



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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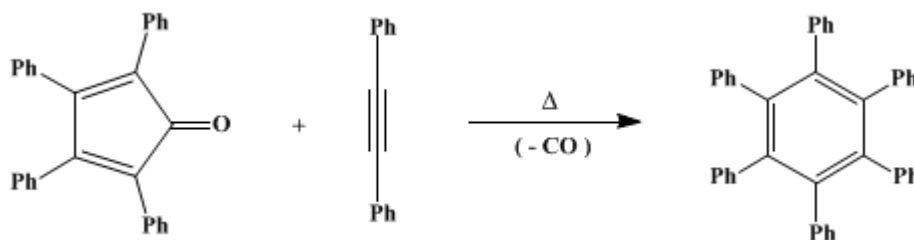
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.604 (1973); Vol. 46, p.44 (1966).

HEXAPHENYLBENZENE

[Benzene, hexaphenyl-]



Submitted by Louis F. Fieser¹

Checked by Chester E. Ramey and V. Boekelheide.

1. Procedure

A 100-ml., round-bottomed, ground-glass flask containing 40 g. of **benzophenone** is heated over a free flame to melt the bulk of the solid, and then 8.0 g. of **tetraphenylcyclopentadienone** (0.021 mole) (**Note 1**) and 8.0 g. of **diphenylacetylene** (0.043 mole) (**Note 2**) are introduced through a paper cone so that no material lodges on the neck or walls. An air condenser is attached, and the mixture is heated over a microburner so that it refluxes briskly but without flooding the condenser (the temperature of the liquid phase is 301–303°). **Carbon monoxide** is evolved, the purple color begins to fade in 15–20 minutes, and the color changes to a reddish brown in 25–30 minutes. When no further lightening in color is observed (after about 45 minutes), the burner is removed and 8 ml. of **diphenyl ether** is added to prevent subsequent solidification of the **benzophenone**. The crystals that separate are brought into solution by reheating, and the solution is let stand for crystallization at room temperature. The product is collected and washed free of brown solvent with **benzene** to give 9.4 g. (84%) of colorless plates, m.p. 454–456° (sealed capillary) (**Note 3**). A satisfactory solvent for recrystallization is **diphenyl ether**, using 7 ml. per gram of product.

2. Notes

1. A synthesis of **tetraphenylcyclopentadienone** is described in *Org. Syntheses, Coll. Vol. 3, 806 (1955)*. However, the following procedure is more convenient. A 250-ml. Erlenmeyer flask is charged with 21 g. of **benzil**, 21 g. of **dibenzyl ketone** (Eastman Organic Chemicals, practical grade), and 100 ml. of **triethylene glycol**, a thermometer is introduced, and the mixture is heated over a free flame until the solid has dissolved. A 10-ml. portion of a 40% solution of **benzyltrimethylammonium hydroxide** in **methanol** is made ready, the temperature of the reaction mixture is adjusted to 100°, the basic catalyst is added, and the mixture is swirled once for mixing and let stand. Within 15–20 seconds the liquid sets to a stiff paste of purple crystals and the temperature rises to 115°. After the temperature has dropped to 80°, the mixture is cooled, thinned by stirring in 50 ml. of **methanol**, and the product is collected and washed with **methanol** until the filtrate is purple, not brown. The yield of product, m.p. 219–220°, is 35.5 g. (93%). Recrystallization can be accomplished with 92% recovery by dissolving the ketone in **triethylene glycol** (10 ml./gram) at 220°.

2. Improvements in the preparation and dehydrohalogenation of **meso-stilbene dibromide** [*Org. Syntheses, Coll. Vol. 3, 350 (1955)*] are as follows. **trans-Stilbene** (20 g.) is heated with 400 ml. of **acetic acid** on the steam bath until dissolved, 40 g. of pyridinium bromide perbromide is added, and the mixture is heated on the steam bath and swirled for 5 minutes. **meso-Stilbene dibromide** separates at once in pearly white plates. The mixture is cooled to room temperature, and the product is collected and washed with **methanol**. The yield of dibromide, m.p. 236–237°, is 32.4 g. (86%). A 250-ml., round-bottomed, ground-glass flask is charged with 32.4 g. of the dibromide, 65 g. of **potassium hydroxide pellets**, and 130 ml. of **triethylene glycol**. A 15 × 125 mm. test tube containing enough of the same solvent to cover the bulb of a thermometer is inserted in the flask. The flask is supported in a clamp,

which is used as a handle for swirling the flask over a free flame to mix the contents and bring the temperature to 160°, when [potassium bromide](#) begins to separate. By intermittent heating and swirling the mixture is kept at 160–170° for 5 minutes more to complete the reaction. The test tube is then removed, dipped into 500 ml. of water in a beaker, and the adhering organic material is rinsed into the beaker with 95% [ethanol](#). The hot reaction mixture is poured into the beaker, and the flask is rinsed alternately with water and with [ethanol](#). After cooling, the crude product is collected, washed with water, and air-dried (16.5 g.). The brown solution of this material in 50 ml. of 95% [ethanol](#) is filtered from a little dark residue, reheated, and let stand for crystallization. A first crop of [diphenylacetylene](#) (11.8 g.) separates in large colorless spars, m.p. 61.5–62.5°. Concentration of the mother liquor yield an additional 2.4 g. of crystals, m.p. 58–59°.

The checkers used [diphenylacetylene](#) provided by Aldrich Chemicals.

3. The melting point is determined conveniently with a Mel-Temp apparatus and a 90–510° thermometer designed for use with it (Laboratory Devices, Post Office Box 68, Cambridge 39, Massachusetts). An evacuated capillary containing a sample is sealed close to the sample to prevent sublimation, and repeated determinations are made with the same sample. The figure 456° is the average of two determinations of the temperature of melting; 454° is the average of two observations of the point of solidification. When the amount of [diphenylacetylene](#) was reduced to 1.2 times the theory, the yield was the same but the melting point was 450–452°.

3. Discussion

[Hexaphenylbenzene](#) has been prepared by heating [tetraphenylcyclopentadienone](#) and [diphenylacetylene](#) without solvent² and by trimerization of [diphenylacetylene](#) with [bis-\(benzotrile\)-palladium chloride](#) and other catalysts.³

4. Merits of the Preparation

[Hexaphenylbenzene](#) can be prepared satisfactorily by strong heating of a mixture of 0.5 g. each of [tetraphenylcyclopentadienone](#) and [diphenylacetylene](#) in a test tube, but the method is unsatisfactory on a larger scale because of the high melting point of the product and the poor heat transfer in a flask. The present procedure demonstrates use of [benzophenone](#) as solvent for a Diels-Alder reaction requiring a temperature of about 300°. When the reaction is completed, addition of a small amount of [diphenyl ether](#) lowers the melting point of [benzophenone](#) sufficiently to prevent this solvent from solidifying.

Other solvents tried and the liquid temperatures of the refluxing mixtures are: [stearic acid](#) (340–365°), [di-*n*-butyl phthalate](#) (320–325°), [phenyl salicylate](#) (290°). The first two solvents are unsatisfactory because of side reactions consuming some of the [tetraphenylcyclopentadienone](#), the third because the addition reaction is too slow.

([Note 1](#)) describes an improvement in the preparation of the starting dienone involving use of a medium of higher solvent power and higher boiling point than [ethanol](#) and of a basic catalyst more convenient than [potassium hydroxide](#) because it is miscible with the solvent employed. ([Note 2](#)) reports two improvements in the preparation of [diphenylacetylene](#). The yield in the conversion of [trans-stilbene](#) to the *meso* dibromide is increased by use of the highly stereoselective reagent pyridinium bromide perbromide. In the dehydrohalogenation step the reaction time is reduced substantially and the yield increased by use of a high-boiling alcohol in place of [ethanol](#).

References and Notes

1. Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138.
 2. W. Dilthey and G. Hurtig, *Ber.*, **67**, 2007 (1934).
 3. A. T. Blomquist and P. M. Maitlis, *J. Am. Chem. Soc.*, **84**, 2329 (1962).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

pyridinium bromide perbromide

meso dibromide

ethanol (64-17-5)

acetic acid (64-19-7)

Benzene (71-43-2)

methanol (67-56-1)

carbon monoxide (630-08-0)

Benzil (134-81-6)

potassium hydroxide,
potassium hydroxide pellets (1310-58-3)

Benzophenone (119-61-9)

potassium bromide (7758-02-3)

phenyl salicylate (118-55-8)

stearic acid (57-11-4)

dibenzyl ketone (102-04-5)

diphenyl ether (101-84-8)

Diphenylacetylene (501-65-5)

benzyltrimethylammonium hydroxide (100-85-6)

Tetraphenylcyclopentadienone (479-33-4)

triethylene glycol (112-27-6)

Hexaphenylbenzene,
Benzene, hexaphenyl- (992-04-1)

bis-(benzonitrile)-palladium chloride

trans-Stilbene (103-30-0)

meso-stilbene dibromide

di-n-butyl phthalate (84-74-2)

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