

CXC.—*A New Method for the Preparation of Aryl Ethers of Glycerol α -Monochlorohydrin.*

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IN the preparation of glycidic aryl ethers by the action of epichlorohydrin on a solution of a phenol in excess of sodium hydroxide (Trans., 1908, **93**, 838; 1909, **95**, 1808), we have invariably observed amongst the products of the reaction a small quantity of a compound containing chlorine, which we assumed to be the glycerol α -monochlorohydrin aryl ether, $\text{Ar}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$.

This fact led us to investigate whether sodium hydroxide might be advantageously employed as a catalytic agent to bring about the addition of a phenol to epichlorohydrin. We find that this is so. In the presence of a small quantity of sodium hydroxide, epichlorohydrin and phenol react at the ordinary temperature with moderate rapidity to form γ -chloro- β -hydroxy- α -phenoxypropane. From a mixture of 94 grams of phenol and 92.5 grams of epichlorohydrin, to which 0.5 gram of sodium hydroxide had been added, we obtained, after the mixture had been kept for about three weeks, 66 grams of chlorohydrin ether, boiling at 151—160°/18 mm.; from this, on fractionation, 49 grams, boiling at 155—156°/16 mm., were obtained.

Fischer and Krämer (Ber., 1908, **41**, 2728), following the method of Lindemann (Ber., 1891, **24**, 2145), have prepared the phenyl ether (γ -chloro- β -hydroxy- α -phenoxypropane) by heating epichlorohydrin with phenol in a closed vessel for forty hours at 160°. They give 152—153°/12 mm. as the boiling point of the pure substance. They obtained, from 500 grams of epichlorohydrin and 600 grams of phenol, 173 grams of crude ether, boiling at 135—155°/12 mm.; the yield of the pure compound is not mentioned.

Fourneau (J. Pharm. Chim., 1910, [vii], **1**, 58) gives 25 to 30 grams as the yield of chlorohydrin ether obtained from 65 grams of phenol by the same method, but no boiling point is mentioned.

Fourneau (*loc. cit.*) has also prepared γ -chloro- β -hydroxy- α -phenoxypropane by boiling phenol with a large excess of epichlorohydrin. The yield mentioned is 20 to 22 grams from 35 grams of phenol, but no information is given with regard to the purity of this product. The boiling point given by Fourneau for the pure substance, $170^{\circ}/21$ mm., appears to be considerably too high.

Using Lindemann's method, and heating for ten hours at 150° , we have obtained about 5 grams of γ -chloro- β -hydroxy- α -phenoxypropane, boiling at 152 — $155^{\circ}/12$ mm., from 47 grams of phenol. We were unable to detect the presence of any phenyl glycid ether, which, according to Lindemann, is one of the products formed when epichlorohydrin is heated with phenol.

EXPERIMENTAL.

γ -Chloro- β -hydroxy- α -phenoxypropane, $C_6H_5 \cdot O \cdot CH_2 \cdot CH(OH) \cdot CH_2Cl$.

Half a gram of sodium hydroxide (1/80 mol.), dissolved in about 5 c.c. of water, was added to a mixture of 94 grams of phenol (1 mol.) and 92.5 grams of epichlorohydrin (1 mol.). The mixture formed a clear solution. After it had been kept for about three weeks at the laboratory temperature, it had still a strongly alkaline reaction. It was then treated with ether; the ethereal solution was shaken with dilute sodium hydroxide solution to remove unchanged phenol, and dried over potassium carbonate. On distillation of the product under diminished pressure, 66 grams of γ -chloro- β -hydroxy- α -phenoxypropane, boiling at 151 — $160^{\circ}/18$ mm., were obtained. The residue in the distilling flask was very small in amount. Fractional distillation of the crude ether gave 49 grams of oil, boiling at 155 — $156^{\circ}/16$ mm. The portion analysed boiled at $156^{\circ}/16$ mm. (Found, C=57.90; H=6.11; Cl=18.85. Calc., C=57.89; H=5.94; Cl=19.01 per cent.) Prepared in this way, the ether forms a colourless, somewhat viscous oil, with a scarcely noticeable odour. On treatment with solid potassium hydroxide, it is converted into phenyl glycid ether.

The *phenylurethane*, $C_6H_5 \cdot O \cdot CH_2 \cdot CH(O \cdot CO \cdot NH \cdot C_6H_5) \cdot CH_2Cl$, was prepared by keeping a mixture of the chlorohydrin ether and phenyl isocyanate for twelve days at the ordinary temperature. The solid mass obtained was treated with warm alcohol. The alcoholic solution was filtered, and the *phenylurethane*, obtained on evaporation of the alcohol, was crystallised several times from light petroleum. It forms needles, melting at 70° :

0.2351 gave 0.1111 AgCl. Cl=11.69.

0.4131 „ 16.65 c.c. N_2 (moist) at 20° and 740 mm. N=4.49.

$C_{16}H_{16}O_3NCl$ requires Cl=11.60; N=4.58 per cent.

1790 ARYL ETHERS OF GLYCEROL α -MONOCHLOROHYDRIN *γ -Chloro- β -hydroxy- α -o-tolyloxypropane,*
 $C_7H_7 \cdot O \cdot CH_2 \cdot CH(OH) \cdot CH_2Cl$.

This substance was prepared by the same method as that employed for the phenyl ether. Fifty-four grams of *o*-cresol (1 mol.), 46 grams of epichlorohydrin (1 mol.), and 0.5 gram of sodium hydroxide (1/40 mol.) were used. After nine days the mixture was still strongly alkaline. The yield of crude substance, boiling at 169—172°/22 mm., was 25 grams. The pure ether forms a colourless, somewhat viscous oil, boiling at 166°/18 mm.:

0.2278 gave 0.1627 AgCl. Cl=17.67.

$C_{10}H_{13}O_2Cl$ requires Cl=17.68 per cent.

The *phenylurethane*, $C_7H_7 \cdot O \cdot CH_2 \cdot CH(O \cdot CO \cdot NH \cdot C_6H_5) \cdot CH_2Cl$, prepared as in the previous case, crystallised from a solution in cold alcohol, on addition of a little water, in needles, melting at 81—82°:

0.2715 gave 0.1203 AgCl. Cl=10.96.

0.2843 „, 10.9 c.c. N_2 (moist) at 20° and 744 mm. N=4.29.

$C_{17}H_{18}O_3NCl$ requires Cl=11.09; N=4.38 per cent.

 γ -Chloro- β -hydroxy- α -p-tolyloxypropane,
 $C_7H_7 \cdot O \cdot CH_2 \cdot CH(OH) \cdot CH_2Cl$.

Fifty-seven grams of *p*-cresol, 46 grams of epichlorohydrin, and 1 gram of sodium hydroxide were used, and the mixture was kept for eight days. The yield of crude substance, boiling at 178—183°/30 mm., was 47.5 grams. The pure ether boils at 165°/14 mm., and forms a colourless, rather viscous oil:

0.2036 gave 0.1447 AgCl. Cl=17.58.

$C_{10}H_{13}O_2Cl$ requires Cl=17.68 per cent.

The *phenylurethane*, $C_7H_7 \cdot O \cdot CH_2 \cdot CH(O \cdot CO \cdot NH \cdot C_6H_5) \cdot CH_2Cl$, prepared as in the previous cases, crystallised from alcohol in needles, melting at 113—114°:

0.2349 gave 0.1051 AgCl. Cl=11.06.

0.3017 „, 11.6 c.c. N_2 (moist) at 17.5° and 751 mm. N=4.40.

$C_{17}H_{18}O_3NCl$ requires Cl=11.09; N=4.38 per cent.

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