



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.

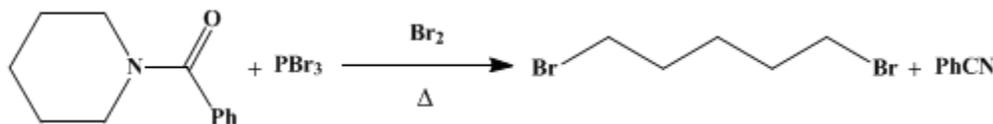
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.428 (1941); Vol. 9, p.70 (1929).

PENTAMETHYLENE BROMIDE

[Pentane, 1,5-dibromo-]



Submitted by J. von Braun

Checked by J. B. Conant and J. S. Andrews.

1. Procedure

In a 500-cc. Claisen distilling flask is placed 80 g. (0.42 mole) of [benzoyl piperidine](#) (p. 99). To this is added with cooling 115 g. (0.43 mole) of [phosphorus tribromide](#); this results in the formation of a light-colored solution. With careful cooling, this solution is treated, with shaking, with 65 g. (20.8 cc., 0.405 mole) of [bromine](#). The flask is now connected for distillation under reduced pressure, and the solution is heated gradually for a few minutes until the rapid evolution of gas ceases. The product is then distilled under reduced pressure. At about 70°/20 mm. a mixture of [pentamethylene bromide](#), [phosphorus oxybromide](#), and [benzonitrile](#) begins to distil over into the receiver; a yellow solid collects in the condenser. This is then followed by a black decomposition product, at which point the distillation is stopped. The distillate is poured upon ice and allowed to stand in order to decompose the [phosphorus oxybromide](#), a process which requires about one hour if carried out in a flask fitted with a reflux condenser and mechanical stirrer.

The heavy oil is removed from the water; it consists of [pentamethylene bromide](#) and [benzonitrile](#). This oily layer is treated with 125 cc. of 40 per cent [hydrobromic acid](#) solution and boiled under a reflux condenser with vigorous stirring for about three hours in order to hydrolyze completely the [benzonitrile](#) to [benzoic acid](#) (Note 1). The mixture is then distilled with steam, an air condenser being placed between the distillation flask and the receiving flask to which is fitted a reflux condenser cooled with water. This apparatus is necessary to avoid clogging of the condenser tubes with the [benzoic acid](#). The [pentamethylene bromide](#) is separated from the water layer, washed with [sodium carbonate](#), dried over [calcium chloride](#), and distilled under reduced pressure. The product boils at 108–110°/20 mm. and amounts to 63–70 g. (65–72 per cent of the theoretical amount).

2. Notes

1. It has been reported that [pentamethylene bromide](#) prepared by the procedure described contains a considerable amount of [benzonitrile](#), and the following procedure is given for removing the nitrile. The crude product, after removal of the [phosphorus oxybromide](#), is washed with water and distilled, the portion boiling up to 105°/10 mm. being collected. The distillate is dissolved in two volumes of ligroin (b.p. 40°) and extracted seven times with concentrated [sulfuric acid](#) — 3 cc. for each 10 cc. of distillate. The ligroin solution is then washed with dilute [sodium hydroxide](#) solution, any emulsions being broken by filtration, dried over [calcium chloride](#), and distilled.¹ Alternatively, it is reported² that the procedure of v. Braun and Steindorff³ removes [benzonitrile](#) satisfactorily. In this procedure the distillate containing the [pentamethylene bromide](#), [benzonitrile](#) and [phosphorus oxybromide](#) is poured carefully into 85–95 cc. of water, while cooling and stirring. The resulting mixture is refluxed for eight to ten hours with occasional additions of 3–4 cc. of [alcohol](#) to decrease resinification. The product is then extracted with [ether](#), washed with [sodium carbonate](#) solution, steam-distilled, dried, and, finally, distilled *in vacuo*. In the laboratory it has been found that shaking [pentamethylene bromide](#) with concentrated [sulfuric acid](#) results in the formation of emulsions. The use of a solvent such as petroleum ether usually prevents the emulsification but lowers the yield of the final product.

3. Discussion

Pentamethylene bromide can be prepared by the action of fuming hydrobromic acid on pentamethylene glycol,⁴ or 1, 5-diphenoxypentane;⁵ by the action of hydrobromic acid on an acetic acid solution of 1,5-diisoamyloxypentane;⁶ and by the action of phosphorus pentabromide on benzoyl piperidine.⁷ Pentamethylene bromide can also be prepared from tetrahydrofurfuryl alcohol by conversion to 1,2-dihydropyran, reduction to 1,5-epoxypentane, and treatment of this last product with hydrogen bromide in glacial acetic acid.⁸

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 99
- Org. Syn. Coll. Vol. 3, 692

References and Notes

1. Johnson, J. Chem. Soc. 1531 (1933). Compare, Clarke, *ibid.* **103**, 1703 (footnote) (1913), Dox and Yoder, J. Am. Chem. Soc. **43**, 1368 (1921).
2. Müller, Ber. **68**, 1013 (1935).
3. v. Braun and Steindorff, Ber. **38**, 2339 (1905).
4. Gustavson and Demjanoff, J. prakt. Chem. (2) **39**, 542 (1889); Haworth and Perkin, Ber. **26**, 2247 (1893); Hochstetter, Monatsh. **23**, 1071 (1902); Müller and Rölz, *ibid.* **50**, 105 (1928).
5. v. Braun and Steindorff, Ber. **38**, 960 (1905).
6. Hamonet, Compt. rend. **138**, 1611 (1904); Bull. soc. chim. (3) **33**, 530 (1905).
7. v. Braun, Ber. **37**, 3211 (1904); v. Braun and Steindorff, Ber. **38**, 2338 (1905); Merck, Ger. pat. 164,365 [Chem. Zentr. II, 1563 (1905)]; Clarke, J. Chem. Soc. **103**, 1703 (footnote) (1913); Dox and Yoder, J. Am. Chem. Soc. **43**, 1367 (1921).
8. Paul, Bull. soc. chim. (4) **53**, 1489 (1933).

Appendix

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

ligroin

alcohol (64-17-5)

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

ether (60-29-7)

benzotrile (100-47-0)

sodium hydroxide (1310-73-2)

HYDROBROMIC ACID,
hydrogen bromide (10035-10-6)

sodium carbonate (497-19-8)
bromine (7726-95-6)
phosphorus tribromide (7789-60-8)
Benzoic acid (65-85-0)
BENZOYL PIPERIDINE (776-75-0)
pentamethylene bromide,
Pentane, 1,5-dibromo- (111-24-0)
pentamethylene glycol (111-29-5)
1,5-epoxypentane (142-68-7)
phosphorus oxybromide
1, 5-diphenoxypentane (40339-96-6)
1,5-diisoamyloxypentane
phosphorus pentabromide (7789-69-7)
tetrahydrofurfuryl alcohol (97-99-4)
1,2-dihydropyran