



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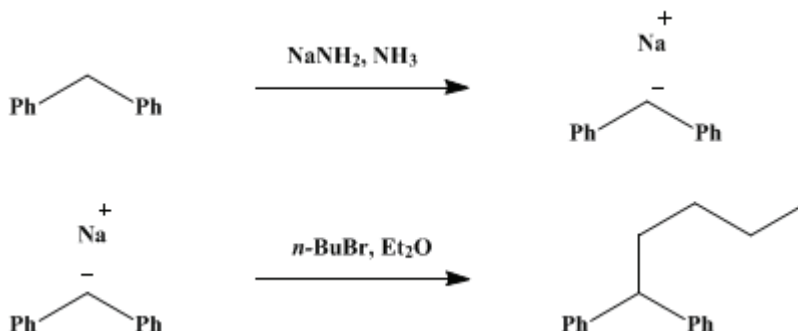
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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1,1-DIPHENYLPENTANE

[Pentane, 1,1-diphenyl-]



Submitted by William S. Murphy, Phillip J. Hamrick, and Charles R. Hauser¹.
Checked by Prithipal Singh and Peter Yates.

1. Procedure

Caution! This preparation should be carried out in a hood to avoid exposure to ammonia.

A suspension of sodium amide (0.275 mole) (Note 1) in liquid ammonia is prepared in the following manner in a 1-l. three-necked flask equipped with an air condenser (Note 2), a sealed mechanical stirrer, and a dropping funnel. Commercial anhydrous liquid ammonia (600 ml.) is introduced by pouring from an Erlenmeyer flask (Note 3). To the stirred liquid ammonia is added a small piece of sodium. After the appearance of a permanent blue color (Note 4) a few crystals of ferric nitrate hydrate (*ca.* 0.1 g.) are added, followed by small pieces of freshly cut sodium (Note 5) until 6.32 g. (0.275 g. atom) has been added. After all the sodium is converted to the amide (Note 6), 42.0 g. (0.250 mole) of diphenylmethane (Note 7) in 20 ml. of anhydrous ether is added (Note 8). The deep red suspension is stirred for 15 minutes. *n*-Butyl bromide (37.6 g., 0.274 mole) (Note 7) in 20 ml. of anhydrous ether is then added dropwise with stirring. The ammonia is allowed to evaporate (Note 9) from the resulting gray suspension. Water (100 ml.) is added carefully (Note 10), then 100 ml. of ether. The ethereal layer is separated, and the aqueous layer is extracted with two further 100-ml. portions of ether. The combined ethereal extracts are dried over Drierite and filtered, and the solvent is removed. The resulting liquid (54.5 g., 97%) is essentially pure 1,1-diphenylpentane (Note 11) and (Note 12) The liquid is distilled with the use of a Claisen distillation head without a fractionating column. The fraction, b.p. 138–139° (1.5 mm.), n_D^{26} 1.5501, weighs 51.6 g. (92%) (Note 13).

2. Notes

1. A 10% excess of sodium amide and *n*-butyl bromide with respect to diphenylmethane was adopted.
2. The checkers used a dry-ice condenser in place of the air condenser.
3. Dry commercial liquid ammonia is conveniently transferred from the cylinder via an Erlenmeyer flask without cooling and without the use of a condenser.
4. A permanent blue color may not remain after the addition of one pellet of sodium because of the presence of traces of moisture. Another pellet is added if necessary.
5. Sodium is cut into small pellets in the atmosphere but weighed under dry benzene or toluene.
6. Conversion is indicated by the discharge of the blue color (*ca.* 30 minutes). The addition of another portion of ferric nitrate hydrate will catalyze the conversion.
7. Freshly distilled diphenylmethane and *n*-butyl bromide were used.
8. The checkers found it important to add the diphenylmethane slowly (*ca.* 20 minutes); fast addition caused the reaction to get out of control.

9. The ammonia is allowed to evaporate overnight. A steam bath may be employed with care to facilitate the evaporation.
10. In the event of the presence of traces of unreacted sodium on the flask, water is added initially with special care.
11. The purity of the 1,1-diphenylpentane is attested by vapor-phase chromatography on a 5-ft. column of 10% Apiezon L on Celite at 200°.
12. Although 1,1-diphenylpentane undergoes air oxidation,² it appears to be stable in a stoppered flask under an inert atmosphere.
13. The checkers observed b.p. 127–129° (1.5 mm.).

3. Discussion

This procedure is an adaptation of one described by Hauser and Hamrick.³ 1,1-Diphenylpentane has been prepared by the catalytic hydrogenation of 1,1-diphenyl-1-pentene^{4,5,6} and in low yield from the reaction of diphenylmethyl bromide with di-*n*-butylmercury.⁷ More recently 1,1-diphenylpentane was prepared by allowing lithium diphenylmethide to react with tri-*n*-butyl orthophosphate.⁸

4. Merits of the Preparation

This procedure illustrates a process which is general for 1,1-diphenyl substituted hydrocarbons. Diphenylmethane has been alkylated³ with benzyl chloride, benzhydryl chloride, α -phenylethyl chloride, β -phenylethyl chloride, isopropyl chloride, 2-ethylbutyl bromide, and *n*-octyl bromide in yields of 99, 96, 97, 88, 86, 96, and 99%, respectively.

The present method is superior to earlier ones in that it is shorter, the chemicals are readily available, and high yields are obtained. The Gilman method⁸ affords a 74% yield but a longer reaction time (1–2 days) and less readily available starting materials make it less convenient.

References and Notes

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3. C. R. Hauser and P. J. Hamrick, Jr., *J. Am. Chem. Soc.*, **79**, 3142 (1957).
4. K. T. Serijan and P. H. Wise, *J. Am. Chem. Soc.*, **73**, 4766 (1951).
5. G. Benoit and F. Eliopoulos, *Bull. Soc. Chim. France*, [5] **18**, 892 (1951).
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Appendix

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

Drierite

lithium diphenylmethide

ammonia (7664-41-7)

Benzene (71-43-2)

ether (60-29-7)

n-butyl bromide (109-65-9)

n-octyl bromide (111-83-1)

toluene (108-88-3)

sodium (13966-32-0)

Diphenylmethane (101-81-5)

benzyl chloride (100-44-7)

β -phenylethyl chloride (622-24-2)

sodium amide (7782-92-5)

diphenylmethyl bromide (776-74-9)

ferric nitrate hydrate

benzhydryl chloride (90-99-3)

isopropyl chloride (75-29-6)

1,1-Diphenylpentane,
Pentane, 1,1-diphenyl- (1726-12-1)

1,1-diphenyl-1-pentene

α -phenylethyl chloride (672-65-1)

di-n-butylmercury (629-35-6)

tri-n-butyl orthophosphate (126-73-8)

2-ethylbutyl bromide (3814-34-4)