267. *The Partial Esterification of Polyhydric Alcohols. Part XIII. Glycerol α-Monophenyl Ether.*

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Specimens of glycerol monophenyl ether prepared by methods already shown (preceding paper) to yield α-isomerides exclusively have been found to possess a double melting point, 54° and 68°, similar to those frequently exhibited by glycerides (see, *e.g.*, Chevreul, "*Recherches chimiques sur les corps gras d'origine animale,*" Paris, 1823; Smits and Bokhorst, *Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 681; Watson, Joglekar, and Rewadikar, *J. Indian Inst. Sci.*, 1930, **13**A, 119, 128) and often attributed to isomeric forms which possess an orthocarboxylic radical (compare Grün, *Ber.*, 1921, **54**, 290; Part VII, J., 1929, 131; Hibbert and Grieg, *Canadian J. Res.*, 1931, **4**, 254; *Ber.*, 1932, **65**, 199). It is believed that this is the first recorded instance of a glycerol *ether* exhibiting the double point; explanations based on orthocarboxylic structure are clearly inapplicable.

Glycerol α-Monophenyl Ether, $PhO\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$.—For references to previous descriptions of this compound, see " Organic Syntheses," 1926, VI, 48.

(*a*) 442 G. of monochlorohydrin were added with mechanical stirring during 2 hours to 376 g. of phenol and 170 g. of sodium hydroxide at 120°; stirring at this temperature was continued for a further hour, and the product was then washed with water and distilled at 145—148°/0·6 mm. (yield, 59%). Recrystallisation of the solidified colourless distillate from benzene–ligroin gave glycerol monophenyl ether, m. p. 67—68°. Fusion and re-solidification caused this figure to change to 53—54°. After 48 hours at room temperature samples of the ether usually again melted at 68°; after 5 months' storage they invariably did so (Found: OH, 20·1. Calc. for $C_9H_{12}O_3$: OH, 20·2%). That it possesses the α-structure is probable from the synthesis adopted (preceding paper) and is confirmed by the mixed melting points described below.

(*b*) 15 G. of glycidyl phenyl ether (preceding paper) were refluxed with 50 c.c. of *N*-sodium hydroxide for 5 hours. The product was extracted with ether, dried with potassium carbonate, and recrystallised from ether–ligroin; m. p. 67°, alone or mixed with the higher-melting form obtained by preparation (*a*). After fusion it melted at 54° and a mixed m. p. determination with the lower melting form obtained by preparation (*a*) also gave this figure.

*αγ-Di-*o*-tolyloxy-β-acetoxypropane.*—This compound, previously described as a liquid (J., 1931, 445), has since crystallised; m. p. 36° after recrystallisation from alcohol.

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