Organic Syntheses

A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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α-GLYCERYL PHENYL ETHER

[1,2-Propanediol, 3-phenoxy-]

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1. Procedure

To 500 cc. of absolute alcohol (Note 1) in a 1-l. flask fitted with a reflux condenser is added gradually 46 g. (2 atoms) of sodium in thin slices (Note 2) at such a rate that the mixture boils steadily. When all the sodium has been added, the mixture is heated on the steam bath until the few remaining pieces of sodium barely react. Pure commercial molten phenol is now added gradually through the condenser until all the sodium has reacted, and then the remainder of 188 g. (2 moles) of phenol is added. This is followed by the addition of 221 g. (2 moles) of redistilled glycerol α-monochlorohydrin (p. 294) in small portions, the rather vigorous reaction being allowed to complete itself before each subsequent addition.

When all has been added, the mixture is heated on the steam bath for about one hour. The end of the reaction is determined by withdrawing a sample, filtering it, and heating the filtrate in which little or no precipitate should form. The mixture is filtered hot by suction through filter cloth or heavy filter paper (Note 3), the precipitate being washed with three 50-cc. portions of absolute alcohol. The filtrate and washings are distilled on the steam bath under slightly reduced pressure until no more alcohol comes over; the residue, which sets to a white waxy solid on cooling, is transferred to a distilling flask and distilled under reduced pressure, the fraction boiling at 175–190°/15 mm. being collected. In this way 235–275 g. of a product melting at 43–49° is obtained. On redistillation, 205–215 g. (61–64 per cent of the theoretical amount) of a fraction which boils at 185–187°/15 mm. and melts at 48–53° is obtained (Note 4).

2. Notes

1. Absolute alcohol (p. 249) is required in order that all the sodium chloride formed may be precipitated and that none may remain to contaminate the product.
2. More rapid solution of the sodium can be obtained if the metal is granulated prior to its addition to the alcohol. This is done by covering the sodium with ten times its weight of dry xylene and heating to 120° in a stout round-bottomed flask.[1] The flask is then well corked, wrapped in a thick, dry cloth, and well shaken for a short time. The metal is thus obtained in the form of small spheres, the size of which is controlled by the time and rapidity of the shaking. A dry bucket should be kept at hand so that the flask can be dropped into it in case of breakage. Not more than 30 g. of sodium should be treated at one time. Vigorous mechanical stirring (Fig. 2, p. 33) may be used to advantage in place of shaking by hand.
3. The precipitate of sodium chloride obtained is very sludgy and filters poorly through fine-fibered papers.
4. Small traces of impurity lower the melting point very considerably, and by repeated recrystallization from anhydrous ether the melting point can be raised to 70°. The product crystallizes from the ether in very long, flexible needles, forming a spongy mass which filters with some difficulty. In order to obtain a high melting point, complete removal of the solvent, preferably by warming to 50° under reduced pressure, is essential.

3. Discussion

α-Glyceryl phenyl ether can be prepared by heating phenol with excess of glycerol and anhydrous

sodium acetate,[2] and by heating phenol with α-monochlorohydrin and caustic alkali.[3]

References and Notes

1. Nef, Ann. **280**, 307 (1894); Read and Lucarini, Ind. Eng. Chem. **17**, 480 (1925).
2. Zivkovic, Monatsh. **29**, 952 (1908).
3. Marle, J. Chem. Soc. **101**, 310 (1912).

Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

Glycerol α-monochlorohydrin

α-monochlorohydrin

caustic alkali

alcohol (64-17-5)

ether (60-29-7)

sodium acetate (127-09-3)

glycerol (56-81-5)

phenol (108-95-2)

sodium chloride (7647-14-5)

sodium (13966-32-0)

xylene (106-42-3)

α-Glyceryl phenyl ether

1,2-Propanediol, 3-phenoxy- (538-43-2)

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