



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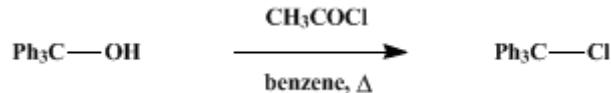
*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 3, p.841 (1955); Vol. 23, p.100 (1943).*

## TRIPHENYLCHLOROMETHANE

### [Methane, chlorotriphenyl-]

#### [A. FROM TRIPHENYLCARBINOL AND ACETYL CHLORIDE]



Submitted by W. E. Bachmann

Checked by R. L. Shriner and Eldred Welch.

#### 1. Procedure

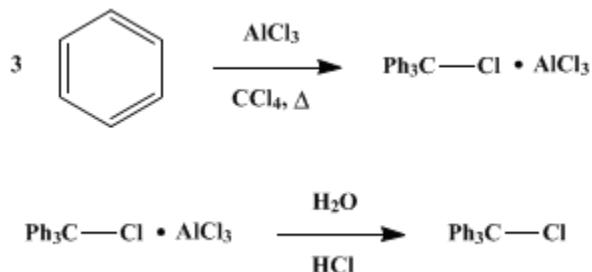
A mixture of 250 g. of pure triphenylcarbinol (p. 839) and 80 ml. of dry benzene is placed in a 1-l. round-bottomed flask provided with a reflux condenser. The condenser is provided with a calcium chloride tube at the top (Note 1). The mixture is heated on a steam bath; when it is hot, 50 ml. of acetyl chloride (Note 2) is added through the top of the condenser. Heating is continued while the mixture is shaken vigorously. In about 5 minutes all the solid triphenylcarbinol disappears and a clear solution results. In the course of 10 minutes, an additional 100 ml. of acetyl chloride is added in 10-ml. portions. The solution is then refluxed for 30 minutes longer.

The solution is cooled by shaking the flask under running water, and during this operation 200 ml. of petroleum ether (Note 3) is added through the top of the condenser; the triphenylchloromethane separates in sugarlike crystals. The mixture is cooled in an ice bath for 1–2 hours, and the product is filtered and washed with 100–150 ml. of petroleum ether (Note 4). The colorless solid, after drying in a desiccator over soda-lime and paraffin (Note 5), weighs 212–224 g. (79–83%) and melts at 111–112° with slight previous softening. An additional 30–37 g. of colorless material may be obtained by concentrating the filtrate to a volume of about 75 ml. For this purpose, the petroleum ether and acetyl chloride are distilled at ordinary pressure, and the acetic acid under reduced pressure. The warm solution is treated with 2 g. of Norit, filtered, and again warmed with 2 g. of Norit. The mixture is filtered, 50 ml. of petroleum ether is added to the filtrate, and the solution is then cooled in an ice bath. The crystals of triphenylchloromethane are collected on a filter and washed with 70 ml. of cold petroleum ether. This second crop of material is pure white, like the first crop; the solid melts at 110.5–112° with previous softening (Note 6). The total yield is 249–254 g. (93–95%).

#### 2. Notes

1. It is best to carry out the reaction under a hood.
2. The acetyl chloride should be of good quality. Good results were obtained with practical acetyl chloride which was distilled just before use.
3. Petroleum ether having a boiling point of 30–60° should be used because it is easily removed from the product.
4. The filtration should be rapid. Triphenylchloromethane is hydrolyzed by moisture in the air.
5. The final product is perfectly colorless and should have no sharp odor. This product is sufficiently pure for most purposes. It may be recrystallized by dissolving it in 100 ml. of hot benzene and cooling the solution after diluting it with 200 ml. of petroleum ether. If the product is kept in a bottle, the stopper should be coated with paraffin in order to keep out the moisture of the air.
6. Triphenylbromomethane may be made in a similar manner by substituting acetyl bromide for the acetyl chloride.

#### [B. FROM BENZENE AND CARBON TETRACHLORIDE, BY THE FRIEDEL-CRAFTS REACTION]



Submitted by C. R. Hauser and Boyd E. Hudson, Jr.  
Checked by R. L. Shriner and Flavius W. Wyman.

## 1. Procedure

A mixture of 2 kg. (2.28 l., 25.6 moles) of dry thiophene-free benzene (Note 1) and 800 g. (470 ml., 5.2 moles) of dry sulfur-free carbon tetrachloride (Note 2) is placed in a 5-l. three-necked flask immersed in an ice bath and equipped with a mercury-sealed mechanical stirrer and a reflux condenser which is connected to a trap for the absorption of hydrogen chloride. The third neck of the flask is connected to a 1-l. Erlenmeyer flask by means of short pieces of large-bore (15-mm.) glass and rubber tubing (see Fig. 19, p. 550). In the Erlenmeyer flask is placed 600 g. (4.51 moles) of fresh resublimed aluminum chloride (Note 3). The Erlenmeyer flask is tilted and gently tapped, so that the aluminum chloride is added in small portions to the reaction mixture, and at such a rate that addition is completed in 1.5–2 hours. The reaction mixture is not allowed to reflux during the addition of the aluminum chloride. Fifteen minutes after all the aluminum chloride has been added, the ice bath is removed, and the reaction is allowed to proceed without further cooling. When no further heat is evolved, the mixture is refluxed until the evolution of hydrogen chloride subsides (about 2 hours). The mixture is then allowed to cool to room temperature.

A 10-l. copper can (22.5 cm. in diameter and 30 cm. deep) (Note 4) is equipped with a powerful mechanical stirrer and a thermometer and is immersed to a depth of 20 cm. in an ice bath. A mixture of 1 l. of thiophene-free benzene and 2 l. of 6 N hydrochloric acid is placed in the copper vessel. The above reaction mixture is added to the vigorously stirred contents of the copper can at such a rate that the temperature does not rise above 25° (about 2 hours is required). When the addition is complete, the reaction flask is rinsed with a little ice water, and the rinsings are added to the hydrolysis mixture. Stirring is continued for 10 minutes longer. The benzene layer is decanted, and the aqueous layer is diluted with 1 l. of ice water. The aqueous layer is extracted with 500 ml. of benzene and is discarded. The combined benzene solutions are washed with 250 ml. of ice-cold hydrochloric acid and are dried for 2 hours in a stoppered flask over 250 g. of anhydrous calcium chloride.

The dried benzene solution is filtered through glass wool into a 5-l. flask fitted with a cork carrying a delivery tube and a thermometer which reaches within 5 cm. of the bottom of the flask. Several boiling chips are added, and the benzene is removed by distillation, slowly towards the last, until the temperature of the boiling residue reaches 120°. The residue is transferred to a 2-l. Erlenmeyer flask with the aid of 40–50 ml. of dry benzene and is cooled to about 40°. Twenty-five milliliters of acetyl chloride (Note 5) is added, and the mixture is heated nearly to the boiling point. The solution is vigorously shaken while it is cooled rapidly to room temperature; it is then chilled in ice water for 2 hours. The solid triphenylchloromethane is crushed thoroughly with a porcelain spatula and is filtered with suction. The filtrate is set aside, and the crystals are washed with three 300-ml. portions of ligroin (b.p. 70–90°) (Note 6). The solvent is removed from the product by allowing it to stand in a vacuum desiccator over mineral oil or paraffin shavings for 24 hours. The crystals are stirred occasionally, and the desiccator is evacuated to 5–10 mm. (Note 7). The light-greenish yellow crystals melt at 111–112° and weigh 870–940 g. (69–75% based on the aluminum chloride).

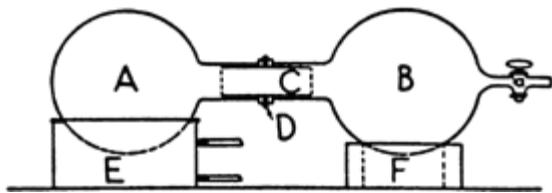
Second crops of crystals may be obtained by distilling, separately, the filtrate and washings until the temperature reaches 110° and 100°, respectively, and cooling the residues rapidly while they are shaken. The crystals are washed with minimum quantities of ligroin (b.p. 70–90°) and are dried as described for

the first crop. The second crop from the filtrate weighs 70–80 g. and melts at 111–112° with sintering at 108°; that from the washings weighs 50–135 g. and melts at 110–111° with sintering at 107°. These second crops are darker in color than the first crop, and of the two second crops, that from the washings is the darker greenish yellow. The total yield of product varies from 1060 g. to 1085 g. (84–86% based on the aluminum chloride) (Note 8).

## 2. Notes

1. The presence of sulfur compounds, especially thiophene, in the reagents leads to low yields and a dark-colored product. A good grade of thiophene-free benzene should be used. The benzene may be dried by distillation or by allowing it to stand over calcium chloride. The benzene which is recovered in this preparation may be used in future runs after it has been extracted with alkali, washed, and dried. Small amounts of carbon tetrachloride in the benzene do not interfere, since the quantities of benzene and carbon tetrachloride used are in excess of the relative quantity of the aluminum chloride.
2. A good grade of commercial carbon tetrachloride (b.p. 75–76°) may be used without a noticeable decrease in yield. However, if a colorless product is desired, sulfur-free C.P. carbon tetrachloride is recommended. The carbon tetrachloride may be dried in the same manner as the benzene.
3. The yield of triphenylchloromethane depends very much upon the quality of the aluminum chloride used. Fresh commercial resublimed aluminum chloride, in powder form, has been used in the preparation described.
4. The high thermal conductivity of copper makes possible rapid removal of heat during the hydrolysis; the presence of copper in the mixture does not appear to produce any undesirable effects. If a metal can is not available, a 3-gal. enameled bucket may be used.
5. A technical grade of acetyl chloride may be used, since the presence of small amounts of acetic acid does not interfere. The acetyl chloride serves to convert into triphenylchloromethane any triphenylcarbinol which may be present.
6. Technical ligroin (b.p. 90–120°) should be extracted several times with concentrated sulfuric acid, washed, and dried before use.
7. The vacuum desiccator shown in Fig. 28 has been in use in the research laboratories of the Eastman Kodak Company for some time, and has been found to be of great convenience when large amounts of materials must be handled. One of two similar round-bottomed flasks (*B*) is provided with a tube for connection to the vacuum pump. Although not necessary, a glass stopcock in this tube is a convenience, and it enables the flask to be used as a large separatory funnel. A glass sleeve *C*, which must not fit too loosely, serves as a guide for the union between the two flasks *A* and *B*. The sleeve carries a rubber gasket (*D*) which is most conveniently cut from an old inner tube. The gasket provides a tight seal for the vacuum, and the sleeve prevents the contact surfaces from slipping sidewise. *Without the guiding sleeve, the assembly is not safe.* Special guiding clamps may be used, but they offer no particular advantage. When in use, flask *A* contains the product and *B* contains the drying agent. *E* is a steam bath, and *F* is any convenient support. The apparatus, assembled from 5-l. stock flasks chosen at random, holds a vacuum of 2 mm. for 24 hours with the aid of a high-grade vacuum grease. This "dumb-bell desiccator" is particularly useful for synthetic work; frequently one operation may be eliminated, for flask *A* may be the vessel in which a reaction, or process of concentration, was performed and the product may be dried without transferring it, or flask *A* may be the vessel in which a subsequent reaction is to be carried out; while the product is drying, it may be stirred by rotating the assembly; and, within limits, the desiccator may be of any size desired. It is desirable to coat the flasks on the outside with a thin film of some soluble plastic, for the hazards are thereby greatly reduced; very little shattering occurred when evacuated flasks so coated were experimentally "imploded." A comparative test, in which a highly hygroscopic syrup was used, indicated that, with this form of vacuum desiccator and with equal amounts of drying agent, operations may be performed about twice as rapidly as in the conventional model. When the flask *A* is warmed gently, the efficiency of the assembly is at least four times that of a conventional desiccator. (F. P. Pingert, private communication.)

Fig. 28.



8. The product may be stored satisfactorily in ordinary screw-top bottles, provided that they are well sealed with paraffin or some similar material. Triphenylchloromethane is slowly hydrolyzed to triphenylcarbinol by the moisture of the air. Partially hydrolyzed triphenylchloromethane may be purified by recrystallization from one-third its weight of benzene containing 5–25% of acetyl chloride. The product is washed with ligroin containing a little acetyl chloride.

### 3. Discussion

Triphenylchloromethane has been made by the action of phosphorus pentachloride,<sup>1</sup> hydrogen chloride,<sup>2</sup> or acetyl chloride<sup>3</sup> upon triphenylcarbinol. It has also been made by the reaction between carbon tetrachloride and benzene in the presence of aluminum chloride<sup>4</sup> or ferric chloride,<sup>5</sup> and by the action of phosphorus pentachloride,<sup>6</sup> or of sulfonyl chloride in the presence of peroxides,<sup>7</sup> upon triphenylmethane. Procedure A is based upon that of Gomberg and Davis;<sup>3</sup> procedure B is a modification of that originally reported by Gomberg<sup>4</sup> and later described by Gattermann and Wieland.<sup>8</sup>

### References and Notes

1. Hemilian, *Ber.*, **7**, 1207 (1874); Fischer and Fischer, *Ann.*, **194**, 257 (1878).
2. Gomberg, *Ber.*, **35**, 2401 (1902).
3. Gomberg and Davis, *Ber.*, **36**, 3925 (1903).
4. Gomberg, *Ber.*, **33**, 3147 (1900).
5. Wertyporoch, Kowalski, and Roeske, *Ber.*, **66**, 1237 (1933).
6. Cone and Robinson, *Ber.*, **40**, 2163 (1907).
7. Kharasch and Brown, *J. Am. Chem. Soc.*, **61**, 2148 (1939).
8. Gattermann and Wieland, *Laboratory Methods of Organic Chemistry*, p. 346, The Macmillan Company, New York, 1937.

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

ligroin

petroleum ether

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

hydrogen chloride,  
hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

Benzene (71-43-2)

phosphorus pentachloride (10026-13-8)

acetyl chloride (75-36-5)

carbon tetrachloride (56-23-5)

copper (7440-50-8)

Norit (7782-42-5)

sulfuryl chloride (7791-25-5)

aluminum chloride (3495-54-3)

ferric chloride (7705-08-0)

Triphenylmethane (519-73-3)

Triphenylchloromethane,  
Methane, chlorotriphenyl- (76-83-5)

Triphenylcarbinol (76-84-6)

Thiophene (110-02-1)

acetyl bromide (506-96-7)

Triphenylbromomethane (596-43-0)