



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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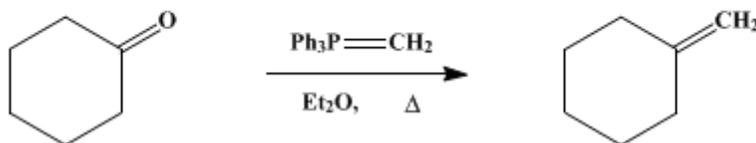
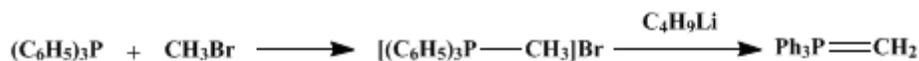
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.751 (1973); Vol. 40, p.66 (1960).

METHYLENECYCLOHEXANE

[Cyclohexane, methylene-]



Submitted by George Wittig and U. Schoellkopf¹.
Checked by John D. Roberts and Martin Vogel.

1. Procedure

A. *Triphenylmethylphosphonium bromide*. A solution of 55 g. (0.21 mole) of *triphenylphosphine* dissolved in 45 ml. of dry *benzene* is placed in a pressure bottle, the bottle is cooled in an ice-salt mixture, and 28 g. (0.29 mole) of previously condensed *methyl bromide* is added (Note 1). The bottle is sealed, allowed to stand at room temperature for 2 days, and is reopened. The white solid is collected by means of suction filtration with the aid of about 500 ml. of hot *benzene* and is dried in a vacuum oven at 100° over *phosphorus pentoxide*. The yield is 74 g. (99%), m.p. 232–233°.

B. *Methylenecyclohexane* (Note 2). A 500-ml. three-necked round-bottomed flask is fitted with a reflux condenser, an addition funnel, a mechanical stirrer, and a gas inlet tube. A gentle flow of *nitrogen* through the apparatus is maintained throughout the reaction. An ethereal solution of *n*-*butyllithium*² (0.10 mole, about 100 ml., depending on the concentration of the solution) and 200 ml. of anhydrous *ether* is added to the flask. The solution is stirred and 35.7 g. (0.10 mole) of *triphenylmethylphosphonium bromide* is added cautiously over a 5-minute period (Note 3). The solution is stirred for 4 hours at room temperature (Note 4).

Freshly distilled *cyclohexanone* (10.8 g., 0.11 mole) is now added dropwise. The solution becomes colorless and a white precipitate separates. The mixture is heated under reflux over-night, allowed to cool to room temperature, and the precipitate is removed by suction filtration. The precipitate is washed with 100 ml. of *ether*, and the combined ethereal filtrates are extracted with 100-ml. portions of water until neutral and then dried over *calcium chloride*. The *ether* is carefully distilled through an 80-cm. column packed with glass helices. Fractionation of the residue remaining after removal of the *ether* through an efficient, low-holdup column (Note 5) gives 3.4–3.8 g. (35–40%) of pure *methylenecyclohexane*, b.p. 99–101°/740 mm., n_D^{25} 1.4470 (Note 6).

2. Notes

1. Eastman Kodak Co. white label *triphenylphosphine* and Matheson Co. *methyl bromide* were used. *Triphenylphosphine* is available from the Metal and Thermit Corp., Rahway, New Jersey.
2. Since this procedure was first published in this series the use of methylsulfinyl carbanion (as the base) in *dimethyl sulfoxide* (as solvent) has been found to give better results in many examples than the base-solvent pair described here.³ The Wittig reaction appears to proceed more rapidly in *dimethyl sulfoxide* and the yields of olefin are frequently superior. For purposes of comparison with the present procedure the procedure of Greenwald, Chaykovsky, and Corey³ was repeated several times with the following deviations from the published procedure. *Triphenylmethylphosphonium bromide* from two different batches was purchased from the Aldrich Chemical Co., Inc. This material contained a small amount (*ca.* 1–2 percent) of *benzene* (as indicated by nmr analysis). Drying as described in part A

reduced the benzene content to less than 1 percent. The apparatus was set up and the purification of cyclohexanone and dimethylsulfoxide was carried out as described in the preparation of methylenecyclohexane oxide (this volume, p. 755). With these modifications the procedure resembled that described by Monson.⁴ In several experiments the *apparent* yields (75–94%) of methylenecyclohexane clustered about the 8.10 g. (84.2%) reported by Greenwald, Chaykovsky, and Corey;³ however, analysis by nmr and glpc showed that the product was a mixture of methylenecyclohexane and benzene in the ratio of 4 to 1. Methylenecyclohexane and benzene may be separated quite easily by distillation (using a spinning-band column) or by preparative gas chromatography on any of several columns (SE-30, di-2-ethylhexyl sebacate, silver nitrate-ethylene glycol). Thus, the *true* yield of methylenecyclohexane was 60–78%. This is a substantial improvement over the yield obtained by the present procedure. The source of the benzene was not determined. Using different batches of the various reagents did not alter the results. Omitting the washing of the sodium hydride with *n*-pentane resulted in a 50–60% reduction in apparent yield (private communication from D. G. McMahan and H. E. Baumgarten).

3. If the triphenylmethylphosphonium bromide is added too rapidly, the evolution of butane causes excessive frothing of the solution.

4. The small amount of precipitate in the orange solution is not unreacted starting material but triphenylphosphinemethylene.

5. The checkers used a 6 × 350 mm. spinning-band column with a total reflux variable take-off head. The band was spun at 1100 r.p.m.

6. The methylenecyclohexane was analyzed by vapor-phase chromatography and found to be better than 99% pure.

3. Discussion

The procedure is a modification of that published.⁵ Methylenecyclohexane has been prepared by the pyrolysis of N,N-dimethyl-1-methylcyclohexylamine oxide, N,N,N-trimethyl-1-methylcyclohexylammonium hydroxide, N,N-dimethylcyclohexylmethylamine oxide, and N,N,N-trimethylcyclohexylmethylammonium hydroxide.⁶ It has also been obtained from the pyrolysis of cyclohexylmethyl acetate⁷ and of cyclohexylideneacetic acid⁸ and from the dehydrohalogenation of cyclohexylmethyl iodide.⁹

References and Notes

1. University of Heidelberg, Heidelberg, Germany.
2. R. G. Jones and H. Gilman, *Org. Reactions*, **6**, 352 (1951).
3. R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).
4. R. S. Monson, "Advanced Organic Synthesis," Academic Press, New York, 1971, p. 105.
5. G. Wittig and U. Schoellkopf, *Ber.*, **87**, 1318 (1954).
6. A. C. Cope, C. L. Bumgardner, and E. E. Schweizer, *J. Am. Chem. Soc.*, **79**, 4729 (1957).
7. D. H. Froemsdorf, C. H. Collins, G. S. Hammond, and C. H. DePuy, *J. Am. Chem. Soc.*, **81**, 643 (1959).
8. O. Wallach, *Ann.*, **359**, 287 (1908).
9. A. Faworsky and I. Borgmann, *Ber.*, **40**, 4863 (1907).

Appendix

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

calcium chloride (10043-52-4)

Benzene (71-43-2)

ether (60-29-7)

Cyclohexanone (108-94-1)

silver nitrate (7761-88-8)

nitrogen (7727-37-9)

ethylene glycol (107-21-1)

methyl bromide (74-83-9)

n-PENTANE (109-66-0)

butane (106-97-8)

n-butyllithium (109-72-8)

sodium hydride (7646-69-7)

dimethyl sulfoxide,
dimethylsulfoxide (67-68-5)

Methylenecyclohexane,
Cyclohexane, methylene- (1192-37-6)

cyclohexylmethyl iodide

cyclohexylideneacetic acid

triphenylphosphinemethylene

N,N-Dimethylcyclohexylmethylamine oxide

triphenylphosphine (603-35-0)

di-2-ethylhexyl sebacate (122-62-3)

triphenylmethylphosphonium bromide (1779-49-3)

Methylenecyclohexane oxide (185-70-6)

N,N-dimethyl-1-methylcyclohexylamine oxide

N,N,N-trimethyl-1-methylcyclohexylammonium hydroxide

N,N,N-trimethylcyclohexylmethylammonium hydroxide

cyclohexylmethyl acetate

phosphorus pentoxide (1314-56-3)

