CC.—*The Action of Potassium Hydroxide on Epichlorohydrin in Presence of Monohydric Phenols.*

By David Runciman Boyd and Ernest Robert Marle.

Under the above title, Zunino has recently published a paper (*Atti R. Accad. Lincei*, 1909, [v], **18**, i, 254), in which certain of the diaryl ethers of glycerol are described.

The author is apparently unaware of the fact that three of the ethers which he describes were prepared some years ago, the diphenyl ether, $OH{\cdot}CH(CH_2{\cdot}OPh)_2$, by Rössing (*Ber.*, 1886, **19**, 63) and Lindeman (*Ber.*, 1891, **24**, 2147), and the di-*o*-tolyl and di-*m*-tolyl ethers by one of us (Boyd, Trans., 1903, **83**, 1137 and 1139). This is the more extraordinary since the question of the constitution of these substances was discussed by us less than a year ago (Trans., 1908, **93**, 838).

Moreover, the statements made by Zunino with regard to the properties of these substances are incorrect.

The diphenyl ether is described as a liquid boiling at 287—288°, whereas it is really a crystalline solid melting at 81—82°, and boiling, with considerable decomposition, at the ordinary pressure at 343—345° (uncorr.).

The di-*o*-tolyl ether is described as a liquid boiling at 296°, whilst, as a matter of fact, it is a solid melting at 36—37°, and boiling at 226°/13 mm.

The di-*m*-tolyl ether is described as boiling at 253—254°, whilst we have found it to boil at 232°/13 mm., and, with considerable decomposition, at 363° under atmospheric pressure.

Two other ethers are described by Zunino, namely, a dithymyl and a dicarvacryl ether, which have not hitherto been prepared. The boiling points assigned to the compounds, however (for the dithymyl ether 215°, for dicarvacryl ether 245°), appeared to us

so improbable that we thought it desirable to investigate the action of epichlorohydrin on thymol in the presence of alkalis.

As a result, we have obtained glycide thymyl ether,

$$O<\begin{matrix}CH\cdot CH_2\cdot O\cdot C_{10}H_{13},\\ |\\ CH_2\end{matrix}$$

and glycerol dithymyl ether, $OH\cdot CH(CH_2\cdot O\cdot C_{10}H_{13})_2$. The former substance is an oil boiling at 158°/16 mm., and the latter is a crystalline solid, melting at 41½—42°, and boiling at 270°/28 mm.

In Zunino's paper, no reference is made to the fact that by the action of epichlorohydrin on phenols in the presence of alkalis two different products may be obtained, namely, (1) the glycide aryl ether, $O<\begin{matrix}CH\cdot CH_2\cdot OR\\ |\\ CH_2\end{matrix}$, and (2) the glycerol diaryl ether,

$$OH\cdot CH(CH_2\cdot OR)_2.$$

We were at first inclined to suppose that the substances obtained by Zunino were really the glycide aryl ethers. However, a comparison of the boiling points recorded with those of the glycide aryl ethers in question shows a wide discrepancy (40—50°), and we can only account for his data by supposing that he was dealing with mixtures of the two substances.

Experimental.

Glycerol Dithymyl Ether, $OH\cdot CH(CH_2\cdot O\cdot C_{10}H_{13})_2$.

This substance was prepared by the method previously described for the diphenyl ether (Trans., 1908, **93**, 840). On pouring the reaction mixture into water, an oil separated. This was extracted with ether, and, after removal of the ether, fractionated under diminished pressure. In this way, a colourless, dense, very viscous oil was obtained, boiling at 270°/28 mm. On keeping, it solidified to a crystalline mass, melting at 41½—42°:

(1) 0·2306 gave 0·6580 CO_2 and 0·1867 H_2O. C = 77·82; H = 9·06.
(2) 0·1297 „ 0·3696 CO_2 „ 0·1069 H_2O. C = 77·70; H = 9·22.

$C_{23}H_{32}O_3$ requires C = 77·52; H = 8·98 per cent.

Thymyl Glycide Ether, $O<\begin{matrix}CH\cdot CH_2\cdot O\cdot C_{10}H_{13}.\\ |\\ CH_2\end{matrix}$

Twenty grams of sodium hydroxide (2 mols.), 35 grams of thymol (rather less than 1 mol.), and 23 grams of epichlorohydrin (1 mol.) were used. The sodium hydroxide was dissolved in 100 c.c. of water, and the thymol added. Epichlorohydrin dissolves completely in this solution, forming a slightly yellow liquid, from which an oil separates on keeping, and rises to the surface. After

four days, the oil was separated, warmed for half an hour with powdered sodium hydroxide on the water-bath, and then dissolved in ether. The ethereal solution was washed with water, dried, and the oil left after evaporation of the ether was fractionated under diminished pressure. A colourless, fairly mobile oil, with a faint odour, was obtained, which boiled at 158°/16 mm. The residue, about half of the original oil, consisted mainly of glycerol dithymyl ether:

(1) 0·2666 gave 0_27440 CO_2 and 0·2114 H_2O. C = 76·10; H = 8·87.
(2) 0·3069 „ 0·8528 CO_2 „ 0·2403 H_2O. C = 75·77; H = 8·77.

$C_{13}H_{18}O_2$ requires C = 75·73; H = 8·74 per cent.

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