LXXVII.—*The Condensation of Epichlorohydrin with Phenols.*

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OUR attention has recently been drawn to a paper on the above subject by Cohn and Plohn (*Ber.*, 1907, **40**, 2597), in which paper the authors describe some experiments on the action of epichlorohydrin on alkaline solutions of phenols, and maintain that, as the result of their experiments, certain data in the literature require correction.

The data which it is proposed to alter are those established by Lindemann (*Ber.*, 1891, **24**, 2145). This investigator found (1) that by the action of epichlorohydrin on a cold solution of phenol in aqueous sodium hydroxide an oil is obtained (b. p. 234°), to which he assigned the formula $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}\begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix}$, and (2) that if epichlorohydrin

is boiled for a short time with an alcoholic solution of phenol and sodium ethoxide a crystalline substance is formed (m. p. 80—81°), to which he assigned the formula $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_5$.

Lindemann further states that the phenyl glycid ether is converted into the glyceryl diphenyl ether by boiling with an alcoholic solution of phenol and sodium ethoxide.

It is now maintained by Cohn and Plohn that the oil and the crystalline compound obtained by Lindemann are really identical; the oil, according to their statement, changing into the crystals if allowed to stand for some time. Moreover, Cohn and Plohn have analysed the crystalline compound, and obtained figures which lead them to assign to it the formula $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}\begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix}$.

These conclusions of Cohn and Plohn we cannot accept.

The formula $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}\begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix}$ for the crystalline compound is quite inconsistent with the results obtained by one of us (Boyd, *Trans.*, 1901, **79**, 1221) in a study of the action of the chlorides of phosphorus on this substance. It was then shown that this compound is converted by means of phosphorus trichloride into a phosphorous acid derivative, the analysis and reactions of which pointed clearly to the formula $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}(\text{OPH}_2\text{O}_2)\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_5$, whilst phosphorus pentachloride transforms it into a substance for which analysis indicates the formula $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_5$.

These results confirm Lindemann's conception of the crystalline compound as a glyceryl diphenyl ether,

In view, however, of the statements of Cohn and Plohn, we have thought it desirable again to prepare and analyse a specimen of the crystalline substance. Our results are in complete agreement with the formula assigned by Lindemann.

With regard to the constitution of the oil, the data in the literature are not so complete. In addition therefore to analysing this substance, we have studied its transformation into glyceryl diphenyl ether by the action of phenol in presence of alkali, and have also investigated its behaviour towards phosphorus pentachloride. Assuming Lindemann's formula $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{O} \end{smallmatrix}$ to be correct, one would expect to obtain a substance of the formula $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CHCl}\cdot\text{CH}_2\text{Cl}$ as the principal product of the action of phosphorus pentachloride. This expectation was fully realised, the yield of phenoxydichloropropane amounting to 63 per cent. of that theoretically possible.

If the oil is allowed to stand in contact with a solution of phenol in aqueous potassium hydroxide, it reacts slowly even in the cold to form glyceryl diphenyl ether, and this change is brought about rapidly on heating an alcoholic solution of it with phenol and sodium ethoxide. From 2.18 grams of the oil, we obtained in this way 3.03 grams of the crystals, or about 85 per cent. of the theoretical yield. These results, we consider, definitely establish the formula $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{O} \end{smallmatrix}$ for the oil.

We are at a loss to account for the statement of Cohn and Plohn that the oil changes into the crystalline compound on standing, except on the supposition that these investigators have never obtained the oil in a pure state. A specimen of pure phenyl glycid ether has been kept in this laboratory for a period of more than six months without undergoing any change.

It appears probable that the origin of the errors into which Cohn and Plohn have been led is to be found in the circumstance that in the preparation of phenyl glycid ether by the action of epichlorohydrin on a solution of phenol in aqueous sodium hydroxide it is scarcely possible to avoid the formation of a considerable amount of the crystalline glyceryl diphenyl ether at the same time.

In the case of the action of epichlorohydrin on *p* cresol, precisely similar relations hold good. The crystalline compound (m. p. 88°), which is stated by Cohn and Plohn to have the formula

is really, as stated by Lindemann, the glyceryl di-*p*-tolyl ether, $\text{C}_7\text{H}_7\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_7\text{H}_7$ (compare Boyd, *loc. cit.*, and

Trans., 1903, **88**, 1140), whilst the *p*-tolyl glycide ether is an oil boiling at 136° under 17 mm. pressure.

EXPERIMENTAL.

Glyceryl Diphenyl Ether, $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_5$.

Twelve grams of sodium (rather more than 0.5 gram-atom) were dissolved in 250 c.c. of alcohol. Ninety-four grams of phenol (1 gram-mol.) were added, and then 45 grams of epichlorohydrin (rather less than 0.5 gram-mol.). The mixture was heated in a water-bath under reflux for four hours, and then poured into water. A white, crystalline solid separated. After recrystallisation from alcohol, it melted at 81—82°. The yield was 90 grams.

It is to be noted that the maximum yield of phenyl glycide ether which is theoretically possible from 45 grams of epichlorohydrin is less than 75 grams:

0.2085 gave 0.5659 CO_2 and 0.1277 H_2O . C = 74.02; H = 6.86.

0.2028 „ 0.5494 CO_2 „ 0.1180 H_2O . C = 73.86; H = 6.52.

$\text{C}_{15}\text{H}_{16}\text{O}_3$ requires C = 73.72; H = 6.62 per cent.

Phenyl Glycide Ether, $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}\begin{smallmatrix} \diagup \text{CH}_2 \\ \diagdown \text{O} \end{smallmatrix}$

Ninety-two and a-half grams of epichlorohydrin (1 mol.) were added to a cold solution of 94 grams of phenol (1 mol.) and 50 grams of sodium hydroxide ($1\frac{1}{4}$ mols.) in 600 c.c. of water.

After twenty-four hours, the oil which had separated was extracted with ether. The ethereal solution was dried over potassium carbonate, the ether evaporated, and the residue, a slightly yellow oil, was fractionated under reduced pressure. In this way, 45 grams of an oil boiling at about 128°/15.5 mm. were obtained.

The oil thus prepared was found to contain a trace of chlorine, due possibly to the presence of a small quantity of glyceryl monochlorohydrin phenyl ether, $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$. Considerable difficulty was experienced in removing the last traces of chlorine, but this was finally accomplished by heating for three-quarters of an hour over powdered sodium hydroxide in a water-bath and subsequently extracting with ether and fractionating in a vacuum.

The pure oil boiled at 133°/23 mm. It distils practically without decomposition at 243—244° (corr.) under atmospheric pressure:

0.2787 gave 0.7354 CO_2 and 0.1618 H_2O . C = 71.96; H = 6.50.

0.2222 „ 0.5859 CO_2 „ 0.1332 H_2O . C = 71.91; H = 6.72.

$\text{C}_9\text{H}_{10}\text{O}_2$ requires C = 71.95; H = 6.73 per cent.

The residue left in the distilling flask after the phenyl glycid ether had passed over was dissolved in hot alcohol, and from this solution about 7.5 grams of crystalline glyceryl diphenyl ether separated on cooling.

Action of Phenyl Glycid Ether on a Cold Solution of Phenol in Aqueous Potassium Hydroxide.

Four grams of phenol were dissolved in 10 c.c. of a solution of potassium hydroxide containing about 2.5 grams, and 2.28 grams of phenyl glycid ether were added to the cold solution. The mixture was allowed to stand for six days with occasional shaking. The oil had then changed almost completely into a mass of crystals; steam was now passed through to remove any unchanged phenyl glycid ether, and the solid product obtained on cooling was crystallised from alcohol. The crystals obtained weighed 3.04 grams and melted at 81–82°. The yield is thus 82 per cent. of that required by theory.

Action of Phenyl Glycid Ether on a Hot Alcoholic Solution of Phenol and Sodium Ethoxide.

Six grams of phenol and 0.2 gram of sodium were dissolved in 25 c.c. of alcohol, 2.18 grams of phenyl glycid ether were added, and the mixture was heated on a water-bath under reflux for fifteen hours. The bulk of the alcohol was then distilled off, and water and potassium hydroxide were added. The solid substance which separated was collected, washed, and drained. It was then dissolved in ether, and the ethereal solution was shaken several times with potassium hydroxide to ensure complete removal of the excess of phenol. After evaporation of the ether, the product was crystallised from alcohol. The melting point of the crystals was 80°, and the yield was 3.03 grams or 85.5 per cent. of the theoretical.

Action of Phosphorus Pentachloride on Phenyl Glycid Ether. Preparation of Phenoxydichloropropane, $C_6H_5 \cdot O \cdot CH_2 \cdot CHCl \cdot CH_2Cl$.

Twenty grams of phenyl glycid ether were dissolved in 50 grams of chloroform, and the solution added by means of a tap-funnel to 40 grams of phosphorus pentachloride contained in a flask provided with a reflux condenser and cooled in a water-bath. The action is energetic at first. After all the solution had been added, the flask was warmed in the water-bath for some time. The mixture was then cooled, and treated with water and potassium hydroxide until alkaline; the chloroform was distilled off, and the residue extracted with ether. The ethereal solution was dried over potassium carbonate, and the slightly

yellow oil obtained on evaporation of the ether was fractionated in a vacuum. Seventeen grams of a colourless, highly refractive oil boiling at 139—140°/13 mm. were obtained. The yield was thus 63 per cent. of that theoretically possible :

0·3731 gave 0·7260 CO₂ and 0·1728 H₂O. C = 53·07 ; H = 5·18.

0·2335 „ 0·4511 CO₂ „ 0·1048 H₂O. C = 52·69 ; H = 5·02.

0·2363 „ 0·3261 AgCl. Cl = 34·12.

0·2716 „ 0·3801 AgCl. Cl = 34·60.

C₉H₁₀OCl₂ requires C = 52·70 ; H = 4·91 ; Cl = 34·58 per cent.

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