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.*

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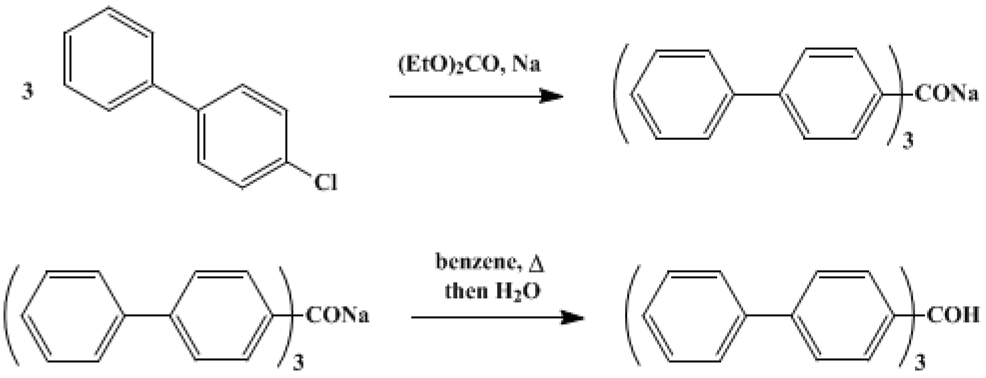
# TRIBIPHENYLCARBINOL

## [Carbinol, tris-(4-phenylphenyl-)]



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## 1. Procedure

In a 3-l. three-necked round-bottomed flask, equipped with a mercury-sealed stirrer and a 12-bulb reflux condenser, are placed 188.5 g. (1 mole) of *p*-chlorobiphenyl (Note 1), 47.2 g. (0.4 mole) of ethyl carbonate (Note 2), and 1.5 l. of anhydrous, thiophene-free benzene. The side tube is closed with a cork, stirring is begun, and the mixture is heated by means of a hot plate (Note 3). As soon as the mixture begins to boil, 2 g. of powdered sodium (Note 4) is added. The reaction starts in 1–2 minutes, as indicated by more vigorous refluxing and a change in color from yellow to brown (Note 5). Powdered sodium is then introduced in small portions, over a period of 1 hour, until an additional 28 g. has been added (total amount of sodium, 30 g.). The reaction mixture is refluxed and vigorously stirred (Note 6) for 2 hours. When the mixture has cooled somewhat, 75 to 100 ml. of absolute ethanol is added. After all the particles of sodium have reacted, 500 ml. of water is added, the condenser is arranged for downward distillation, and the benzene and unchanged *p*-chlorobiphenyl are removed by distillation from a steam bath (Note 7). The crude product remaining in the flask is separated by filtration, washed with 100–200 ml. of water, and pressed as dry as possible. The solid is dissolved in 600 ml. of xylene in a 1-l. distilling flask, and the solution is subjected to distillation until 25 to 50 ml. of distillate (xylene and water) has been collected. The solution is cooled somewhat, 1 to 2 g. Norit is added, and then the mixture is boiled for 5 minutes. The hot solution is filtered rapidly and the filtrate is cooled. The product is collected by filtration, washed with 25 to 50 ml. of cold xylene then with 200 ml. of petroleum ether, and dried. The tribiphenylcarbinol forms small white crystals which melt at 207–208°. The product weighs 57–65 g. (35–40%) (Note 8).

## 2. Notes

1. Technical *p*-chlorobiphenyl was purified by recrystallizing 300 g. of it from 750 ml. of petroleum ether. The recovery was 240–250 g.
2. Technical ethyl carbonate was washed successively with 10% aqueous sodium carbonate and saturated calcium chloride solution. It was then dried with magnesium sulfate and distilled. The fraction boiling at 124–125° was used.
3. A hot plate should be used to reduce the fire hazard. All flames in the vicinity should be extinguished.
4. The powdered sodium is prepared by melting 30 g. of the clean metal under 1 l. of dry xylene. The mixture is then stirred vigorously with a metal stirrer until the sodium is powdered.
5. If anhydrous reagents are used and the benzene solution is boiling, the reaction starts immediately. The reaction must start before more sodium is added.
6. The stirring must be sufficiently vigorous to prevent caking on the sides of the flask.

7. Unchanged *p*-chlorobiphenyl steam-distils along with the benzene. It is essential that it be removed, since a pure product is difficult to obtain by crystallization if unchanged chloro compound is present.

8. Better yields may be obtained in small-scale preparations if sodium chips are used. A solution of 19 g. of *p*-chlorobiphenyl, 5 g. of ethyl carbonate, and 50 ml. of anhydrous thiophene-free benzene is heated on a steam bath until refluxing begins. During 30 minutes 5 g. of sodium, cut into particles about 0.5 mm. square and 2 mm. thick, is dropped through the condenser. After the mixture has refluxed for 12 hours, it is decomposed and the product is isolated as described above, but with one-tenth the amounts of solvents. The yields range from 7 to 9 g. (47 to 55%), but the long period of refluxing required and the tedious cutting of the sodium chips make this method of value for small-scale preparations only. A large-scale run by this method gave only a 31% yield.

## 3. Discussion

Tribiphenylcarbinol has been prepared by the action of 4-xenylmagnesium iodide upon 4,4'-diphenylbenzophenone, or upon the methyl ester of *p*-phenylbenzoic acid;[1] and by the action of *p*-chlorobiphenyl upon ethyl carbonate in the presence of powdered sodium[2] or sodium wire.[3]

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## References and Notes

1. Schlenk, *Ann.*, **368**, 295 (1909).
2. Morton and Stevens, *J. Am. Chem. Soc.*, **53**, 4028 (1931); Morton and Emerson, *J. Am. Chem. Soc.*, **59**, 1947 (1937); Morton and Wood, private communication.
3. Bachmann and Wiselogle, *J. Org. Chem.*, **1**, 372 (1936).

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

petroleum ether

4-xenylmagnesium iodide

ethanol (64-17-5)

calcium chloride (10043-52-4)

Benzene (71-43-2)

sodium carbonate (497-19-8)

Norit (7782-42-5)

sodium,
sodium wire (13966-32-0)

xylene (106-42-3)

magnesium sulfate (7487-88-9)

ethyl carbonate

TRIBIPHENYLCARBINOL

Carbinol, tris-(4-phenylphenyl-) (5341-14-0)

p-chlorobiphenyl (2051-62-9)

4,4'-diphenylbenzophenone

methyl ester of p-phenylbenzoic acid (720-75-2)