Organic Syntheses

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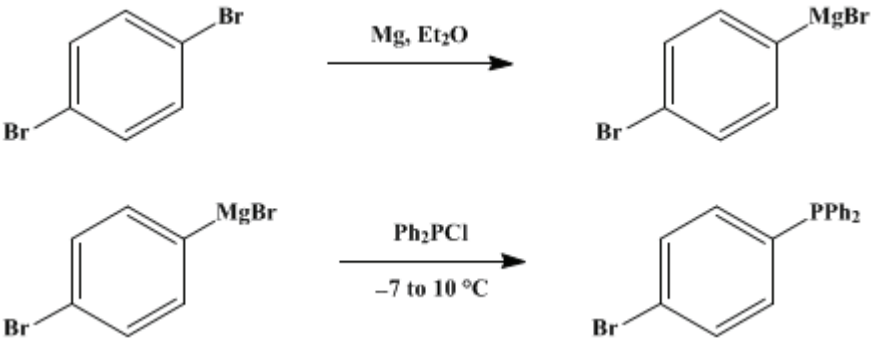
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.049.0066

Organic Syntheses, Coll. Vol. 5, p.496 (1973); Vol. 49, p.66 (1969).

DIPHENYL-*p*-BROMOPHENYLPHOSPHINE

[Phosphine, (*p*-bromophenyl)diphenyl]



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1. Procedure

A dry 1-l. round-bottomed flask with five outlets is equipped with a sealed stirrer, a 500-ml. dropping funnel, a reflux condenser attached to a calcium chloride tube, an inlet for dry nitrogen (a weak stream of which is maintained through all the reaction until the hydrolysis step), and a thermometer reaching close to the bottom. In the flask are placed 9.0 g. (0.38 g. atom) of magnesium turnings, a crystal of iodine, and about 25 ml. of dry ether. With stirring, about 15 ml. of a solution of 88.5 g. (0.38 mole) of *p*-dibromobenzene (Note 1) in 500 ml. of dry ether (Note 2) is added at once. When the reaction has started, the remaining ether solution is added at a rate which maintains rapid refluxing. After the *p*-dibromobenzene has been added, the mixture is stirred at room temperature for 1.5 hours.

The mixture is then cooled by means of an ice-sodium chloride bath. When the internal temperatures has reached −7°, a solution of 71.8 g. (0.33 mole) of chlorodiphenylphosphine (Note 3) in 100 ml. of dry ether is added at such a rate that the internal temperature does not exceed +10°. The addition requires about 1.25 hours. The cooling bath is then removed and stirring continued for 1.5 hours. The flask is then again immersed in an icesodium chloride bath, and 150 ml. of a cold saturated aqueous ammonium chloride solution is added slowly. The ether is decanted and the remainder acidified with hydrochloric acid and extracted three times with 125 ml. of benzene each (Note 4). From the combined ether and benzene solutions, the solvents are evaporated and the residue is distilled at reduced pressure. After the low-boiling material, some *p*-dibromobenzene distills and crystallizes in the distillation bridge. At 2×10^{-2} mm., heating is continued until the phosphine reaches the stillhead. At this stage the distillation is interrupted, the stillhead and condenser containing *p*-dibromobenzene replaced by a clean, short distillation bridge without condenser, and the phosphine distilled at 2×10^{-2} to 10^{-3} mm., no forerun being taken (Note 5). The main bulk distills at 180–185° (2×10^{-2} mm.). The colorless, oily distillate begins to crystallize in the receiving flask during or shortly after the distillation (Note 6) and weighs 81–83 g. (73–77% yield) (Note 7), m.p. 64–71°. This material is sufficiently pure for further reactions, *e.g.*, Grignard reaction. A sample may be recrystallized from methanol to give colorless needles, m.p. 79–80°.

2. Notes

1. A commercial product, m.p. 88–89°, was used without purification.
2. The *p*-dibromobenzene may be dissolved by heating the ether to reflux. If substantially less ether is used, part of the compound will crystallize out at room temperature.
3. A commercial product from Aldrich Chemical Company was used without purification.

4. When a larger excess of Grignard reagent was used, a polymer insoluble in either phase was observed.
5. Dividing the distillate into a forerun and a constant-boiling main fraction did not improve the melting point of the latter, 66 g. (62%) of phosphine being obtained. The forerun likewise consisted mainly of the phosphine.
6. The distillation apparatus should be taken apart and to a hard glass which blocks the joints and can hardly be removed from the flask.
7. No improvement of the yield was obtained when a 50% excess of Grignard reagent was used.

3. Discussion

This preparation[2] is an example of the general and versatile synthesis of *t*-phosphines of Michaelis[3] which, however, is usually not applicable for aromatic phosphines substituted with –M substituents. The synthesis is an interesting case of the Grignard reaction in that it includes the addition of a Grignard reagent to an "inorganic" single bond and makes use of the mono-Grignard reagent of a dihalogen compound with two equivalent halogen atoms. Similarly, from the mono-Grignard reagents of *m*-dibromobenzene in ether[4] and of *p*-dichlorobenzene in tetrahydrofuran,[5] diphenyl-*m*-bromophenyl-[4] and diphenyl-*p*-chlorophenylphosphine[2] were prepared in yields of 58 and 84%, respectively.

A slightly higher yield of diphenyl-*p*-bromophenylphosphine has been reported using more expensive reagents (tetrahydrofuran and butyllithium rather than ether and magnesium turnings).[6] An alternative route consists of a Friedel-Crafts type of reaction of bromobenzene with phosphorus trichloride and reaction of the resulting dichloro-*p*-bromophenylphosphine with phenylmagnesium bromide. The submitter found this sequence less convenient, and the overall yield is given as only 21%.[7,8,9] In addition, this path fails for the *meta* isomer, and with other substituents the first step yields a mixture of isomers.[11] On the other hand, some phosphines containing – *M* substituents were prepared by making use of the second step.[12,13] A more facile synthesis of such phosphines starts from the title compound[2] or its *meta* isomer,[4] the key step being a second Grignard reaction with subsequent carbonation to give the diphenylphosphinobenzoic acids[2,4] which are also accessible by several other, apparently less convenient and more expensive, routes.[8,12,13,14,15] *p*-Diphenylphosphinobenzoic acid has been used in place of triphenylphosphine in a modification of the Wittig olefination, giving rise to a phosphine oxide which is scarcely soluble in organic solvents and easily soluble in aqueous carbonate solution, and therefore facilitates separation of the olefin from the phosphine oxide.[10]

References and Notes

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

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

methanol (67-56-1)

ether (60-29-7)

ammonium chloride (12125-02-9)

magnesium turnings (7439-95-4)

nitrogen (7727-37-9)

iodine (7553-56-2)

bromobenzene (108-86-1)

phosphorus trichloride (7719-12-2)

Phenylmagnesium bromide (100-58-3)

butyllithium (109-72-8)

Tetrahydrofuran (109-99-9)

triphenylphosphine (603-35-0)

phosphine oxide

chlorodiphenylphosphine (1079-66-9)

p-dibromobenzene (106-37-6)

p-dichlorobenzene (106-46-7)

m-dibromobenzene (108-36-1)

Diphenyl-p-bromophenylphosphine,
Phosphine, (p-bromophenyl)diphenyl (734-59-8)

diphenyl-m-bromophenyl-

diphenyl-p-chlorophenylphosphine

dichloro-p-bromophenylphosphine

p-Diphenylphosphinobenzoic acid (2129-31-9)