Delaunois.[9] The density curve is quite normal in this region.

The refractive index does not possess a maximum but for both refractive index and surface tension the deviations from the ideal are very great.

The eutectic point at 0.152 mole fraction of dioxane and a temperature of −14.9° agrees well with that found by Gillis and Delaunois. However, these workers report a peculiar trend in the curve between 0.8 and 1.0 mole fraction dioxane. This has not been confirmed and the results obtained here are in excellent agreement with those found by Bell and Wolfenden.[10] Gillis and Delaunois in calling attention to this peculiar irregularity base their conclusions on one point only which may well be in error by 10%. Further, it is difficult to understand why they report two densities for their pure dioxane at 20°, namely, 1.0345 and 1.03215. The maximum deviation from the ideal linear freezing-point curve, Fig. 3, occurs at 0.37 mole fraction of dioxane corresponding to the maximum found in the density measurements.

Values for the vapor pressure of pure dioxane, Table III, are higher at low temperatures and lower at higher temperatures than the corresponding values given by Herz and Lorentz.[2] The vapor pressure may be expressed by means of the equation

(9) Gillis and Delaunois, *Rec. trav. chim.*, **53**, 186 (1934).
(10) Bell and Wolfenden, *J. Chem. Soc.*, 822 (1935).

$$\log_{10} P \text{ (mm.)} = -1933.8/T + 8.0588$$

with a maximum deviation of one per cent. over the temperature range 10 to 80°.

Dioxane itself is a very normal liquid. The Eötvös constant as calculated is 2.11 for the temperature range investigated. The parachor is 205.7, which agrees fairly well with the calculated value of 202.1. The molecular refraction according to the expression of Lorentz and Lorenz gives an experimental value of 21.678, which is in excellent agreement with the theoretical value of 21.690.

The authors wish to express their appreciation to Dr. J. O. Morrison, of Yale University, for furnishing the purified dioxane.

Summary

1. The density, surface tension and total vapor pressure of the dioxane–water system were investigated for the temperature range 10 to 80°.

2. The partial vapor pressure and the index of refraction for this system were determined at 25°.

3. The freezing point curve of the dioxane–water system was studied.

4. The dioxane–water system was discussed and the possible errors of other workers in the case of freezing points, density and fluidity were pointed out.

The Reaction of 2,3-Epoxybutane with the Grignard Reagent

BY D. L. COTTLE AND LEO S. POWELL

The rearrangement of certain ethylene oxides in Grignard reactions is well known. Among the simple alkyl or aryl substituted ethylene oxides, 2,3-epoxybutane,[1] 1,2-epoxy-2-methylpropane,[2] 1,2-epoxy-2-methylbutane,[3] 1,2-epoxy-2-phenylpropane,[4] and styrene oxide,[5] have been reported to rearrange in Grignard reactions to produce one alcohol, while 1,2-epoxypropane[6–8] and 1,2-epoxybutane[8] have been reported not to rearrange.

(1) L. Henry, *Compt. rend.*, **145**, 406 (1907).
(2) L. Henry, *ibid.*, **145**, 21 (1907).
(3) Fourneau and Tiffeneau, *ibid.*, **145**, 438 (1907).
(4) Tiffeneau, *ibid.*, **140**, 1460 (1905).
(5) Fourneau and Tiffeneau, *ibid.*, **146**, 698 (1908).
(6) Hess, *Ber.*, **46**, 3117 (1913).
(7) Levene and Walti, *J. Biol. Chem.*, **90**, 81 (1931).
(8) Levene and Walti, *ibid.*, **94**, 367 (1931).

In order to explain the rearrangement of cyclohexene oxide in a methylmagnesium iodide reaction reported by Bedos, Bartlett and Berry[9] adopted the Blaise[10] structure for the primary intermediate.[11,12]

(9) Bartlett and Berry, THIS JOURNAL, **56**, 2683 (1934).
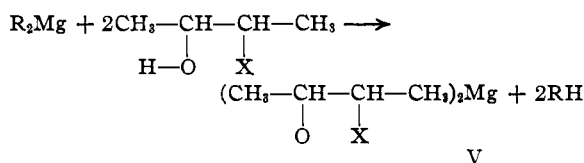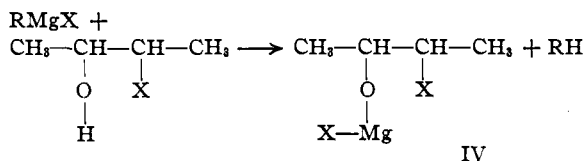(10) Blaise, *Compt. rend.*, **134**, 552 (1902).
(11) This theory was criticized by Grignard [*Bull. soc. chim.*, [3] **29**, 944 (1903)] who preferred to depict the oxide ring as breaking at much higher temperatures. Boord and Summerbell readvanced the Blaise theory (Columbus, Ohio, meeting of The American Chemical Society, May, 1929) and Ribas and Tapia placed it on a more secure basis as a result of extensive experiments with ethylene oxide, epichlorohydrin and 3-methoxy-1,2-epoxypropane [*Anal. soc. españ. fis. quim.*, **30**, 778 (1932): **30**, 944 (1932)].
(12) Boord and Summerbell and Ribas and Tapia suggested as likewise possible the structures BrMgOCH₂CH₂Br and Mg(OCH₂CH₂Br)₂ for ethylene oxide intermediates.

$$\begin{array}{c} CH_2 \\ CH_2 \end{array} \Big< \begin{array}{c} CH_2-CH_2 \\ CH_2-CHX \end{array} \Big> CHOMgR$$

I
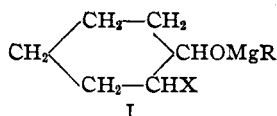
These workers further assumed that I rearranged to cyclopentylformaldehyde instead of reacting through replacement of the halogen by the methyl group. These assumptions were based on experimental work by Bedos[13,14] who found that the alkoxide formed from cyclohexene chlorohydrin and ethylmagnesium bromide gave a 40% yield of cyclopentylformaldehyde when the ether was evaporated from its mixture with magnesium bromide. The oxide treated similarly with magnesium bromide etherate gave a 34% yield of aldehyde. These magnesium bromide reaction mixtures, both chlorohydrin and oxide, reacted vigorously with methylmagnesium iodide to form methylcyclopentylcarbinol.

If the reaction path outlined by Bartlett and

$$MgX_2 +$$
$$CH_3-CH-CH-CH_3 \longrightarrow CH_3-CH-CH-CH_3$$
$$\quad\quad\quad \searrow\!O\!\swarrow \quad\quad\quad\quad\quad\quad |\quad\; |$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad O\quad X$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad |$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad X-Mg$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad II$$

$$RMgX +$$
$$CH_3-CH-CH-CH_3 \longrightarrow CH_3-CH-CH-CH_3$$
$$\quad\quad\quad \searrow\!O\!\swarrow \quad\quad\quad\quad\quad\quad |\quad\; |$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad O\quad X$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad |$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad R-Mg$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad III$$

$$RMgX +$$
$$CH_3-CH-CH-CH_3 \longrightarrow CH_3-CH-CH-CH_3 + RH$$
$$\quad\quad |\quad\; | \quad\quad\quad\quad\quad\quad\quad\quad\quad |\quad\; |$$
$$\quad\quad O\quad X \quad\quad\quad\quad\quad\quad\quad\quad O\quad X$$
$$\quad\quad |\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad |$$
$$\quad\quad H \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad X-Mg$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad IV$$

$$R_2Mg + 2CH_3-CH-CH-CH_3 \longrightarrow$$
$$\quad\quad\quad\quad\quad\; |\quad\; |$$
$$\quad\quad\quad\quad\; H\!-\!O\quad X$$
$$\quad\quad\quad\quad (CH_3-CH-CH-CH_3)_2Mg + 2RH$$
$$\quad\quad\quad\quad\quad\quad\quad\; |\quad\; |$$
$$\quad\quad\quad\quad\quad\quad\quad\; O\quad X$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad V$$
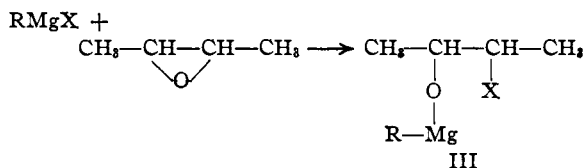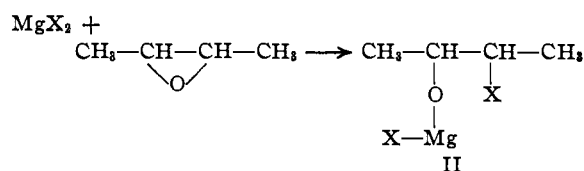
(13) Bedos, *Compt. rend.*, **189**, 255 (1929).

(14) Berry and Bartlett are confused in the history of this reaction for they credit Bedos with their explanation as well as with the experimental work. There is nothing in the reference[13] cited by Berry and Bartlett or in other articles by Bedos to indicate that he wished to advance the explanation credited to him. The statement by Berry and Bartlett[9] (p. 2684), "Bedos has further elucidated the mechanism of this rearrangement by showing that, as in the aliphatic series, the primary product of reaction between cyclohexene oxide and a Grignard reagent is the halohydrin derivative....," is misleading in another respect inasmuch as in only one case, 1,2-epoxy-2-methylbutane, are there sufficient data in the literature to support a qualified explanation of an aliphatic ethylene oxide rearrangement. Moreover, no reference is given to the work of Ribas and Tapia of 1932 which is the only successful attempt to refute the unsatisfactory theory advanced by Grignard in 1903.

Berry is applicable to 2,3-epoxybutane, 3-bromo-2-butanol should react with a Grignard reagent and yield a tertiary alcohol since Henry[1] obtained tertiary amyl alcohol when methylmagnesium bromide reacted with the oxide. The intermediates, II and III, would have structures similar or identical to IV and V.

We found that 3-bromo-2-butanol reacted with the second mole of ethylmagnesium bromide without application of heat, and the end-products consisted of 2-butanone, postulated by Henry as an intermediate in the oxide reaction, and 3-methyl-3-pentanol. We were unable to isolate any 3-methyl-2-pentanol, which would have resulted from a replacement of the halogen by the alkyl group of the Grignard reagent. Thus, the explanation of Berry and Bartlett applies to 2,3-epoxybutane.

The Grignard reaction of this bromohydrin without application of heat undoubtedly is due to the secondary bromine atom. Ethylene bromohydrin is well known to require higher temperatures for reaction of the bromine atom.[15] The magnesium salt of 3-bromo-2-butanol, prepared from 2,3-epoxybutane and magnesium bromide in ether benzene solution decomposed practically quantitatively at slightly above room temperature. The product was 2-butanone. Rector[16] was able to prepare 3-bromo-2-butanol in 60% yield by this method by working at 0°.

Although the Blaise theory is satisfactory in predicting the behavior of 3-bromo-2-butanol the isolation by Henry, Fourneau and Tiffeneau and others of only one alcohol in the oxide reactions which involved rearrangements is not in satisfactory agreement with known experimental data. Ribas and Tapia[11] found in treating 2 moles of ethylene oxide with one of ethylmagnesium bromide in the cold that the magnesiumalkyl bond also reacted. Later, Bartlett and Berry[9] obtained no rearrangement in the reaction of cyclohexene oxide with diethylmagnesium or dimethylmagnesium. Ribas and Tapia obtained a 5% yield of n-butyl alcohol when ethylene oxide was reacted with ethylmagnesium bromide in a 1 to 1 ratio in the cold. This may be assumed to represent the percentage of reaction of C_2H_5Mg bond when in competition with a similar quantity of MgBr bond. Consequently, we considered it probable that small amounts of normal products

(15) Grignard, *Bull. soc. chim.*, [3] **34**, 918 (1905); Conant and Kirner, THIS JOURNAL, **46**, 240 (1924).

(16) Rector, Master of Science Thesis, Rutgers University, 1933.

in the rearrangements cited were overlooked by the early workers.

2,3-Epoxybutane was selected for investigation of this and related points for the following reasons: the recent description[17] of a source of pure 2-butene made its preparation in larger than usual quantities feasible; 3-bromo-2-butanol is the only bromohydrin that it can form; and the difference in boiling points of the possible alcohols produced by the Grignard reagent is greater than if a higher molecular weight oxide were used.

In the present work 2,3-epoxybutane was found to react with diethylmagnesium and dimethylmagnesium to yield secondary alcohols. These results are in complete agreement with the predictions of Bartlett and Berry[9] and have been reported by other investigators.[18] Secondary alcohols were also isolated in 2,3-epoxybutane reactions with ethylmagnesium chloride and bromide and methylmagnesium bromide. A trace of secondary alcohol probably was present in an ethylmagnesium iodide experiment. A tertiary alcohol also was produced in each of these reactions. That the formation of the secondary alcohol was due to a direct reaction of the alkylmagnesium bond with the oxide was demonstrated by the absence of the secondary alcohol in the 3-bromo-2-butanol reaction with ethylmagnesium bromide. The formation of appreciable yields of the tertiary alcohol (see Table I) without heating of the bromide and iodide reactions was predicted on the basis of the results obtained with 3-bromo-2-butanol.

TABLE I

Expt.	RMgX	Yield, % Secondary alcohol	Tertiary alcohol
1	C_2H_5MgCl	27[a]	30[a]
2	C_2H_5MgBr	2	31
3	C_2H_5MgI	Trace	27
4	CH_3MgBr	7[a]	44[a]

[a] Based on refractive index of the mixture.

In view of the discovery by Brönsted and co-workers[19] that of the aqueous potassium halides, iodide adds faster than bromide and bromide faster than chloride to glycid and epichlorohydrin it is not surprising that of the three ethyl Grignard reagents, the iodide gave the least alkylmagnesium reaction. However, several factors

need evaluation before a valid conclusion can be drawn.

The discovery by Schlenk and Schlenk[20] that the dioxane precipitate from a Grignard solution behaved like a Grignard reagent with esters and ketones caused us to treat 2,3-epoxybutane with the precipitate from an ethylmagnesium bromide solution. The precipitate contained a larger amount of magnesium halide bond compared with magnesiumalkyl than the original Grignard and a tertiary alcohol with very little if any of the secondary was expected. However, the precipitate was apparently too insoluble for reaction and dissociated to form soluble diethylmagnesium for only the secondary alcohol was formed.

In the reaction of 3-bromo-2-butanol there was obtained, besides 2-butanone, a small amount of liquid which boiled around 155–165°. From the boiling point, reduction of permanganate and the formation of a solid with semicarbazide solution this product contained an octenone. Pariselle and Simon[21] obtained a similar product in the reaction of isopropylmagnesium bromide with 2-butanone and analogous observations have been made by many other workers although generally with Grignard reagents with more complex alkyls than ethyl. In the present work similar material was obtained from the reaction of 2,3-epoxybutane with ethylmagnesium iodide and of 2-butanone with diethylmagnesium. In the latter reaction the yield of alcohol was only 8%.

Experimental

The Preparation of Crude 3-Bromo-2-butanol.—Bromine water was treated with 2-butene by the method given by Read and Williams[22] for ethylene bromohydrin. 2-Butene, generated by heating 4 moles of 2-butanol with 60% sulfuric acid,[17] was passed into the bottom of a well stirred, 5-liter, 3-necked flask which contained 4 liters of water. At the same time, air, regulated by a needle valve, carried bromine into the reaction vessel at such a rate as to give the solution a faint yellow color. The air and butene bubbles were broken up by Jena G-4 gas distribution tubes. In order to prevent the dibromide from extracting the butene and bromine from the water the flask was fitted with a siphon for the intermittent removal of the by-product.

At the end of the reaction the remaining dibromide was separated and the water layer saturated with salt and extracted with ether. After drying over sodium sulfate the ether was expelled on a water-bath. The residue, in 7 preparations, averaged 164 g. or 27% of the theoretical based on the 2-butanol used.

(17) Young and Lucas, THIS JOURNAL, **52**, 1964 (1930); cf. Komarewsky, Johnstone and Yoder, ibid., **56**, 2705 (1934), and Young and Winstein, ibid., **58**, 102 (1936).

(18) Norton and Hass, ibid., **58**, 2147 (1936).

(19) Brönsted, Kilpatrick and Kilpatrick, ibid., **51**, 443 (1929).

(20) Schlenk and Schlenk, Ber., **62B**, 920 (1929).

(21) Pariselle and Simon, Compt. rend., **173**, 88 (1921).

(22) Read and Williams, J. Chem. Soc., **117**, 359 (1920).

The Preparation of 2,3-Epoxybutane.—Crude 3-bromo-2-butanol (360 g.) was added drop by drop to a well-stirred solution of 450 g. of sodium hydroxide in 1050 cc. of water in a 2-liter, 3-necked flask heated on a water-bath. The oxide and some water distilled over at 50–60°. After drying over potassium carbonate it was fractionated with a 3-bulb Snyder column and gave a 75% yield of oxide, b. p. 55–59°, $n^{20}D$ 1.3765, d^{20}_{20} 0.8144.

The Preparation of Pure 3-Bromo-2-butanol.—The method of Thayer, Marvel and Hiers[23] for the preparation of ethylene bromohydrin was used. 2,3-Epoxybutane (66 g.) was added to 172 cc. of 48% hydrobromic acid kept at 0–2°. The yield was 123 g. or 88% of the theoretical of 3-bromo-2-butanol, b. p. 46–50° (8 mm.); $n^{20}D$ 1.4780, d^{20}_{20} 1.4500.

Anal. Calcd. for C_4H_9OBr: Br, 52.24. Found: Br, 52.2, 52.3.

This compound has been prepared previously.[24]

The Preparation of Reference Compounds.—In order to facilitate the identification of the various alcohols obtained in the experiments described below it was necessary to prepare some new urethans.

3-Methyl-3-pentanol was prepared from ethylmagnesium bromide and 2-butanone. The α-naphthyl urethan was prepared by heating 1 g. of the alcohol with 1.7 g. of α-naphthyl isocyanate for three hours. It melted at 83.5°.

Anal. Calcd. for $C_{17}H_{21}O_2N$: N, 5.17. Found: N, 5.05, 4.85.

The phenylurethan, similarly prepared, melted at 43.5°.

Anal. Calcd. for $C_{13}H_{19}O_2N$: N, 6.33. Found: N, 6.37, 6.32.

3-Methyl-2-pentanol was prepared from *s*-butylmagnesium bromide and acetaldehyde by an adaptation of the method for 3-methyl-2-butanol.[25]

The α-naphthylurethan melted at 72°.

Anal. Calcd. for $C_{17}H_{21}O_2N$: N, 5.17. Found: N, 5.21, 4.98.

3-Methyl-2-butanol was prepared according to the directions of Drake and Cooke.[25] The α-naphthylurethan melted at 108–109°.

Anal. Calcd. for $C_{16}H_{19}O_2N$: N, 5.45. Found: N, 5.39, 5.24.

The phenylurethan melted at 68°.

Anal. Calcd. for $C_{12}H_{17}O_2N$: N, 6.76. Found: N, 6.67, 6.87.

These derivatives and the α-naphthylurethan of 2-methyl-2-pentanol, described by Neuberg and Kansky,[26] were used in mixed melting point determinations with urethans prepared from the products of the experiments described below.

The Reaction of 3-Bromo-2-butanol with Ethylmagnesium Bromide.—The bromohydrin (0.65 mole), prepared from the oxide and hydrobromic acid, was added drop by drop to 480 cc. of an ice-cooled ether solution containing 1.3 moles of ethylmagnesium bromide. A precipitate

gradually formed which filled half of the solution. Soon after removal of the ice-bath the reaction mixture refluxed violently for an hour. After standing overnight it was hydrolyzed, the ether extract dried over sodium sulfate and the ether removed on the water-bath. The residue was treated with 30% sodium hydroxide in order to remove unchanged bromohydrin. After extracting with ether and drying over potassium carbonate distillation was made through a 6-bulb Snyder column.

A portion of a 1.0-g. fraction boiling at 65–78° gave a semicarbazone which melted at 138–139°. A mixed melting point with an authentic semicarbazone of 2-butanone did not vary.

The fraction distilling at 121–122° weighed 17.4 g. which corresponds to a 26% yield of alcohol. It was identified as 2-methyl-2-pentanol. The 122–131° fraction weighed 0.9 g. and the material boiling from 131–136°, 0.6 g. The latter gave an α-naphthylurethan melting at 81.5°. A mixture with the α-naphthylurethan of 3-methyl-3-pentanol melted at 82.5°. When a mixture of equal quantities of 3-methyl-3-pentanol and 3-methyl-2-pentanol was reacted with α-naphthyl isocyanate no derivative melting above 52° could be obtained.

A residue of 1.0 cc. was investigated and is reported below.

The Reaction of 2,3-Epoxybutane with Magnesium Bromide.—One mole of oxide was added drop by drop to 1 mole of magnesium bromide, prepared in 300 cc. of ether by the method of Zelinsky[27] and diluted with 300 cc. of benzene. The original object of this experiment was the preparation of 3-bromo-2-butanol but cooling was inefficient and the hydrolysis product consisted of 16 g. of uninvestigated liquid which did not volatilize on the steam-bath. 2-Butanone was extracted from the ether and benzene distillate with sodium bisulfite and identified by the melting point of its semicarbazone and a mixed melting point determination. The oxide dissolved in ether and benzene did not give a precipitate with sodium bisulfite.

The Reaction of 2,3-Epoxybutane with Diethylmagnesium and Dimethylmagnesium.—The oxide was added drop by drop to the dialkylmagnesium in ether in an atmosphere of tank nitrogen using ordinary Grignard technique.

To 0.105 mole of dimethylmagnesium, prepared according to the method of Gilman and Schulze,[28] in 200 cc. of ether was added 0.20 mole of oxide. After addition of the oxide the reaction mixture was refluxed for a short time. A crude yield of 6.1 g. or 35% of the theoretical of alcohol identified as 3-methyl-2-butanol was obtained.

Diethylmagnesium, in 1 liter of ether (0.62 mole), was prepared from ethylmagnesium bromide by filtering off the dioxane precipitate. The oxide (0.62 mole) was added and the solution concentrated by distillation to 200 cc. of clear solution. On hydrolysis it gave a 50 g. or 79% yield of alcohol, b. p. 132–34°. In a similar experiment in which part of the alcohol was dehydrated during distillation, the alcohol was identified as 3-methyl-2-pentanol.

The Reaction of 2,3-Epoxybutane with the Grignard Reagents.—In each of the four experiments reported in Table I the ratio of Grignard reagent to solution was approximately 1 mole to 300 cc. The amount of the reagent

(23) Thayer, Marvel and Hiers, *Organic Syntheses*, **6**, 12–14 (1926).

(24) Fourneau and Puyal, *Bull. soc. chim.*, [4] **31**, 427 (1922); Likhosherstov and Alekseev, *C. A.*, **28**, 3054 (1934).

(25) Drake and Cooke, *Organic Syntheses*, **12**, 48–50 (1932).

(26) Neuberg and Kansky, *Biochem. Z.*, **20**, 448 (1909).

(27) Zelinsky, *Chem. Zentr.*, **74**, II, 277 (1903).

(28) Gilman and Schulze, THIS JOURNAL, **49**, 2329 (1927).

was determined by the titration method of Gilman and co-workers.[29] The oxide was added drop by drop to the reagent cooled in ice and the mixture allowed to come to room temperature. On warming up to room temperature a reaction set in which refluxed the ether violently for about an hour in each case. With the exception of the methylmagnesium bromide experiment, which stood overnight, the reaction mixtures were hydrolyzed at the end of this spontaneous reaction and worked up as described under the 3-bromo-2-butanol experiment.

The results were obtained with the following quantities of oxide and Grignard reagent: no. 1, 0.68 mole; no. 2, 0.30 mole; no. 3, 0.86 mole; no. 4, 1.0 mole. The yields of tertiary alcohol in expts. 2 and 3 were calculated on the basis of the product boiling at 121–122°. In expt. 2, the secondary alcohol boiled at 132–140°. The yields of secondary and tertiary alcohol in expts. 1 and 4 were determined from the refractive indices of the alcohol mixtures which were previously separated by distillation from low and high boiling substances. These mixtures then were fractionated until sufficient quantities of pure alcohols were obtained for the formation of a sharp melting α-naphthyl or phenylurethan. These derivatives were identified further by mixed melting point determinations with authentic samples. Experiment 3 produced 1 g. boiling at 131–140°, which gave an α-naphthylurethan melting at 56–66° after many recrystallizations. The experience with this material was similar to that recorded in the 3-bromo-2-butanol experiment for synthetic mixtures of the two possible alcohols. Experiment 3 also produced a residue of 4 g., the investigation of which is reported below.

The Reaction of 2,3-Epoxybutane with a Dioxane Precipitate from Ethylmagnesium Bromide.—The dioxane precipitate from a diethylmagnesium preparation by calculation contained 0.80 mole of active ethylmagnesium bromide. Enough ether was added to facilitate stirring and 0.80 mole of oxide added. At the end of nine to ten hours of refluxing the reaction mixture gave a negative Gilman and Schulze[30] test for R–Mg bond. The hydrolysis product was treated in the same manner as that in the 3-bromo-2-butanol experiment. Fractionation showed 0.6 g. boiling at 110–120°, 0.3 g. at 120–125°, 1.6 g. at 125–130° and 7.6 g. at 130–135°. The first two and last fractions gave sharp-melting α-naphthylurethans of 3-methyl-2-pentanol. The yield of alcohol based on the fractions boiling from 125–135° was 11% of the theoretical.

The Reaction of 2-Butanone with Diethylmagnesium.—2-Butanone (0.46 mole) was added to 0.195 mole of diethylmagnesium in 300 cc. of ether. The reaction mixture set to a gelatinous mass after standing overnight. At this time it gave a positive Gilman and Schulze color test. It was hydrolyzed and treated in the usual manner and 7.9 g. or a yield of 8% of 3-methyl-3-pentanol, b. p. 118–124°, and some unreacted ketone were obtained. There also was obtained 10.1 g. of some higher boiling material the investigation of which is reported below.

Examination of the Residues.—The major portion of the residues collected from the 3-bromo-2-butanol, ethylmagnesium iodide and diethylmagnesium experiments distilled at 155–165°. All three of these small fractions gave a test

for unsaturation with potassium permanganate, evolved hydrogen bromide when treated with bromine in carbon tetrachloride and gave a small yield of crystals when treated with an excess of semicarbazide solution. After thorough washing with water, alcohol and chloroform, in all of which they were quite insoluble, they melted with decomposition at 250.5–251.5°, corr. The melting point varied with the rate of heating.

2-Butanone was treated with ethoxymagnesium bromide and the product, b. p. 170–173°, gave a good yield of crystals with semicarbazide solution which melted at the same temperature. This appears to be a new derivative of a 2-butanone condensation product.[31]

Anal. Calcd. for $C_9H_{17}N_3O$: N, 22.95. Found: N, 22.79, 22.76.

Mixtures of the latter with the crystals from the three residues mentioned above did not cause a change in melting point behavior.

Summary

1. The reaction of 3-bromo-2-butanol with ethylmagnesium bromide produced only the tertiary alcohol.

2. In complete agreement with the prediction of Berry and Bartlett, secondary alcohols were obtained from the reaction of 2,3-epoxybutane with diethylmagnesium and dimethylmagnesium.

3. The reaction of 2,3-epoxybutane with ethylmagnesium chloride and bromide and methylmagnesium bromide produced both secondary and tertiary alcohols. Henry obtained only the tertiary alcohol in the latter case.

4. The formation of tertiary alcohols in the Grignard reactions is interpreted as the result of a rearrangement of the halohydrin derivatives, *i. e.*, the Blaise intermediate, formed from the reaction of the magnesium halide bond with the oxide.

5. 2,3-Epoxybutane and magnesium bromide in ether and benzene solution produced 2-butanone. The same ketone was isolated in the reaction of 3-bromo-2-butanol with ethylmagnesium bromide.

6. 3-Bromo-2-butanol and 2,3-epoxybutane gave appreciable yields of alcohols when treated with Grignard reagents without the application of heat.

7. The reaction of 2,3-epoxybutane with ethylmagnesium iodide, of 2-butanone with diethylmagnesium and of 3-bromo-2-butanol with ethylmagnesium bromide produced, in addition to 3-methyl-3-pentanol, condensation products of 2-butanone.

(29) Gilman, Wilkinsno, Fishel, and Meyers THIS JOURNAL, **45**, 156 (1923).

(30) Gilman and Schulze, *ibid.*, **47**, 2002 (1925).

(31) Colonge, *Bull. soc. chim.*, [4] **49**, 432 (1931). This paper summarizes the data on semicarbazones of the octenones from 2-butanone. All of the semicarbazones listed melt below the melting point of our derivative.

8. 3-Methyl-2-pentanol was the only alcohol obtained from the reaction of 2,3-epoxybutane with a dioxane precipitate from ethylmagnesium bromide.

9. Some new urethans of 3-methyl-2-pentanol, 3-methyl-3-pentanol and 3-methyl-2-butanol were described.

The Isolation of 1,2-Diketones from the Ozonization of Disubstituted Acetylenes

BY THOMAS L. JACOBS

In a recent paper, Hurd and Christ[1] have discussed the course of the ozonization of acetylenes. They formulate the reaction as proceeding through a 1,2-diketone which is assumed to be oxidized by the hydrogen peroxide produced from the decomposition of the ozonide. From the six acetylenes ozonized, they isolated only acids in yields of 42–61%. The isolation of glyoxal in 81% yield from the ozonization of acetylene[2] is the only instance in which a 1,2-dicarbonyl compound actually has been obtained.

I have ozonized diphenylacetylene and benzylphenylacetylene[3] under carefully controlled conditions, and have isolated benzil and benzylphenyl diketone. At −78° the action of ozone on diphenylacetylene produced an unstable ozonide which decomposed to a black tar shortly after the solvent was removed. When the ozonization was carried out in petroleum ether at 5–15°, the product was a yellow oil which on hydrolysis gave benzoic acid in 65% and benzil in 5% yield. The unstable ozonide apparently produced the same yellow oil as an intermediate when treated with water. When benzylphenylacetylene ozonide, prepared at −30 to −40°, was decomposed with water, the sole products were a mixture of acids and tar. From the acid mixture were isolated benzoic acid in 60% and phenylacetic acid in 10% of the theoretical yield.

$$C_6H_5C{\equiv}CCH_2C_6H_5 \xrightarrow[\text{H}_2\text{O}]{\text{O}_3} C_6H_5COOH + C_6H_5CH_2COOH$$
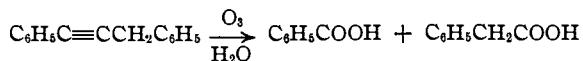
When the product of ozonization was decomposed with neutral potassium iodide solution, benzylphenyl diketone was isolated in 25% yield. In addition, a small amount of acidic material and

much tar were obtained. One attempt was also made to decompose the ozonide by distillation under reduced pressure. A mixture of acid and neutral material resulted, from which a low yield of a mixture of acids was obtained. The neutral portion was accidentally lost.

Ozone was never absorbed completely by any of the acetylenes investigated. The rate of absorption was nearly constant until one mole of ozone had been taken up for each mole of acetylene treated, and then began to fall off rapidly. In one experiment in which the ozonization was continued beyond this point, the initial absorption was 83% and dropped to 25%, but decreased only slowly from this point. The residual absorption probably represents attack of the benzene rings.

The isolation of 1,2-diketones does not prove that such compounds are always intermediates in the production of acids by the ozonization of acetylenes, but the brilliant yellow color of the oil which appears during the preparation or decomposition of the ozonides does suggest that this is the case. In this connection it should be noted that benzil is not attacked by ozone under the conditions of the experiments. The detailed mechanism postulated for the reaction by Hurd and Christ[1] assumes the formation of only monomolecular species, and this appears subject to some question. The amorphous character of the unstable product of ozonization at low temperatures indicates that it is probably polymeric.

An extension of the investigation has been temporarily interrupted, and a report of experiments already completed is made at this time in consideration of the publication of Hurd and Christ.[1]

Experimental

An ozonizer of the Henne[4] type yielding 6.5 to 8% of ozone when oxygen was supplied at 18 to 14 liters per hour was used. Ozone concentrations were determined by the

(1) Hurd and Christ, J. Org. Chem., 1, 141 (1936).
(2) Briner and Wunenburger, Helv. Chim. Acta, 12, 786 (1929).
(3) The synthesis, properties and reactions of this compound and related acetylenes will be described in a paper by Johnson, Schwartz and Jacobs. See also Schwartz, Cornell Thesis, 1931; Jacobs, Cornell Thesis, 1935.
(4) Henne, THIS JOURNAL, 51, 2676 (1929).