



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](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.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

*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. 2, p.478 (1943); Vol. 11, p.84 (1931).*

## *n*-PENTANE



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### 1. Procedure

In a 5-l. flask, placed on a steam bath and fitted with a mechanical stirrer, a separatory funnel, a thermometer well (Note 1), and a calcium chloride tube, is placed 182 g. (7.5 gram atoms) of magnesium turnings. To this are added a crystal of iodine and 100 cc. of a solution of 1133 g. (7.5 moles) of 2-bromopentane (Note 2) in 750 g. of *n*-butyl ether (Note 3). The stirrer is started, and the flask is heated with steam until the reaction starts. This may take from fifteen minutes to one hour; the flask must be watched quite closely because the reaction, when once started, is very vigorous and evolves a large amount of heat. As soon as the reaction has started, 750 g. of *n*-butyl ether is added and then the balance of the solution of 2-bromopentane in *n*-butyl ether is added at such a rate that the temperature is kept at 50–60°. External cooling is used in order to allow more rapid addition of the 2-bromopentane. After addition is complete (about three hours), the mixture is heated on a steam bath for one hour.

In the meantime, a 12-l. flask containing a solution of 450 cc. of concentrated sulfuric acid in 3 l. of water is placed on a steam bath and fitted with a stirrer, a separatory funnel, and an efficient ice-cooled condenser set for distillation. The stirrer is started, and the solution of the Grignard reagent, prepared above, is added. The acid solution is allowed to become warm but is kept below the boiling point by external cooling. After all the Grignard reagent has been added, the mixture is heated on the steam bath until no more pentane distils. The reaction flask is allowed to cool, and the *n*-butyl ether layer is separated, transferred to a 5-l. flask connected with the condenser, and heated with a free flame until the boiling point of the *n*-butyl ether is reached (Note 4). The combined distillate is separated from a small amount of water, washed twice with 125-cc. portions of cold, concentrated sulfuric acid, and allowed to stand overnight with anhydrous potassium carbonate. After removing the potassium carbonate, the *n*-pentane is fractionated twice through an efficient 100-cm. fractionating column. The yield is 270–290 g. (50–53 per cent of the theoretical amount) of a product which boils at 35.5–36.5°.

### 2. Notes

1. A closed glass tube containing mercury was used as a thermometer well. It was inserted with the end in the reaction mixture. The thermometer was placed in the well with the bulb in the mercury.
2. The 2-bromopentane used in this preparation was prepared by the action of hydrobromic acid on secondary amyl alcohol (methyl *n*-propyl carbinol) obtained from Stanco Distributors, Inc. Other commercial straight-chain amyl alcohols when converted to the bromides gave a pentane boiling at 33–35°, showing that a considerable quantity of isopentane was present.
3. The use of *n*-butyl ether allows the ready separation of the pentane by distillation. The butyl ether used in this preparation boiled at 142–144°.

4. About 70 per cent of the *n*-butyl ether is recovered readily and may be purified by distillation.

### 3. Discussion

*n*-Pentane has been obtained in many ways, but the reactions which are of preparative interest are few. They include the reduction of 2-bromopentane with zinc and hydrochloric acid;<sup>1</sup> the reduction of 3-iodopentane with zinc and hydriodic acid;<sup>2</sup> the catalytic reduction of pyridine at 50°;<sup>3</sup> the reduction of *n*-amylene;<sup>4</sup> and the decomposition of *sec.*-amylmagnesium bromide with ammonium chloride.<sup>5</sup> The use of *n*-butyl ether in the procedure described above, which eliminates the problem of separating *n*-pentane and ethyl ether,<sup>5</sup> was suggested by a paper of Marvel, Blomquist, and Vaughn.<sup>6</sup>

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### References and Notes

1. Clarke and Talbot, unpublished results.
  2. Karvonen, Acta Chem. Fennica, **3**, 101 (1930) [C. A. **25**, 2412 (1931)].
  3. Skita and Brunner, Ber. **49**, 1598 (1916).
  4. Fettindustrieges. m. b. H., Ger. pat. 329,471 [Frdl. **13**, 178 (1916-21)]; Wibaut and collaborators, Rec. trav. chim. **58**, 337 (1939).
  5. Fischer and Klemm, Z. physik. Chem. A **147**, 275 (1930).
  6. Marvel, Blomquist, and Vaughn, J. Am. Chem. Soc. **50**, 2810 (1928).
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### Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

secondary amyl alcohol

potassium carbonate (584-08-7)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

ethyl ether (60-29-7)

ammonium chloride (12125-02-9)

magnesium turnings (7439-95-4)

HYDROBROMIC ACID (10035-10-6)

mercury (7439-97-6)

iodine (7553-56-2)

pyridine (110-86-1)

zinc (7440-66-6)

hydriodic acid (10034-85-2)

butyl ether,  
n-butyl ether (142-96-1)

Pentane,  
n-PENTANE (109-66-0)

methyl n-propyl carbinol (6032-29-7)

3-iodopentane (1809-05-8)

n-amylene

2-bromopentane (107-81-3)

isopentane (78-78-4)

sec.-amylmagnesium bromide