The Reaction of Epichlorohydrin with the Grignard Reagent. Some Derivatives of Cyclopropanol

By Glenn W. Stahl[1] and D. L. Cottle

Cyclopropanol was reported[2] recently as one of the products of the reaction of magnesium 1-bromo-3-chloro-2-propoxide with ethylmagnesium bromide. During an effort to obtain larger quantities of the alcohol by the same reaction it was found impossible to obtain the yields previously reported. The discovery by Kharasch[3] and coworkers that small amounts of certain metallic halides catalyze oxidation–reduction reactions involving Grignard reagents led us to assume that the previous work in this Laboratory was done with magnesium of a different purity. Addition of small amounts of ferric chloride to subsequent reaction mixtures led not only to cyclopropanol fractions comparable in size to those previously reported but also to much shorter reaction times than those formerly observed. When magnesium of a special purity was used no gas was evolved and no cyclopropanol was obtained.

Attempts to purify the cyclopropanol have resulted in failure. One sample gave a Zerewitinoff value that indicated an 87% content of cyclopropanol. Its change to propionaldehyde has been confirmed and the aldol condensation product of propionaldehyde, 2-methyl-2-penten-1-al, also was obtained on treating the alcohol with potassium carbonate. On the other hand, it was possible to prepare the phenyl-, *p*-nitrophenyl- and α-naphthylurethans, the *p*-nitrobenzoate, the 3,5-dinitrobenzoate and the allophanate. Their analyses and the non-agreement of their properties with the properties of derivatives of other simple alcohols leave unchanged the previously reported conclusion that cyclopropanol is a product of the reaction.

Attempts to purify cyclopropanol are being continued.

Experimental

The Preparation of Cyclopropanol.—The propoxide was prepared and treated with ethylmagnesium bromide as described previously. The yields of crude cyclopropanol. material soluble in water and boiling at 100–103°, averaged 6.0% of the theoretical in four experiments each involving 1 mole of epichlorohydrin and 6.3% in six experiments each involving 1 mole of 1-bromo-3-chloro-2-propanol. The time of standing at room temperature varied from eight days to fifty days and the ratio of ethylmagnesium bromide from two to three moles per mole of propoxide. These factors appear to be unimportant if the reaction is allowed to stand until the evolution of gas ceases.

An experiment in which the product, from 1 mole of epichlorohydrin and 1 mole of magnesium bromide, containing 0.0014 mole of ferric chloride, was treated with 3 moles of ethylmagnesium bromide, ceased evolving gas at the end of one-half hour and gave a yield of cyclopropanol of 43%. Another experiment with 1.66 moles of epichlorohydrin, 1.66 moles of magnesium bromide, and 5 moles of ethylmagnesium bromide, which contained 0.0015 mole of ferric chloride, was complete in two hours and gave a crude yield of 31%. The former reaction was exceedingly difficult to control.

Ethylmagnesium bromide, prepared from 3 gram atoms of distilled and sublimed magnesium, obtained from the Dow Chemical Company, was added to the product from 1 mole of epichlorohydrin and 1 mole of magnesium bromide and allowed to stand for twenty-eight days. No gas was evolved and the 2.5 g. of product boiling at 96–104° was insoluble in water.

Attempts to Purify Cyclopropanol.—The best conditions described previously were modified by treating the fractions boiling at 85–105° with water and removing the water insoluble material. The alcohol was removed from the water by repeated salting out and distillation. The final product distilled at 100–103° and was invariably contaminated with a halogen-containing compound. One sample in a Zerewitinoff determination gave a value which indicated that it was 87% cyclopropanol.[4] All preparations showed densities and refractive indices in the neighborhood of the values previously reported.

The Preparation and Analysis of Derivatives.—All of the following derivatives were prepared from material which was obtained in the experiments to which no ferric chloride was added.

Cyclopropanol (10 g.), which had been standing for some days over 2.0 g. of anhydrous potassium carbonate, was converted to a higher boiling substance which gave a semicarbazone melting at 187–188° and was found to be identical with a semicarbazone of 2-methyl-2-penten-1-al prepared from propionaldehyde by the method of Doebner.[5]

Anal. Calcd. for $C_7H_{13}N_3O$: C, 54.2; H, 8.44. Found: C, 53.9; H, 8.36.

The phenyl-, *p*-nitrophenyl and α-naphthyl urethans were prepared by using an excess of the alcohol and keeping the reaction mixtures cold. The phenyl and α-naphthyl urethans were recrystallized from diisoamyl ether and the phenyl urethan melted at 101.5–102.0° (*Anal.* Calcd. for $C_{10}H_{11}NO_2$: N, 7.91; C, 67.7; H, 6.27. Found: N, 7.84; C, 68.0; H, 6.37) and the α-naphthyl urethan at 100.5–101.5° (*Anal.* Calcd. for $C_{14}H_{13}NO_2$: N, 6.16; C, 74.0; H, 5.77. Found: N, 5.98; C, 73.4; H, 5.89). The *p*-nitrophenyl urethan, recrystallized from benzene, melted at 159–160°. (*Anal.* Calcd. for $C_{10}H_{10}N_2O_4$: C, 54.1; H, 4.54. Found: C, 53.8; H, 4.43.)

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[2] Magrane and Cottle, This Journal, **64**, 484 (1942).

[3] Kharasch and Fields, *ibid.*, **63**, 2316 (1941).

[4] We are indebted to Mr. William Hollyday for this determination; compare *Ind. Eng. Chem., Anal. Ed.*, **14**, 774 (1942).

[5] Doebner, *Ber.*, **35**, 1144 (1902).

The *p*-nitrobenzoate and the 3,5-dinitrobenzoate were prepared from the alcohol and acyl chloride in pyridine and were much more easily obtained than the urethans. Some decomposition took place during the reaction but it was insignificant compared to that which took place in less basic solvents. The *p*-nitrobenzoate melted at 72.0–72.5° (*Anal.* Calcd. for $C_{10}H_9NO_4$: N, 6.77; C, 57.9; H, 4.38. Found: N, 6.80; C, 57.5; H, 4.59) and the 3,5-dinitrobenzoate melted at 108–109° (*Anal.* Calcd. for $C_{10}H_8N_2O_8$: N, 11.1; C, 47.6; H, 3.20. Found: N, 11.2; C, 47.4; H, 3.35).

The allophanate, prepared according to the method of Béhal,[6] sublimed at 179–181° with decomposition. *Anal.* Calcd. for $C_5H_8N_2O_3$: N, 19.4; C, 41.6; H, 5.59. Found: N, 19.6; C, 41.3; H, 5.63.

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(6) Béhal, *Compt. rend.*, **168**, 945 (1919).

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RECEIVED JUNE 25, 1943

An Examination of the Fatty Oil from Buffalo Gourd Seed

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The ground leaves, stems, fruit and root of the Buffalo gourd plant (*Cucurbita foetidissima*) are very attractive to several species of cucumber beetles.[3] During an examination of the plant for its attractive principle, the physical and chemical characteristics of the oil from the seeds were determined. The plant is a member of the same genus to which the pumpkin belongs. Although pumpkin seed oil has been studied extensively, no examination of the oil from *Cucurbita foetidissima* seeds has been reported.

The seeds, resembling small pumpkin seeds, contain 29.7% of an oil extractable by ether. The crude ether-extracted oil has a yellowish-green color in thin layers and a brownish-red color in moderately thick layers. The oil has a bland, fatty taste, and a peculiar fatty odor. The physical and chemical constants of the crude oil are given in Table I. The percentages of saturated and unsaturated acids were determined by the lead-salt–ether method,[4] and corrections were made for the small amount of unsaturated acids that are precipitated and weighed with the saturated acid fraction.

There is only a very small amount of glycerides of volatile acids present, as indicated by the low Reichert–Meissl and Polenske numbers. The low acetyl value, 7.51, indicates a small amount of glycerides of hydroxylated acids. The percentage of insoluble acids, 92.4, has been corrected for unsaponifiable matter and does not represent insoluble acids + unsaponifiable matter (Hehner number), which is commonly reported.

In general the characteristics of the oil are similar to those of pumpkin seed oil as reported by Riebsomer and Nesty.[5]

TABLE I

PHYSICAL AND CHEMICAL CONSTANTS OF BUFFALO GOURD SEED OIL

Density (30°), g./cc.	0.9179
Refractive index (Abbe 30°)	1.4728
Iodine number (Hanus)	140.8
Saponification value	190.2
Soluble acids, %	0.2
Insoluble acids, %	92.4
Acid value	16.5
Unsaponifiable matter, %	1.74
Reichert–Meissl number	0.23
Polenske number	0.14
Iodine number of unsaturated acids	151.2
Unsaturated acids (basis of oil), cor., %	85.67
Saturated acids (basis of oil), cor., %	5.59
Acetyl value	7.51

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(3) Elmore and Campbell, *J. Econ. Entomol.*, **29**, 830 (1936).

(4) Jamieson, "Vegetable Fats and Oils," 1932, p. 351.

(5) Riebsomer and Nesty, THIS JOURNAL, **56**, 1784 (1934).

BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE
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U. S. DEPARTMENT OF AGRICULTURE
BELTSVILLE, MD.
RECEIVED MAY 21, 1943

NEW COMPOUNDS

Germanium (Iso)cyanate

The method used by Forbes and Anderson[1] for preparing the (iso)cyanates of silicon, boron and phosphorus has been found to be satisfactory for the preparation of germanium (iso)cyanate.[2] 59.1 g. of germanium tetrachloride was dissolved in 200 cc. of benzene, and 167 g. (an equivalent quantity) of powdered silver (iso)cyanate was added in small portions through a reflux condenser with shaking. The reaction proceeded rapidly with the evolution of considerable heat. The mixture was heated on a water-bath for one hour, allowed to cool, and filtered, the residue being washed with benzene. The filtrate was fractionally distilled and a yield of 45.3 g. (68%) of germanium (iso)-cyanate was obtained as a fraction boiling between 195 and 199°. This gave no test for chloride. It behaved like a pure compound and was evidently not a mixture of the

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(1) Forbes and Anderson, THIS JOURNAL, **62**, 761 (1940).

(2) The term (iso)cyanate is used here to refer to a product which may be the cyanate, isocyanate, or a mixture of the two.