

3. Long fiber cotton has been oxidized with potassium dichromate and potassium permanganate, extracted with 17.5% sodium hydroxide and the optical rotations have been determined.

4. Photomicrographs showing fiber breakdown are given.

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### THE ALIPHATIC DIOLEFINS. III. THE BEHAVIOR OF $\Delta$ -1,5-HEXADIENE AND $\Delta$ -2,4-HEXADIENE TOWARD HYDROCHLORIC ACID

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In a previous paper from this Laboratory,<sup>2</sup> it was shown that  $\Delta$ -1,5-hexadiene, when treated with sulfuric acid, gives either esters of hexanediol-2,5 and its internal ether, or polymers, according to the temperature and acid concentration employed. It was shown, further, that the polymers are not formed from the hydrocarbon, but are condensation products of the internal ether. The behavior of this hydrocarbon toward hydrochloric acid is analogous. Mainly a mixture of 5-chloro-1-hexene and 2,5-dichlorohexanes is formed, together with some diallyl oxide and a trace of its condensation products. On the other hand, the conjugated isomer,  $\Delta$ -2,4-hexadiene, gives a mixture of monochlorohexenes and polymers. No dichlorohexanes are obtained.

#### Experimental Work

**The Action of Hydrochloric Acid on  $\Delta$ -1,5-Hexadiene.**—Wurtz<sup>3</sup> obtained a mixture of 5-chloro-1-hexene, boiling at 130–140°, and 2,5-dichlorohexane, boiling at 170–180°, when he treated  $\Delta$ -1,5-hexadiene with concentrated hydrochloric acid in sealed tubes. Both were analyzed for chlorine.

In our work 100 cc. of diallyl was shaken with 500 cc. of concentrated hydrochloric acid for 120 hours. A deep green layer of 96 cc. resulted. It was washed with 15%

TABLE I  
 CONSTANTS OBTAINED FOR THE COMPOUNDS

	5-Chloro-1-hexene		2,5-Dichlorohexane	
	Boiling point, °C. (mm.)	28–30 (13)	43–45 (45)	56–58 (9)
Density, $d_4$	0.9141 <sup>20°</sup>	0.8891 <sup>25°</sup>	1.0686 <sup>0°</sup>	1.0441 <sup>25°</sup>
Index of refr., $n_D$	1.4332 <sup>15°</sup>	1.4305 <sup>20°</sup>	1.4279 <sup>25°</sup>	1.4487 <sup>15°</sup>
Molecular refr.	Calcd. 34.34	Found 34.31	Calcd. 39.32	Found 39.64

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<sup>2</sup> Cortese, *Ber.*, **62**, 504 (1929).

<sup>3</sup> Wurtz, *Ann. chim. phys.*, [4] **3**, 155 (1864).

sodium chloride, 5% sodium hydroxide, again with 15% sodium chloride, dried over calcium chloride and fractionally distilled. The yield of combined chloro compounds was found to be 80%, 57% being the dichloro and 23% the monochloro. The rest of the yield could be accounted for as diallyl oxide with a small amount of its polymeric condensation products.

**Meso-2,5-dichlorohexane.**—As our product of 2,5-dichlorohexane was evidently a mixture of stereoisomers, it was desirable to isolate the two forms. This was done by chilling to  $-50^{\circ}$  and separating the crystals which deposited from the mother liquor by means of the centrifugal filtration device of E. L. Skau.<sup>4</sup> The solid form obtained was presumably the meso form, thus isolated for the first time. It was recrystallized from pentane and distilled. Constants of the meso form: b. p. 177.8–178.2° (corr. at 751.8 mm.); f. p. (by cooling curve) 18.7°; m. p. (by heating curve) 18.7°;  $d_4^{25}$  1.0459.

The liquid residue (mother liquor from the meso crystalline form) now presumably enriched in the racemic form was distilled and a fraction obtained having a boiling range of one degree. That it had a slightly higher boiling point and lower density than the original mixture is shown by the data given—liquid residue: b. p. 176.4–177.4° (corr. at 751.1 mm.);  $d_4^{25}$  1.0431;  $d_4^{26}$  1.0675.

### Behavior of $\Delta$ -2,4-Hexadiene toward Hydrochloric Acid

I. **Toward Concentrated Aqueous Acid.**—Fifty cc. of hydrocarbon was shaken with 250 cc. of concentrated acid for twenty hours. The 50-cc. dark violet layer was washed with 10% sodium hydroxide, 15% sodium chloride, shaken with calcium chloride and dried over pearl ash. It was separated into three portions by fractionation.

(1). 13 g.: b. p. 21–25° at 6.5 mm.; colorless, mild rancid odor; turns yellow on standing. B. p. 122–126° at 760 mm.;  $d_4^{20}$  0.9111;  $d_4^{25}$  0.8865;  $n_D^{15}$  1.4417;  $n_D^{25}$  1.4360. It titrated for one double bond. Molecular refraction found, 34.92; calculated, 34.31. It was evidently a mixture of monochlorohexenes.

(2). 10 g.: b. p. 81–84° at 4.5 mm.; light yellow; faint parsley odor; deeper yellow on standing. B. p. 213–223° at 760 mm. Distillate intense violet, fumes with hydrogen chloride and has strong odor of parsley. (Vacuum distilled sample):  $d_4^{24}$  0.9002;  $d_4^{25}$  0.8801;  $n_D^{24}$  1.4670. Titrated for one double bond, if assumed to be the dimer. *Anal.* (Parr bomb.). Calcd. for dichlorohexanes: Cl, 45.8 and for dimer monochloride ( $C_8H_{10}$ )<sub>2</sub>HCl:Cl, 17.7. Found: Cl, 15.7.

Shaking with excess standard sodium hydroxide and titrating the unused alkali with standard acid, using phenolphthalein as the indicator, showed that the chlorine content is practically all hydrolyzable in the cold by *N*/10 sodium hydroxide.

Both density and boiling point exclude the possibility of dichlorohexanes. This fraction probably consists of a mixture largely of dimer monochloride, some dimer and a little free hydrochloric acid.

(3). Tar residue.

II. **Toward Alcoholic Hydrochloric Acid.**—Five cc. of  $\Delta$ -2,4-hexadiene was dissolved in 50 cc. of 95% alcohol saturated with hydrochloric acid gas. The opalescent solution very soon developed a pink color. In one hour it was deep violet with colorless oil drops settling out. In three hours it was opaque deep purple with more oil drops. After one week it was deep purple-red, but the odor of unchanged hydrocarbon was very strong. It was diluted with water, which changed the color to light yellow. The yellow oil was washed with water, dried with pearl ash and distilled. It was found that only two-fifths of the hydrocarbon had been attacked; one-half of this was ac-

<sup>4</sup> For a description of this device, together with its use in separating the meso-2,5-dichlorohexane described here, see Skau, *J. Phys. Chem.*, **33**, 951 (1929).

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.<sup>5</sup>

### Summary

1. Hydrochloric acid reacts with  $\Delta$ -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  $\Delta$ -2,4-hexadiene to give a mixture of monochlorohexanes and polymeric products of the hydrocarbon.

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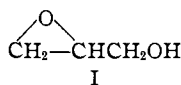
## STUDIES OF GLYCIDOL. I. PREPARATION FROM GLYCEROL MONOCHLOROHYDRIN<sup>1</sup>

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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.



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

<sup>5</sup> Cf. McCullough and Cortese, *THIS JOURNAL*, 51, 225 (1929).

<sup>1</sup> 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.