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.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 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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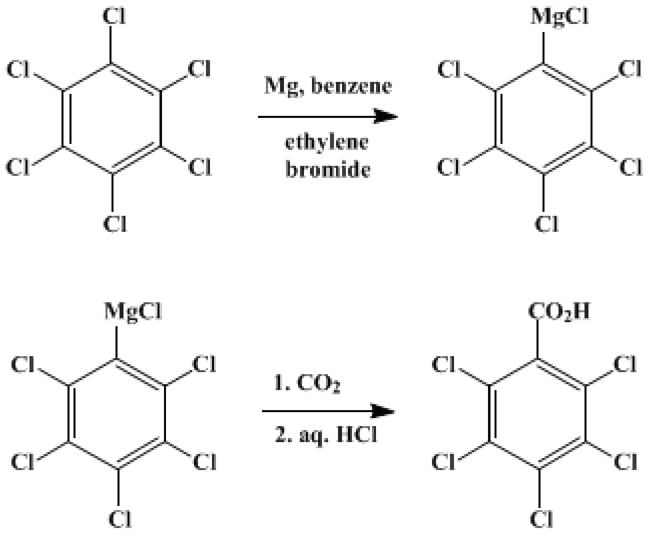
PENTACHLOROBENZOIC ACID

[Benzoic acid, pentachloro-]



Submitted by D. E. Pearson and Dorotha Cowan[1].
Checked by Virgil Boekelheide and Fred G. H. Lee.

1. Procedure

Magnesium turnings (39 g., 1.6 g. atoms) and hexachlorobenzene (142.4 g., 0.5 mole, m.p. 228–229°) in 1 l. of dry ether are brought to gentle reflux in a 3-l. three-necked flask heated by a Glascol® mantle at 20 volts (Note 1). Ethylene bromide (188 g., 1.0 mole) in 200 ml. of dry benzene is added through a Hershberg funnel[2] over a period of 48 hours (about 1 drop/25 seconds) (Note 2). Efficient stirring is maintained throughout the period of addition, during which the reaction mixture turns dark brown and forms a precipitate. The mixture is cooled to room temperature, and carbon dioxide, generated from dry ice and dried by passage through anhydrous calcium chloride, is added under the surface of the stirred mixture for at least 3 hours and at such a rate as to minimize clogging of the entrance tube (Note 3). After this addition 10% aqueous hydrochloric acid is added slowly until the mixture is strongly acid. The ether and benzene are removed by distillation, and the crude pentachlorobenzoic acid left in the water is removed by filtration and is washed free of salts with water. The dark-brown damp acid is converted to the ammonium salt by repeated extraction with hot dilute ammonium hydroxide (1 part by volume of concentrated ammonium hydroxide and 2 parts of water) followed by decantation. The combined decanted solutions are treated with Norit® while still hot, filtered, and then strongly acidified while still hot with concentrated hydrochloric acid. The precipitated acid is digested for at least several hours (Note 4). After the suspension has been cooled, the crude brown-colored acid is removed by filtration, washed with cold water, and air-dried to give 113 g. (77%) of product. The crude acid is recrystallized from 900 ml. of 50% aqueous methanol to yield 95 g. (65%) of tan-colored needles, m.p. 202–206° (Note 5).

2. Notes

1. The atomic proportions of magnesium are not related to the mole quantity of hexachlorobenzene in this or any other entrainment reaction. The excess magnesium (1.1 g. atoms in this case) is used to react with ethylene bromide and leave 0.5 g. atom of clean-surfaced magnesium. Ordinarily 1 mole of entrainment reagent is used per mole of "inert" halide, but for this preparation 2 moles of entrainment reagent per mole of halide gives a better yield.

2. Little attention is needed provided that the capillary tube is fitted properly. The capillary tube of the

Hershberg dropping funnel should be about 4.5 in. long, and a Band S 24 platinum wire should be inserted to fit very snugly.
Rather than a Hershberg funnel, a commercial constant addition funnel (Kontes Glass Co., Vineland, N.J.) can be used.
3. A T-tube in the carbon dioxide stream serves to bypass the gas if its rate of addition is too rapid. Also, the T-tube is large enough to permit the insertion of a plunger to dislodge particles within the mouth of the tube.
4. Without digestion the acid will contain appreciable amounts of the ammonium salt. In an alternative method of purification the crude acid is converted to the insoluble sodium salt. The sodium salt can be recrystallized from 95% ethanol to give flaky white crystals, m.p. 339–340°. Digestion of the sodium salt with 1 part of concentrated hydrochloric acid and 1 part of water yields the free acid. From 10 g. of crude acid, 7.3 g. of purified acid can be obtained from the sodium salt. The free acid is reported to crystallize well from toluene and light petroleum ether.[3]
5. The melting point is reported variously in the range from 199° to 208°.[4] The acid is colorless if purified by conversions through the sodium salt (Note 4), but the yield is lower.

3. Discussion

Pentachlorobenzoic acid has been prepared by oxidation of pentachlorotoluene with nitric acid and mercury,[3] by oxidation of pentachlorobenzaldehyde by potassium permanganate,[5] and by chlorination of tetrachlorophthalyl chloride[6] and of dichlorobenzoic acids.[7] Pentachlorobenzoic acid recently has been prepared by the exhaustive chlorination of benzoic acid in sulfuric acid containing iodine.[8] The present procedure has been adapted from that of Pearson, Cowan, and Beckler.[9]

4. Merits of the Preparation

Ethylene bromide has been demonstrated to be as efficient as ethyl bromide as an entrainment agent.[9] Its use is advantageous because a second Grignard reagent is not introduced in the reaction mixture—only magnesium bromide. An additional feature of this preparation and of most preparations involving entrainment agents is the slow rate of addition of the entrainer, which permits adequate time for the "inert" halide (in this preparation, hexachlorobenzene) to react on the bright, clean surfaces of the magnesium turnings.

Although pentachlorophenylmagnesium chloride can be made in tetrahydrofuran without the use of the entrainment method, the Grignard reagent in this solvent does not react with carbon dioxide to give pentachlorobenzoic acid in good yield.[10]

References and Notes

1. Department of Chemistry, Vanderbilt University, Nashville, Tennessee.
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Appendix

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

petroleum ether

ethanol (64-17-5)

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

methanol (67-56-1)

ether (60-29-7)

magnesium,
magnesium turnings (7439-95-4)

nitric acid (7697-37-2)

potassium permanganate (7722-64-7)

Ethyl bromide (74-96-4)

Benzoic acid (65-85-0)

mercury (7439-97-6)

carbon dioxide (124-38-9)

platinum wire (7440-06-4)

iodine (7553-56-2)

Norit (7782-42-5)

toluene (108-88-3)

ethylene bromide (106-93-4)

ammonium hydroxide (1336-21-6)

magnesium bromide (7789-48-2)

Tetrahydrofuran (109-99-9)

Pentachlorobenzoic acid,

Benzoic acid, pentachloro- (1012-84-6)

hexachlorobenzene (118-74-1)

pentachlorotoluene (877-11-2)

pentachlorobenzaldehyde

tetrachlorophthalyl chloride

pentachlorophenylmagnesium chloride