



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.

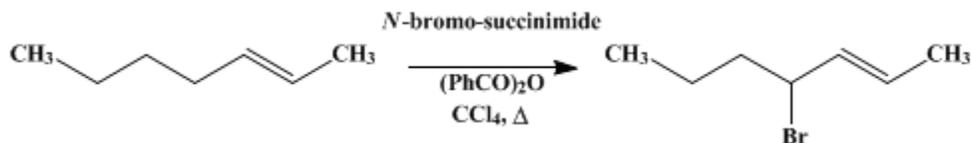
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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4-BROMO-2-HEPTENE

[2-Heptene, 4-bromo-]



Submitted by F. L. Greenwood, M. D. Kellert, and J. Sedlak¹.

Checked by John D. Roberts and A. T. Bottini.

1. Procedure

In a 500-ml. round-bottomed flask fitted with a stirrer, nitrogen inlet tube, and reflux condenser are placed 40 g. (0.41 mole) of 2-heptene, 48.1 g. (0.27 mole) of N-bromosuccinimide, 0.2 g. of benzoyl peroxide, and 250 ml. of carbon tetrachloride (Note 1). The reaction mixture is stirred and heated under reflux in a nitrogen atmosphere for 2 hours (Note 2). The succinimide is removed by suction filtration, washed twice with 15-ml. portions of carbon tetrachloride and the carbon tetrachloride washings are combined with the filtrate (Note 3). The carbon tetrachloride solution is transferred to a 500-ml. Claisen flask modified so that the distilling arm carries a 25 × 300 mm. section packed with glass helices. The capillary is attached to a source of nitrogen and the carbon tetrachloride removed at 36–38°/190 mm. (Note 4).

The residue is transferred to a 125-ml. Claisen flask modified so that the distilling arm carries an 18 × 180 mm. section packed with glass helices. Nitrogen is led into the capillary, and, after a forerun of 1–3 g., there is collected 28–31 g. (58–64%) of 4-bromo-2-heptene, b.p. 70–71°/32 mm., n_D^{25} 1.4710–1.4715 (Note 5). A residue of 7–10 g. remains in the distilling flask (Note 6).

2. Notes

1. The 2-heptene was the pure grade material purchased from Phillips Petroleum Company, Bartlesville, Oklahoma. This olefin is comparable to material prepared by a Boord synthesis. The N-bromosuccinimide was obtained from Arapahoe Chemicals, Inc., Boulder, Colorado. The benzoyl peroxide was used as received from Distillation Products, Rochester, New York. The carbon tetrachloride was reagent grade, from J. T. Baker Chemical Company, Phillipsburg, New Jersey.
2. The reaction is not rapid, and benzoyl peroxide is necessary to effect reaction. Longer reflux times lead to darkening of the reaction mixture.
3. The succinimide recovered corresponded to 97–98% of the theoretical amount and analyzed for 0.4% active bromine.
4. Removal of the carbon tetrachloride at a lower pressure results in loss of product. Distillation at a pressure much above 200 mm. causes considerable darkening of the liquid. Carbon tetrachloride removed at the higher pressure gives no precipitate with aqueous silver nitrate; this indicates the absence of product.
5. When first distilled, the product is nearly colorless. On standing under nitrogen in the refrigerator for several days, the material acquires a pale yellow color. Evidence for the identity of the product as 4-bromo-2-heptene is outlined in Reference ².
6. This includes the liquid wetting the helices as well as the small amount of dark residue in the flask.

3. Discussion

Ziegler and coworkers³ indicated that allylic methylene groups undergo bromine substitution more readily than allylic methyl groups. This has been shown² to be true, and the treatment of 2-heptene with N-bromosuccinimide gives rise to 4-bromo-2-heptene.

References and Notes

1. Tufts University, Medford, Massachusetts.
 2. Greenwood and Kellert, *J. Am. Chem. Soc.*, **75**, 4842 (1953).
 3. Ziegler et al., *Ann.*, **551**, 80 (1942).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

silver nitrate (7761-88-8)

bromine (7726-95-6)

carbon tetrachloride (56-23-5)

nitrogen (7727-37-9)

benzoyl peroxide (94-36-0)

Succinimide (123-56-8)

N-bromosuccinimide (128-08-5)

4-Bromo-2-heptene,
2-Heptene, 4-bromo- (22118-57-6)

2-heptene