



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.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

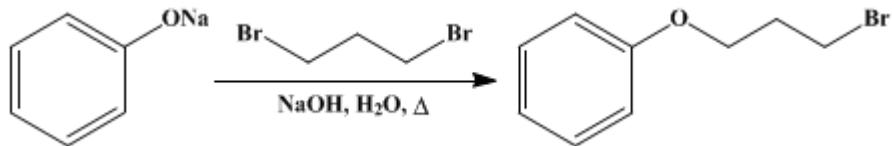
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.435 (1941); Vol. 9, p.72 (1929).

γ -PHENOXYPROPYL BROMIDE

[Propane, 1-bromo-2-phenoxy-]



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1. Procedure

In a 5-l. round-bottomed flask, fitted with a stopper carrying a long reflux condenser, a mechanical stirrer (Note 1), and a separatory funnel, are placed 2 l. of water (Note 2), 1 kg. (4.95 moles) of trimethylene bromide (p. 30) (Note 3), and 370 g. (3.9 moles) of phenol. The stirrer is started, and the mixture is heated to boiling. To the boiling solution is added a solution of 150 g. (3.75 moles) of sodium hydroxide in 500 cc. of water at such a rate that all is added in about one hour. The mixture is refluxed for five to six hours longer to complete the reaction, then cooled, and the upper water layer is separated and discarded.

The lower layer consists of trimethylene bromide, phenoxypropyl bromide, and diphenoxypyropane. This mixture is distilled under reduced pressure, a Claisen flask with a modified side arm (p. 130) being used. The first fraction is collected up to 136°/20 mm.; it consists of water and recovered trimethylene bromide with a little phenoxypropyl bromide (Note 4). The water is separated and discarded. The recovered trimethylene bromide weighs 340–450 g. (Note 5). The next fraction is pure phenoxypropyl bromide, which boils at 136–142°/20 mm. The yield is 495–600 g. (84–85 per cent of the theoretical amount based on the trimethylene bromide not recovered) (Note 6). On cooling, the phenoxypropyl bromide crystallizes to a white solid, m.p. 7–8°. A small amount (50–80 g.) of diphenoxypyropane is left as a residue in the distilling flask.

2. Notes

1. The reaction may be run without stirring, but a longer period of refluxing is necessary and the yield is lower.
2. If less water is used in the reaction mixture, sodium bromide separates.
3. The large excess of trimethylene bromide must be used in order to avoid the formation of large amounts of diphenoxypyropane.
4. Phenoxypropyl bromide attacks rubber stoppers quite readily, and the side arm of the distillation flask should be set in (p. 130), in order to avoid contamination of the distillate.
5. The use of recovered trimethylene bromide does not result in so good a yield of phenoxypropyl bromide, because a little phenoxypropyl bromide is already present and during the reaction is converted to diphenoxypyropane.
6. Phenoxyethyl bromide may be made in a similar manner. Two kilos (10.7 moles) of ethylene bromide, 785 g. (8.5 moles) of phenol, and 2 l. of water, upon treatment with 375 g. (9.4 moles) of sodium hydroxide, yield 960–970 g. of phenoxyethyl bromide (55–56 per cent of the theoretical amount) boiling at 125–130°/18 mm.

3. Discussion

γ -Phenoxypropyl bromide can be prepared by the action of sodium phenoxide on trimethylene bromide in alcohol solution.¹ The procedure described has been published.²

References and Notes

1. Lohmann, Ber. **24**, 2631 (1891); Salonina, Ber. **26**, 2987 (1893); v. Braun and Beschke, Ber. **39**, 4120 (1906).
2. Marvel and Tanenbaum, J. Am. Chem. Soc. **44**, 2647 (1922).

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

alcohol (64-17-5)

sodium hydroxide (1310-73-2)

phenol (108-95-2)

sodium bromide (7647-15-6)

Trimethylene bromide (109-64-8)

ethylene bromide (106-93-4)

sodium phenoxide

γ -Phenoxypropyl bromide,
phenoxypropyl bromide (588-63-6)

Propane, 1-bromo-2-phenoxy-

diphenoxypyropane

Phenoxyethyl bromide (589-10-6)