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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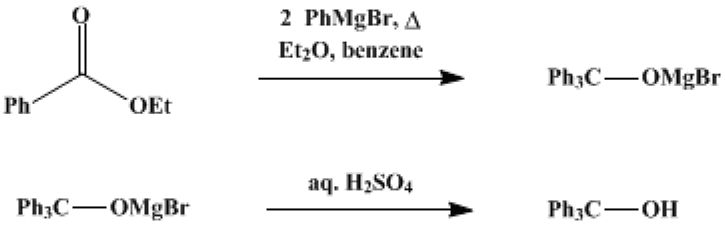
TRIPHENYLCARBINOL

[Carbinol, triphenyl-]



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1. Procedure

In a 2-l. three-necked flask, fitted with a separatory funnel, a reflux condenser, and a mercury-sealed stirrer, 27 g. (1.1 gram atoms) of magnesium, 181 g. (122 ml., 1.15 moles) of bromobenzene, and a total of 450 ml. of anhydrous ether (Note 1) are converted into phenylmagnesium bromide by the procedure described in *Org. Syntheses* Coll. Vol. **1**, 226 (1941). Calcium chloride tubes are used to prevent the entrance of moisture through the condenser and the separatory funnel during the addition. In order to dissolve all the magnesium it may be necessary, in some instances, to continue stirring for longer than the prescribed 10 minutes after addition is complete.

To the Grignard solution, 75 g. (71.5 ml., 0.5 mole) of ethyl benzoate in 200 ml. of dry benzene (Note 2) is added at such a rate that the mixture refluxes gently. The flask is cooled in a pan of cold water during the addition, which requires about an hour. After the addition is complete, the mixture is refluxed for an hour on a steam bath. The reaction mixture is cooled in cooled an ice-salt bath and then poured slowly, with constant stirring, into a mixture of 1.5 kg. of cracked ice and 50 ml. of concentrated sulfuric acid. The mixture is stirred at intervals until all the solid that separates at the benzene-water interface has dissolved. If necessary, 50 g. of ammonium chloride is added to facilitate the decomposition of the magnesium salt, and additional benzene may be added if the amount present is insufficient to dissolve all the product. When the solids have disappeared, the benzene layer is separated and washed, successively, with 200 ml. of water, 200 ml. of a 5% solution of sodium bicarbonate, and finally with 200 ml. of water. The solvents are removed as completely as possible by distillation on a steam bath, and the remaining solution or solid mass is steam-distilled to remove biphenyl and unchanged bromobenzene. The product is filtered, washed with water, and dried. The crude triphenylcarbinol, which weighs 120–125 g., is recrystallized from carbon tetrachloride (4 ml. of solvent per gram of solid). The weight of the first crop of colorless triphenylcarbinol is 110–115 g. (Note 3). A second crop may be obtained by heating the filtrate with a gram of Norit, then concentrating to about 125 ml. and cooling the solution. The total yield of triphenylcarbinol melting at 161–162° is 116–121 g. (89–93%) (Note 4).

2. Notes

1. Commercial anhydrous ether, before it is used, should be dried over slices of sodium, and the bromobenzene should be dried by distillation.
2. The benzene may be dried over anhydrous magnesium sulfate.
3. Triphenylcarbinol separates from carbon tetrachloride with solvent of crystallization. The solvent is readily lost on exposure of the crystals to air. The weight mentioned is that of the solvent-free product.
4. Practically the same yield of triphenylcarbinol was obtained from benzophenone and phenylmagnesium bromide; in this reaction only one-half as much Grignard reagent is required as that needed for the reaction with ethyl benzoate. To the cooled Grignard reagent prepared from 13.5 g. (0.55 gram atom) of magnesium, was added a solution of 91 g. (0.5 mole) of benzophenone in 200 ml. of dry

benzene at such a rate that the mixture refluxes gently. After the mixture had been refluxed for 1 hour, the isolation of the triphenylcarbinol was carried out in the manner described above.

3. Discussion

Triphenylcarbinol has been obtained by the reaction between phenylmagnesium bromide and benzophenone,[1] methyl benzoate,[2] phosgene,[3] or ethyl or butyl pyrocarbonate;[4] by action of phenylsodium on benzophenone, benzoyl chloride, ethyl chlorocarbonate, or ethyl benzoate;[5] by hydrolysis of triphenylchloromethane;[6] and by oxidation of triphenylmethane.[7]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 841

References and Notes

1. Acree, *Ber.*, **37**, 2755 (1904).
2. Ullmann and Münzhuber, *Ber.*, **36**, 406 (1903).
3. Sachs and Loevy, *Ber.*, **36**, 1588 (1903).
4. Shamshurin, *J. Gen. Chem., U.S.S.R.*, **13**, 569 (1943); [*C. A.*, **39**, 700 (1945)].
5. Acree, *Am. Chem. J.*, **29**, 594 (1903).
6. Meissel, *Ber.*, **32**, 2422 (1899).
7. Law and Perkin, *J. Chem. Soc.*, **93**, 1637 (1908); Schwarz, *J. Am. Chem. Soc.*, **31**, 848 (1909).

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

ethyl or butyl pyrocarbonate

sulfuric acid (7664-93-9)

Benzene (71-43-2)

ether (60-29-7)

ammonium chloride (12125-02-9)

sodium bicarbonate (144-55-8)

magnesium (7439-95-4)

carbon tetrachloride (56-23-5)

Norit (7782-42-5)

benzoyl chloride (98-88-4)

Benzophenone (119-61-9)

sodium (13966-32-0)

phosgene (75-44-5)

bromobenzene (108-86-1)

Biphenyl (92-52-4)

ethyl benzoate (93-89-0)

phenylsodium

Phenylmagnesium bromide (100-58-3)

methyl benzoate (93-58-3)

ethyl chlorocarbonate (541-41-3)

Triphenylmethane (519-73-3)

Triphenylchloromethane (76-83-5)

Triphenylcarbinol,
Carbinol, triphenyl- (76-84-6)

magnesium sulfate (7487-88-9)