## Summary

The non-catalytic polymerization and hydrogenation of ethylene has been studied, the former between 450 and 600° and the latter between 550 and 600°. The polymerization reaction probably first produces butylene. It gives evidence of being of the chain type, and is certainly not conventional in its mechanism. The hydrogenation reaction appears to be closely coupled with the polymerization. Its rate is of the same order. Ethylene which would have polymerized is largely converted to ethane in presence of hydrogen.
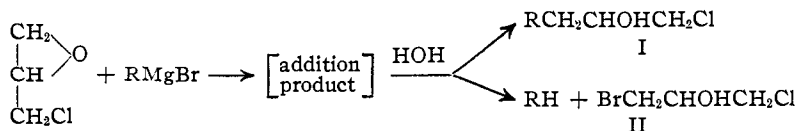
PRINCETON, NEW JERSEY

---

# THE REACTION OF VARIOUS GRIGNARD REAGENTS WITH EPICHLOROHYDRIN. THE PREPARATION OF SOME NEW CHLOROHYDRINS

BY C. FREDERICK KOELSCH AND S. M. McELVAIN

The reaction between epichlorohydrin and various Grignard reagents has been studied by Fourneau and Tiffeneau.[1] These investigators reported that they were unable to isolate any product formed by the development of a new carbon to carbon linkage when Grignard reagents derived from ethyl, propyl, butyl or amyl bromides were allowed to react with epichlorohydrin; in all cases the sole products obtained were the hydrocarbons formed by the hydrolysis of the Grignard reagent used, and glycerol chlorobromohydrin. However, when phenyl-, benzyl- or $p$-anisylmagnesium bromide was allowed to react with epichlorohydrin, they found that an appreciable yield of a chlorohydrin with a structure (I) could be isolated along with the hydrocarbon and glycerol chlorobromohydrin (II). These reactions may be indicated thus

$$\begin{array}{c} CH_2 \\ | \phantom{xx} \diagdown O \\ CH \diagup \\ | \\ CH_2Cl \end{array} + RMgBr \longrightarrow \left[ \begin{array}{c} \text{addition} \\ \text{product} \end{array} \right] \xrightarrow{HOH} \begin{array}{l} \nearrow RCH_2CHOHCH_2Cl \\ \phantom{\nearrow RCH_2CH} I \\ \searrow RH + BrCH_2CHOHCH_2Cl \\ \phantom{\searrow RH + BrCH_2CH} II \end{array}$$

In a previous paper[2] from this Laboratory it was shown that it was possible to isolate a chlorohydrin with the structure of I from the reaction of ethylmagnesium bromide and epichlorohydrin. Since this result was so different from that obtained by Fourneau and Tiffeneau, it seemed advisable to extend the study of the reaction to some of the higher alkyl

---

[1] Fourneau and Tiffeneau, *Bull. soc. chim.*, [4] **1**, 1227 (1907).

[2] Koelsch and McElvain, THIS JOURNAL, **51**, 3390 (1929).

groups and to ascertain, if possible, the effect of the structure of the group upon the course of the reaction.

This paper is a report of the results obtained by the reaction of epichlorohydrin with Grignard reagents prepared from sixteen different organic halides. The halide, the amount of epichlorohydrin used and the yields of the chlorohydrins (based on the amount of epichlorohydrin used) that were isolated are summarized in Table I. The numbers preceding each halide are used in the subsequent tables and discussion to designate the corresponding chlorohydrin or its derivative.

TABLE I

REAGENTS, QUANTITIES AND YIELDS

| | RX | Amount[a] of epichloro-hydrin used, g. | Yield of chlorohydrin g. | % | | RX | Amount[a] of epichloro-hydrin used, g. | Yield of chlorohydrin g. | % |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $C_2H_5Br$[b] | 92.5 | 23.0 | 19 | 9 | $(C_2H_5)_2CHCl$ | 29.4 | 5.7 | 10.9 |
| 2 | $n$-$C_3H_7I$[c] | 44 | 2.5[d] | 3.9[d] | 10 | $C_6H_{11}Cl$[e] | 40.6 | 11.9 | 15.3 |
| 3 | $iso$-$C_3H_7I$[c] | 32.5 | 0 | 0 | 11 | $C_6H_{11}CH_2Cl$[e] | 24.0 | 14.7 | 29.9 |
| 4 | $iso$-$C_3H_7Br$ | 42.0 | 0 | 0 | 12 | $C_6H_{10}(CH_3)Cl$ (1,1)[e] | 5.7 | 0 | 0 |
| 5 | $n$-$C_4H_9Cl$ | 46.2 | 12.0 | 16.0 | 13 | $C_6H_5Br$ | 25.9 | 8.7 | 18.2 |
| 6 | $sec.$-$C_4H_9Cl$ | 38.8 | 3.8 | 9.0 | 14 | $C_6H_5CH_2Cl$ | 31.0 | 19.7[f] | 32.0 |
| 7 | $tert.$-$C_4H_9Cl$ | 23.0 | 0 | 0 | 15 | $C_6H_5(CH_2)_2Cl$ | 28.0 | 7.9 | 12.8 |
| 8 | $n$-$C_5H_{11}Cl$ | 39.8 | 21.0 | 29.8 | 16 | $C_6H_5(CH_2)_3Cl$ | 20.0 | 11.5 | 25.0 |

[a] The amount of epichlorohydrin used was equivalent to the amount of RMgX actually present after the reaction of RX and Mg. [b] Koelsch and McElvain, Ref. 2. [c] The iodide was used in order that chloro-iodohydrin be formed, the higher boiling point of which permitted a better separation of the chlorohydrin by fractional distillation. The latter compound boils too near to the dichlorohydrin and the chlorobromohydrin for satisfactory fractionation. The chlorides were used in the other cases because the chlorohydrins formed have higher boiling points than glycerol dichlorohydrin, and as the size of R increases the greater the difference in the boiling points becomes. [d] This chlorohydrin was not quite pure. It was analyzed as the 3,5-dinitrobenzoate. [e] Cyclohexyl. [f] 7.8 g. of a tarry residue, not volatile at 5 mm.,[3] which was not further investigated, was left after the distillation of this chlorohydrin.

The structures of the chlorohydrins formed have been definitely established in a few cases. The chlorohydrin resulting from the action of ethylmagnesium bromide on epichlorohydrin has been shown[2] to have a structure corresponding to I. Fourneau and Tiffeneau[1] showed that phenylmagnesium bromide and $p$-anisylmagnesium bromide produced chlorohydrins with the structure of I. The chlorohydrin resulting from the action of $n$-butylmagnesium chloride on epichlorohydrin has the same boiling point as 1-chloroheptanol-2 which has been prepared[4] by an entirely different reaction. 1-Chloro-3-cyclohexylpropanol-2 was prepared

[3] This fact indicates that the residue was not 1,5-diphenylpentanol-3; cf. Borsche and Wollemann, Ber., 45, 3721 (1912).

[4] V. Braun and Schirmacher, ibid., 56B, 1847 (1923).

by the addition of hypochlorous acid[5] to 3-cyclohexylpropene-1. This chlorohydrin was found to be identical with the one obtained by the action of cyclohexylmagnesium chloride on epichlorohydrin.

In these representative cases it is seen that the new carbon to carbon linkage is established on the primary carbon atom of epichlorohydrin to produce a chlorohydrin with the structure of I. For this reason it was assumed that other chlorohydrins had this structure rather than the isomeric structure, $ClCH_2CHRCH_2OH$.

## Experimental

**Preparation of the Alkyl Halides.**—The iodides were prepared from the alcohols with phosphorus and iodine. The other halides were prepared by the action of the halogen acids on the corresponding alcohols, except in the case of cyclohexylchloromethane. This halide was prepared by the action of thionyl chloride on cyclohexylcarbinol in the presence of diethylaniline. The physical properties of 3-chloropentane and cyclohexylchloromethane differed materially from those reported in the literature for these compounds. Wagner and Saytzeff[6] prepared 3-chloropentane by the action of phosphorus pentachloride on diethylcarbinol. They report the following constants for this halide: b. p. 103–105° (759 mm.); $d_0$ 0.916; $d_{21}$ 0.895. These values appear in the "International Critical Tables." The constants found for this compound in the present work are: b. p. 96–97° (729 mm.); $d_{25}^{25}$ 0.8724; $n_D^{25}$ 1.4073; $M_D$ calcd. 30.064; found, 30.057. Gutt[7] prepared cyclohexylchloromethane from cyclohexylcarbinol and phosphorus pentachloride and reported the following constants: b. p. 98–99° (100 mm.); $d_4^{22}$ 0.9637; $n_D^{22}$ 1.4565; $M_D$ calcd., 37.17; found, 37.41. The 3-chloro-pentane prepared in the present work has the following constants: b. p. 67–68° (20 mm.); $d_{25}^{25}$ 0.9815; $n_D^{25}$ 1.4630; $M_D$, calcd., 37.168; found, 37.179.

**Preparation of the Chlorohydrins.**—To 0.25–0.5 atom of magnesium turnings covered with 100–200 cc. of ether was added a few cc. of a solution of an equivalent amount of the halide in twice its volume of ether. A small crystal of iodine was added and the reaction was started by heating. The remainder of the halide solution was added slowly with stirring and the mixture then refluxed for half an hour on a water-bath. The solution of the Grignard reagent was cooled and transferred to a long, graduated, cylindrical dropping funnel, where its volume was measured. Two cc. of the solution was pipetted out and added to 5 cc. of 1.0 N hydrochloric acid dissolved in 20 cc. of water. The solution was warmed to dissolve the magnesium hydroxide and to remove the ether, and the excess acid was titrated with $N/10$ sodium hydroxide solution.[8] In the preparation of the Grignard reagents from the tertiary alkyl halides, the quantity of ether used was twice that given above, and the magnesium chloride etherate formed as a by-product in the preparation of the Grignard reagent was removed by centrifuging and decanting the supernatant liquid.

The Grignard reagent was added from the dropping funnel to a solution of an equivalent amount of epichlorohydrin in an equal volume of ether, the rate of addition being

---

[5] Michael has shown [*J. prakt. Chem.*, [2] **64**, 105 (1901)] that in the addition of hypochlorous acid to an unsymmetrical olefin, the hydroxyl group of the hypochlorous acid becomes attached to the carbon atom poorer in hydrogen. This generalization is in accord with the fact that the two chlorohydrins mentioned above are identical.

[6] Wagner and Saytzeff, *Ann.*, **179**, 321 (1875).

[7] Gutt, *Ber.*, **40**, 2067 (1907).

[8] *Cf.* Gilman and others, THIS JOURNAL, **45**, 153 (1923).

regulated so that the mixture refluxed gently. After the addition was completed, the refluxing was continued on a water-bath for one hour; finally the mixture was allowed to stand at room temperature for twenty-four hours. The mixture was then hydrolyzed with ice and dilute sulfuric acid and the ether layer separated. The ether solution was washed with dilute sodium carbonate solution and finally with water. The ether was distilled off through a fractionating column, and the residue was fractionally distilled under diminished pressure. The product was separated by repeated fractional distillation into: (a) the chlorohydrin, (b) glycerol dichlorohydrin (or the corresponding bromo- or iodo- compound), and in some cases (c) the hydrocarbon formed by the hydrolysis of the Grignard reagent. Fractions (b) and (c) were identified by boiling points and densities. The yields of the chlorohydrins (fraction a) are shown in Table I and the physical constants and analyses in Table II.

TABLE II

PHYSICAL CONSTANTS AND ANALYSES OF THE CHLOROHYDRINS

| No. | Chlorohydrin | Boiling point, uncorrected °C. | Mm. |
|---|---|---|---|
| 2 | 1-Chlorohexanol-2 | 72–74 | 12 |
| 5 | 1-Chloroheptanol-2 | 92–94 | 13 |
| 6 | 1-Chloro-4-methylhexanol-2 | 82–84 | 13 |
| 8 | 1-Chloro-octanol-2 | 104–107 | 13 |
| 9 | 1-Chloro-4-ethylhexanol-2 | 103–104 | 15 |
| 10 | 1-Chloro-3-cyclohexylpropanol-2 | 122–124 | 11 |
| 11 | 1-Chloro-4-cyclohexylbutanol-2 | 142–144 | 12 |
| 13 | 1-Chloro-3-phenylpropanol-2 | 142–144 | 23 |
| 14 | 1-Chloro-4-phenylbutanol-2 | 158–160 | 23 |
| 15 | 1-Chloro-5-phenylpentanol-2 | 152–154 | 8 |
| 16 | 1-Chloro-6-phenylhexanol-2 | 147–148 | 2.5 |

| No. | Formula | $d_{25}^{25}$ | $n_D^{25}$ | $M_D$ Calcd. | Found | Chlorine (Carius), % Calcd. | Found |
|---|---|---|---|---|---|---|---|
| 5 | $C_7H_{15}OCl$ | 0.9931 | 1.4474 | 40.79 | 40.73 | 23.6 | 23.9 |
| 6 | $C_7H_{15}OCl$ | 0.9915 | 1.4503 | 40.79 | 40.83 | 23.6 | 23.5 |
| 8 | $C_8H_{17}OCl$ | 0.9715 | 1.4485 | 45.39 | 45.36 | 21.6 | 21.2 |
| 9 | $C_8H_{17}OCl$ | 0.9828 | 1.4528 | 45.39 | 45.23 | 21.6 | 21.4 |
| 10 | $C_9H_{17}OCl$ | 1.0533 | 1.4854 | 47.89 | 48.06 | 20.1 | 20.1 |
| 11 | $C_{10}H_{19}OCl$ | 1.0305 | 1.4832 | 52.50 | 52.70 | 18.6 | 18.0 |
| 13 | $C_9H_{11}OCl$ | 1.1528 | 1.5470 | 46.71 | 46.90 | 20.8 | 20.0 |
| 14 | $C_{10}H_{13}OCl$ | 1.1203 | 1.5375 | 51.41 | 51.48 | 19.2 | 19.3 |
| 15 | $C_{11}H_{15}OCl$ | 1.0895 | 1.5320 | 56.17 | 56.45 | 17.9 | 17.9 |
| 16 | $C_{12}H_{17}OCl$ | 1.0710 | 1.5262 | 60.77 | 60.78 | 16.6 | 16.2 |

Preparation of the 3,5-Dinitrobenzoates.—These esters were obtained practically quantitatively by the following procedure. To a mixture of 1.0 g. of the chlorohydrin with 0.8 of the theoretical amount of 3,5-dinitrobenzoyl chloride was added 5 cc. of dry pyridine. The mixture was stoppered and shaken, and allowed to stand overnight. Water was then added and the separated oil taken up in ether. The ethereal solution was washed with dilute hydrochloric acid, water, dilute sodium carbonate solution and finally again with water. The ether was evaporated off and the residual ester was crystallized from alcohol until its melting point was not changed by further crystallization. The melting points and analyses of these esters are given in Table III.

3-Cyclohexylpropylene-1,2-oxide.—It seemed that the structure of the chlorohydrin derived from cyclohexylmagnesium chloride and epichlorohydrin might be

TABLE III

ANALYSES AND MELTING POINTS OF THE 3,5-DINITROBENZOATES OF THE CHLOROHYDRINS

| No.[a] | M. p., °C. (uncorr.) | Formula | Chlorine (Carius), % Calcd. | Found |
|---|---|---|---|---|
| 2 | 65–66 | $C_{13}H_{15}O_6N_2Cl$ | 11.0 | 10.7 |
| 5 | 59 | $C_{14}H_{17}O_6N_2Cl$ | 10.3 | 10.5 |
| 6 | 49–50 | $C_{14}H_{17}O_6N_2Cl$ | 10.3 | 10.3 |
| 8 | 55 | $C_{15}H_{19}O_6N_2Cl$ | 9.9 | 10.0 |
| 9 | Oil | $C_{15}H_{19}O_6N_2Cl$ | ... | ... |
| 10 | 95–96 | $C_{16}H_{19}O_6N_2Cl$ | 9.59 | 9.58 |
| 11 | 107–108 | $C_{17}H_{21}O_6N_2Cl$ | 9.23 | 9.32 |
| 13 | 120–121 | $C_{16}H_{18}O_6N_2Cl$ | 9.75 | 9.72 |
| 14 | Oil | $C_{17}H_{15}O_6N_2Cl$ | ... | ... |
| 15 | 106–107 | $C_{18}H_{17}O_6N_2Cl$ | 9.04 | 9.01 |
| 16 | Oil | $C_{19}H_{19}O_6N_2Cl$ | ... | ... |

[a] The numbers in this column indicate the 3,5-dinitrobenzoates of the correspondingly numbered chlorohydrins of Table II.

definitely established by converting it into 3-cyclohexylpropylene-1,2-oxide which has been described by Rességuier.[9] Accordingly a solution of 8.87 g. (0.05 mole) of the chlorohydrin in dry ether was treated with 2.2 g. (0.057 mole) of finely powdered sodium hydroxide. The flask was stoppered tightly and shaken intermittently for four hours. The mixture was then allowed to stand for twelve hours at room temperature, after which it was refluxed for thirty minutes. The reaction mixture was then cooled and filtered and the solid residue washed with three 10-cc. portions of dry ether. After removal of the ether the remaining oxide was distilled. The distillate weighed 3.69 g. and boiled at 197–200° (740 mm.); $d_{25}^{25}$ 0.9357, $n_D^{25}$ 1.4572; $M_D$, calcd., 41.008; found, 40.859.

*Anal.* Subs., 0.2707: $CO_2$, 0.7670; $H_2O$, 0.2792. Calcd. for $C_9H_{16}O$: C, 77.13; H, 11.43. Found: C, 77.25; H, 11.51.

Rességuier reports the following constants for this oxide: b. p. 182–185°; $d_0$ 1.003. Since the constants of the oxide as found in the present work differ so markedly from those of Rességuier, and since the chlorohydrin from which the oxide was derived is shown below to be 1-chloro-3-cyclohexylpropanol-2, it is necessary to conclude that Rességuier's oxide was quite impure.

1-Chloro-3-cyclohexylpropanol-2 from 3-Cyclohexylpropene-1.—Since it was not possible to establish the structure of the chlorohydrin by comparing the oxide derived from it with Rességuier's 3-cyclohexylpropylene-1,2-oxide, it was necessary to prepare 1-chloro-3-cyclohexylpropanol-2. This was accomplished in the following manner. A solution of hypochlorous acid was prepared according to the directions of Wohl.[10] To 500 cc. of this solution (titrating 1.9% HOCl) was added 22 g. of 3-cyclohexyl-propene-1 (prepared from allyl bromide and cyclohexylmagnesium chloride), the temperature being kept at about 10° during the addition. The mixture was stirred for two hours and allowed to stand at room temperature overnight. The heavy oil was separated. The aqueous portion of the reaction mixture was extracted twice with 50-cc. portions of ether and the oil obtained from these extracts after evaporating off the ether was added to the main portion. The oil was washed with a little sodium bisulfite solution and finally with a little water. It was then distilled at 13 mm. and the following fractions collected: 118–123° (8.8 g.); 123–133° (3.3 g.); residue, not volatile without decom-

[9] Rességuier, *Bull. soc. chim.*, [4] 15, 175 (1914).

[10] Wohl, *Ber.*, 40, 94 (1907).

position (14.5 g.).   One gram of the fraction boiling at 118–123° was converted into the 3,5-dinitrobenzoate, which melted at 95–96°.   The melting point of a mixture of this 3,5-dinitrobenzoate with the 3,5-dinitrobenzoate of the chlorohydrin prepared from epichlorohydrin and cyclohexylmagnesium chloride was 95–96°.   This comparison leaves no doubt as to the structure of the latter compound.

Oxidation of 1-Chloro-4-phenylbutanol-2 to Benzoic Acid.—In view of the frequent formation of *o*-tolyl compounds from benzylmagnesium chloride and carbonyl compounds,[11] it seemed advisable to determine whether the chlorohydrin resulting from the action of benzylmagnesium chloride on epichlorohydrin contained the phenyl or the tolyl radical.   This was done by oxidizing the chlorohydrin with potassium permanganate to benzoic acid, which was identified by its melting point and neutral equivalent.

## Discussion of Results

The yield of chlorohydrin obtained by the reaction of epichlorohydrin with an alkylmagnesium halide seems to depend on the structure and on the molecular weight of the latter.   The Grignard reagents derived from the primary alkyl halides gave much higher yields than those derived from secondary alkyl halides, while those from the tertiary alkyl halides gave such small yields of chlorohydrins (if any at all) that these compounds could not be isolated from the reaction mixtures.   Apparently the nature of the halogen is not without effect on the yield.   Although no particular study was made of this effect, the reaction of *n*-propylmagnesium iodide with epichlorohydrin to give a yield of only 3.9% indicates that the alkylmagnesium iodides give a smaller yield of chlorohydrin than do the chlorides or bromides.   It was also noted that as the weight of the alkyl radical became greater, the yield of chlorohydrin was raised (*cf.* Nos. 5, 8, 11; Nos. 4, 6, 9 and 10, Table I).   The introduction of an aromatic group into the Grignard reagent caused the yield in some cases to rise above, and in others to fall below, that which would be expected from a Grignard reagent containing an alkyl group of an equal size.   There appears to be a certain periodicity in the yield of chlorohydrin from these phenyl-substituted Grignard reagents (Nos. 13, 14, 15 and 16, Table I) but the data at hand are hardly sufficient to warrant any definite conclusions on this point.

## Summary

1.   The reaction between epichlorohydrin and sixteen different Grignard reagents has been studied.   It has been shown that 1,2-chlorohydrins are formed when the Grignard reagents are derived from primary and secondary (except isopropyl) alkyl halides.

2.   The effect of the structure of the Grignard reagent on the course of the reaction is discussed.

MADISON, WISCONSIN

[11] Gilman and Harris, THIS JOURNAL, **49**, 1825 (1927).