counted for as the monochlorohexenes and one-half as polymeric products. The violet colors always observed are due to the action of the acid on the polymers formed.[5]

Summary

1. Hydrochloric acid reacts with Δ-1,5-hexadiene to give a mixture of 5-chloro-1-hexene, 2,5-dichlorohexanes, diallyl oxide and a trace of its condensation products.
2. From the 2,5-dichlorohexane the meso form was separated as pure crystals.
3. Hydrochloric acid reacts with Δ-2,4-hexadiene to give a mixture of monochlorohexanes and polymeric products of the hydrocarbon.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

STUDIES OF GLYCIDOL. I. PREPARATION FROM GLYCEROL MONOCHLOROHYDRIN[1]

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The usefulness of ethylene oxide in synthetic work has been demonstrated in convincing fashion during the past few years, and for this reason a peculiarly attractive field of investigation is offered by a study of the closely related glycidol, I (epihydrin alcohol). This compound has not been readily available, nor have its chemical properties been adequately studied. Its synthesis has therefore been carefully investigated by the writers with a view to an extensive study of its addition reactions.

I

We have found that any practicable method of synthesis must needs use glycerol monochlorohydrin as the starting material. While both the alpha and beta-isomers of monochlorohydrin are converted into glycidol by the removal of hydrogen chloride, it is of considerable academic importance to know whether or not both isomers are formed in a given reaction used for the preparation of one or the other. There have been no simple tests which would differentiate the two compounds and no solid derivatives of the isomeric monochlorohydrins have been sufficiently described in the literature to make their preparation a safe criterion of structure. In the course of the present investigation the presence of the two isomers in a chlorohydrin mixture has been determined by a qualitative method, which depends upon the fact that the phenylurethans of the isomeric compounds are decidedly different in their properties. The phenylurethan of the alpha-isomer

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[5] *Cf.* McCullough and Cortese, THIS JOURNAL, **51,** 225 (1929).

[1] Constructed from part of the thesis presented by T. H. Rider to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy, 1928.

melts at 129°, while that of the beta-isomer melts at 133°. Mixtures of the two melt from 115–121°. Furthermore, the two compounds show decidedly different crystal structures.

The Preparation of Glycerol α-Monochlorohydrin.—Either gaseous hydrogen chloride or aqueous hydrochloric acid may be used in the direct synthesis of glycerol monochlorohydrin from glycerol. The yields previously reported in the literature have never exceeded 70% with the exception of certain patent claims which appear to be quite inaccurate.

As the result of preliminary work we regarded the reaction using aqueous hydrochloric acid as being the most practical. Even in this method, however, the maximum yield of monochlorohydrin can be obtained from a single run only with the concomitant production of an undesirably large amount of dichlorohydrin. To overcome this waste of glycerol, we have developed a new procedure for the reaction between glycerol and aqueous hydrochloric acid, catalyzed by acetic acid. The conditions are so regulated as to give a maximum formation of monochlorohydrin with a minimum of the dihalogenated product. After isolation of the monochlorohydrin, the rather large glycerol-containing residue is used again. It is desirable to combine the residues from two such reactions and use this mixture as raw material for a third. (*Note.*—Mixing the residue from one reaction with fresh glycerol for the next leads to a rapid accumulation of polyglycerides.) By following closely a set of conditions which was evolved from an extensive study of many factors, yields of 85–88% may consistently be obtained.

The Preparation of Glycidol.—It has been stated above that syntheses of glycidol from intermediates[2] other than monochlorohydrin are in general impracticable. Of these less desirable reactions, mention might be made of Breslauer's method which utilizes epichlorohydrin, but which gives poor yields and a product of doubtful purity.

A number of reagents may be used, with more or less success, to remove hydrogen chloride from monochlorohydrin. Nef[2] has reported 70% yields of glycidol by the use of alcoholic potassium hydroxide. The procedure of Nef calls for the mixing of solutions of monochlorohydrin and potassium hydroxide in 95% alcohol at room temperature, filtering off the precipitated salt after fourteen hours, and separating the alcohol and glycidol by distillation.

A study of the reaction has shown that this yield can be obtained only when several changes are made in Nef's procedure. Absolute alcohol, rather than 95%, should be used; the reactants should be thoroughly

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[2] Grün, *Ber.*, **59**, 690 (1926); Prileschauew, *ibid.*, **42**, 4811 (1909); Nef, *Ann.*, **335**, 1 (1904); Jowanowitsch, *Monatsh.*, **6**, 467 (1885); Richter, *Ber.*, **10**, 697 (1877); Gegerfelt, *Bull. soc. chim.*, [1] **23**, 160 (1875); Laufer, *Jenaer. Zeitschrift*, **10**, 2, Spl. S. 141; Breslauer, *J. prakt. Chem.*, **20**, 188 (1879).

cooled before mixing; the glycidol should be isolated within thirty minutes, and the solvent alcohol removed under diminished pressure. Distillation at atmospheric pressure is attended with the formation of a considerable quantity of glycerol monoethyl ether. By the use of this modified procedure a crude yield of 79% can be obtained.

Unfortunately the great solubility of glycidol in alcohol is a factor which militates against the success of this method. It is impossible to obtain a sharp fractionation of the reaction mixture under reduced pressure and consequently, in order to secure a product free from alcohol, a large amount of glycidol is lost in the solvent fraction. Thus the yield of 79% is reduced to 64% upon further distillation, and the product retains some alcohol.

Since the absence of water from the reaction mixture is desirable from theoretical considerations, an alcoholic solution of sodium ethylate was used in place of the alcoholic potash solution. The yields were higher, and glycidol of a reasonable degree of purity was obtained in amounts 65–68% of the theoretical.

The use of alcohol as a solvent is undesirable, first, because it conduces always to the formation of glycerol monoethyl ether and, second, because it is impossible to isolate all of the glycidol from the alcoholic solution. We have studied the action of solid potassium hydroxide and also solid sodium ethylate on ethereal solutions of monochlorohydrin. When solid potash in the form of a fine powder is stirred with an ethereal solution of monochlorohydrin, a water layer is formed. We have found that in the partition of glycidol between water and ether, there is very little glycidol in the ether layer, consequently in this reaction there is a concentration of the product in the water layer. Since this solution is strongly alkaline it produces a comparatively large amount of hydrolysis, and the yield of glycidol is reduced to 50% of the theoretical.

While the action of solid pulverized sodium ethylate[3] on ethereal solutions of monochlorohydrin does not produce a second liquid phase, the yields are lower than with the solid potash. Since the yields are likewise lower than in the reaction using an alcoholic solution of sodium ethylate, it must be assumed that there is a relatively large amount of direct replacement of halogen by the ethoxy radical. This hypothesis was substantiated by the isolation of rather large amounts of glycerol ethyl ether from the products of reaction, more indeed than was found in the case of a carefully controlled reaction run in alcohol solution.

The presence of both water and alcohol in the reaction mixture may be obviated by reacting metallic sodium with an ethereal solution of monochlorohydrin. This reaction has been studied to a limited extent by Reboul,[4]

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[3] A method, similar in principle, utilizes monosodium glycerate, *cf.* Nivière, *Compt. rend.*, **156**, 1628 (1913). We have obtained 25–27% yields by this procedure.

[4] Reboul, *Ann. chim.*, [3] **60**, 1 (1860).

Bigot[5] and Nivière.[6] The last mentioned claims yields of 55%, while the other investigators state that the yields are low. The yield given by Nivière, and obtained by reacting equimolecular proportions of sodium and monochlorohydrin, could not be duplicated by the writers. When the reaction was continued until the sodium was completely reacted, the precipitate of salt, originally granular, became extremely pasty, and the reaction was increasingly slow, it being almost impossible to cause the last pieces to react. The pasty nature of the precipitate was due to the formation of ether-insoluble polymerization products. By stopping the reaction before the sodium was completely reacted, the salt precipitate remained granular and the yields of glycidol were much higher. For this reason a series of reactions was carried out in which different amounts of sodium were used. The results of these reactions are shown in the accompanying graph, in which the moles of sodium reacting with one mole of monochlorohydrin are plotted against the yield calculated from the latter.

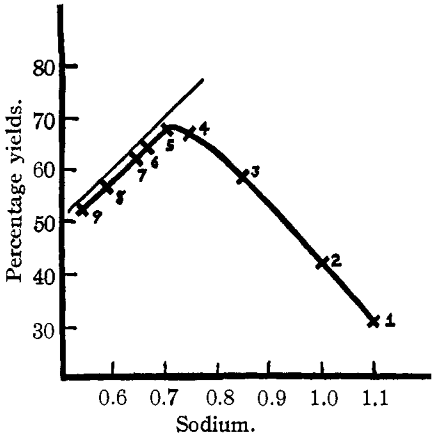

Fig. 1.

The thin diagonal line represents the limiting yields with the amount of sodium used. Thus it is clearly seen that sodium plays two roles, the first to produce glycidol, and the second to destroy it. There are two factors by the control of which the rate of destruction may be made negligible when compared to the rate of formation. The first of these, the mass action factor, entails the use of a reduced amount of sodium. Not only must the total quantity be less than the theoretical, but the sodium should be used in the form of a fine wire, so that the reaction will proceed with reasonable rapidity. The second factor is the temperature at which the reaction is carried out. The optimum temperature is 10–15°. Below 0° the formation proceeds so slowly that it is not practicable to use this temperature. Above 25° the rate of formation is increased, but the rate of destruction becomes correspondingly greater, so that no glycidol can be isolated from the reaction mixture.

With the method of preparation finally adopted, there is considerable monochlorohydrin in excess over the amount of sodium. After removal of the solvent and the distillation of the glycidol from the reaction mixture, an average of one-quarter of a mole of monochlorohydrin may be recovered.

[5] Bigot, *Ann. chim.*, [6] **22**, 433 (1891).

[6] Nivière, *Bull. soc. chim.*, **15**, 464 (1914).

Redistilled glycidol is obtained in yields of 90% calculated from the chlorohydrin actually used. Not only is this yield a great improvement over those previously reported, but the reaction product is obtained in a high degree of purity. Indeed, the impurity of the glycidol resulting from some procedures has led to erroneous statements in the literature concerning its chemical and physical properties.

Glycidol may be conveniently identified by means of its phenyl- and α-naphthylurethans. The former melts at 60° and the latter at 102°.

Experimental Part

The Phenylurethans of the Isomeric Glycerol Monochlorohydrins.—Phenyl isocyanate is stirred with a slight excess of chlorohydrin, or a mixture of isomeric chlorohydrins. When the reactants form a homogeneous solution the mixture is heated on a steam-bath until there is no longer an obvious odor of phenyl isocyanate. The reaction mixture is dissolved in a rather large volume of acetone and water added until the solution is cloudy. If enough water has been added to throw out an oil, the whole colloidal solution is filtered on a coarse folded filter paper, which retains the oil. This filtered colloidal solution, on standing, separates a flocculent solid, which is filtered off and recrystallized from high-boiling petroleum ether. When the urethan has been prepared from a mixture[7] of the isomeric α- and β-glycerol monochlorohydrins, the isomeric urethans may be separated by fractional crystallization from a solvent consisting of a mixture of acetone and high-boiling petroleum ether. More convenient, however, is another method of separation. The mixed urethans, if allowed to crystallize slowly from a solution in high-boiling petroleum ether, separate in different forms. The β-urethan deposits first, in dense clusters, which adhere to the sides of the flask, while the α-isomer precipitates in a flocculent form, which will, for the most part, remain suspended in the solvent so that a decantation will effect a good separation. By repeating this procedure the two forms may be separated completely, as evidenced by microscopic examination. The phenylurethan of α-monochlorohydrin melts at 128–129° and remelts at 129°. The phenylurethan of β-monochlorohydrin melts at 131–133° and remelts at 133°.

Anal. Calcd. for $C_{10}H_{12}O_2NCl$: N, 6.10; Cl, 15.5. Found: α-urethan—N, 6.14, 6.15; Cl, 15.0, 15.2. β-urethan—N, 6.2; Cl, 15.6.

Glycerol α-Monochlorohydrin.—Glycerol is mixed with three and three-quarters parts by weight of concentrated hydrochloric acid (sp. gr. 1.19) and one-tenth part by weight of glacial acetic acid. The mixture is heated on a steam-bath for a period of ten hours, after which it is distilled. The water fraction is removed under the vacuum produced by a water pump (10–15 mm.), during heating by steam. The fractionation is automatic and heating is continued as long as there is a distillate. The residue is now distilled, preferably through a short column. The chlorohydrin is collected from 117–130° at 15 mm. (100–112° at 3–5 mm., or about 81° at 0.5 mm.) and the residue saved. Provided the first distillation has been carried to completion, in the second distillation the temperature should rise rapidly to the boiling point of the chlorohydrin, so that there is no need for a further cut of low-boiling material. The residues from two such reactions are combined and hydrochloric and acetic acids added in the same proportions by weight that were mixed with glycerin in the original preparations. This reaction mixture is heated for a period of fourteen or fifteen hours instead of ten. The distillations are carried out in the same manner. The combined yields from the two original runs

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[7] Such as that derived from the action of hypochlorous acid on allyl alcohol.

and the re-working of the residues is 85–88%, and the density of the once distilled material is 1.317.

Anal. Calcd. for $C_3H_7O_2Cl$: Cl, 32.09. Found: Cl, on crude product, 27.40 to 32.21; Cl, on redistilled material, 32.10, 32.07.

Purified monochlorohydrin, prepared according to the new procedure, has d^{25} 1.3217; n^{25}_{D} 1.4811; it remains liquid at −17°, and freezes to a glass in liquid air. It is miscible in all proportions with ether, water, alcohol and acetone. It is soluble in hot benzene and very slightly soluble in cold benzene, petroleum ether, xylene, heptane, diphenylmethane and diphenyl ether. When distilled at a pressure of 0.53 mm., the temperature of distillation is 80.9°.

Glycidol. (a) **By the Action of Alcoholic Potassium Hydroxide on Monochlorohydrin.**—One mole of potassium hydroxide is dissolved in 400 cc. of absolute alcohol and the solution cooled in an ice-bath. A cold solution of one mole of glycerol α-monochlorohydrin in 200 cc. of absolute alcohol is added during stirring. The reaction mixture is allowed to stand for twenty to thirty minutes, after which it is filtered. The alcohol is removed under reduced pressure and the glycidol distilled from the residue. The first collection is made from 60–100° at a pressure of approximately 10 mm. It is necessary to redistil this product at least twice to remove the alcohol completely, the final collection being made from 65–66°, at a pressure of 2–2.5 mm. The yield of redistilled glycidol is about 60%. The preparation of solid urethans for characterization purposes is given below.

(b) **By the Action of Alcoholic Sodium Ethylate on Monochlorohydrin.**—One mole of metallic sodium is dissolved in 400 cc. of absolute alcohol and the solution cooled in an ice-bath. A cold solution of one mole of glycerol α-monochlorohydrin in 200 cc. of absolute alcohol is added during stirring. The resulting solution is allowed to stand for about an hour, when it should be neutral, and the precipitate coagulated. The solution is then filtered and the alcohol removed under reduced pressure. The glycidol is then distilled as described in the previous reaction. The yield of redistilled glycidol is 65–68% of the theoretical. The purity was determined by the preparation of the phenyl- and α-naphthylurethans.

(c) **By the Action of Metallic Sodium on Monochlorohydrin.**—One mole of glycerol monochlorohydrin is dissolved in 600–800 cc. of strictly anhydrous ether. This solution is placed in a three-necked round-bottomed flask equipped with a mechanical stirrer through the central neck. One of the side necks is equipped with a baffle to make the stirring more effective. The flask is placed in a bath of running cold water at 10–12°. A maximum of seven-tenths of a mole of metallic sodium in the form of a fine wire is now introduced so that it winds around the stirrer and is thus swept through the solution, keeping the surface clean. The solution is stirred vigorously until the sodium is entirely reacted (from six to eight hours). The salt is then filtered off and thoroughly washed with fresh anhydrous ether. The ether is removed and the glycidol distilled as previously described. One redistillation gives a product of high purity, in yields of 95% calculated from the amount of sodium used. After distillation of the glycidol from the reaction mixture, a large amount of unused monochlorohydrin may be recovered by further distillation of the residue. The yield of glycidol, calculated from the weight of monochlorohydrin actually used—that is, the difference between the weight added and that recovered—is about 90% of redistilled material, boiling over a range of one to two degrees.

Anal. Calcd. for $C_3H_6O_2$: C, 48.62; H, 8.17. Found: C, 48.66; H, 8.13.

Glycidol is soluble in ether, alcohol, water, acetone, chloroform and benzene; it is but slightly soluble in petroleum ether and xylene. At a pressure of 2–2.5 mm. it distils at 65–66°, and at a pressure of 1 mm., using an oil-bath at 72°, it distils at a temperature of 41°. Glycidol, as thrice distilled in a vacuum in a stream of dry nitrogen, has d^{25} 1.1143 and n_D^{25} 1.4302. Thus purified it does not reduce Fehling's solution, nor does it give a mirror with ammoniacal silver nitrate either at room temperature or on warming. Tests for the isomeric acetol are negative. Glycidol is fairly stable, when pure, toward distilled water or absolute alcohol, even when heated on a steam-bath for an hour. It is slowly polymerized by pyridine, with evolution of heat, to a water-soluble black tar. With solid calcium chloride it polymerizes more rapidly, with great evolution of heat, to a water-soluble red tar. Several of the properties described by the writers are at variance with the previous literature. Thus Hanriot[8] reports that glycidol is insoluble in benzene and is polymerized by a trace of moisture. Gegerfelt[2] and Breslauer[2] state that it gives a mirror with ammoniacal silver nitrate, and other such references are found. It is evident that the glycidol used by the majority of investigators has been of doubtful purity.

Phenylurethan of Glycidol.—Equimolecular amounts of phenyl isocyanate and glycidol are heated on a steam-bath in ethereal solution for twelve hours. On removal of the ether an oil is obtained which solidifies when stirred with cold water. It is soluble in ether, alcohol and acetone, and insoluble in water and cold petroleum ether. It crystallizes from high-boiling petroleum ether in colorless needles which melt at 60°. The yield is over 90%.

Anal. Calcd. for $C_{10}H_{11}O_3N$: N, 7.25. Found: N, 7.20, 7.20.

α-Naphthylurethan of Glycidol.—Equimolecular amounts of α-naphthyl isocyanate and glycidol are heated on the steam-bath for twelve hours in the absence of a solvent. By dissolving the residue in acetone and then adding cold water, the solid urethan is obtained in good yields. It may be purified by recrystallization from high-boiling petroleum ether, out of which it separates in colorless needles which melt at 102°. The solubilities are similar to those of the phenylurethan.

Anal. Calcd. for $C_{14}H_{13}O_3N$: N, 5.76. Found: N, 5.57, 5.76.

Summary

1. The writers have prepared the phenylurethans of the isomeric glycerol α- and β-monochlorohydrins, and have found that these derivatives are suitable for a qualitative differentiation of the two forms.

2. Glycerol α-monochlorohydrin has been prepared by a new and simple procedure which gives yields considerably higher than those heretofore obtained.

3. Various methods for the preparation of glycidol, or epihydrin alcohol, have been investigated and a method is described whereby pure glycidol may be obtained in yields of 90% through the interaction of monochlorohydrin and metallic sodium.

4. The properties of glycidol have been described, and attention called to several errors found in the previous literature.

5. The phenyl- and α-naphthylurethans of glycidol have been prepared and found suitable for its identification.

New Haven, Connecticut

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[8] Hanriot, *Ann. chim.*, [5] **17**, 62 (1879).