A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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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.

DOI:10.15227/orgsyn.030.0095

Organic Syntheses, Coll. Vol. 4, p.910 (1963); Vol. 30, p.95 (1950).

TETRAPHENYLARSONIUM CHLORIDE HYDROCHLORIDE

[Arsonium chloride, tetraphenyl-, hydrochloride]

$$3\ C_6H_5Cl \xrightarrow[\text{benzene, }\Delta]{\text{Na, }AsCl_3} (C_6H_5)_3As$$

$$(C_6H_5)_3As \xrightarrow[\text{acetone}]{H_2O_2} (C_6H_5)_3AsO$$

$$(C_6H_5)_3AsO \xrightarrow{C_6H_5MgBr,\ \Delta} (C_6H_5)_4AsOMgBr$$

$$(C_6H_5)_4AsOMgBr \xrightarrow{HCl,\ \Delta} (C_6H_5)_4AsCl \bullet HCl$$

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1. Procedure

Caution! All steps in the following preparations should be performed under a hood, since volatile arsenic compounds may be liberated.

A. *Triphenylarsine.* In a 2-l. round-bottomed three-necked flask is placed 130 g. (5.65 g. atoms) of powdered sodium[2] covered with 900 ml. of benzene. The flask is fitted with an Allihn condenser, a mercury-sealed mechanical Hershberg stirrer, and a 500-ml. dropping funnel in which is placed a mixture of 170 g. (0.94 mole) of arsenic trichloride and 272 g. (2.42 moles) of chlorobenzene. About 10 ml. of the arsenic trichloride-chlorobenzene mixture is dropped into the flask, and the reaction mixture is stirred and heated on a steam bath until it darkens and boils spontaneously. The steam bath is removed, and the remainder of the arsenic trichloride-chlorobenzene mixture is added dropwise, with stirring, over a period of 1–1.5 hours at such a rate that gentle boiling is maintained (Note 1). When the addition is complete, the mixture is stirred and heated under reflux on a steam bath for 12 hours.

The reaction mixture is filtered while hot through a large Büchner funnel, and the filtrate is collected in a 3-l. filter flask. The residue (Note 2) is washed on the funnel with two 200-ml. portions of hot benzene, pressed as dry as possible, and then transferred to a 1-l. beaker, boiled with 300 ml. of benzene, and filtered, the same funnel and flask being used. This extraction process is repeated twice.

The combined benzene filtrates are subjected to distillation from a steam bath to remove the benzene. The flask containing the residual red oil is connected to a water pump and heated under reduced pressure in an oil bath at 110–120° for 2 hours to remove unreacted starting materials. When cooled, the crude triphenylarsine solidifies to a light brown solid which melts at 57–59°. The yield is 230–240 g. (93–97%). The crude product is dissolved in 650–700 ml. of hot 95% ethanol and placed in a refrigerator overnight. The crystals are collected on a Büchner funnel and washed with 50 ml. of cold 95% ethanol. The yield is 218–225 g. (88–91%) of white crystals which melt at 61°.

B. *Triphenylarsine oxide.* In a 500-ml. round-bottomed flask equipped with a mechanical stirrer, a thermometer, and a 100-ml. dropping funnel is placed 100 g. (0.33 mole) of the recrystallized triphenylarsine (Note 3) dissolved in 200 ml. of acetone. To the solution 46 g. (0.41 mole) of 30% hydrogen peroxide is added dropwise, with stirring, over a period of 20–30 minutes. A water-ice bath is used to maintain the temperature at 25–30°. When the addition is complete, stirring is continued for 30 minutes, and the acetone is then removed by distillation.

The flask containing the residual yellow oil is fitted with a water trap and condenser, and 120 ml. of benzene is added. The water is then removed by azeotropic distillation (Note 4). When the removal of water is complete, the triphenylarsine oxide is crystallized by cooling the flask in an ice bath for 1.5–2 hours. The light-brown crystals are collected on a Büchner funnel and washed on the funnel with 25 ml. of cold benzene. The crude product weighs 97–98.5 g. (91–93%) and melts at 186–188°. The crude product is transferred to a porcelain dish and triturated with 50 ml. of benzene, collected on a Büchner funnel, pressed as dry as possible, and washed with 25 ml. of cold benzene. After drying in the air, the triphenylarsine oxide amounts to 89–92 g. (84–87%) of white crystals, melting at 189°.

C. *Tetraphenylarsonium chloride hydrochloride.* In a 2-l. round-bottomed three-necked flask fitted with a condenser, a mercury-sealed mechanical Hershberg stirrer, and a dropping funnel is placed 40 g. (0.124 mole) of triphenylarsine oxide dissolved in 1 l. of hot benzene. To this solution there is added with vigorous stirring a solution of phenylmagnesium bromide which is prepared from 34.6 g. (0.22 mole) of bromobenzene, 6.0 g. (0.25 g. atom) of magnesium, and 200 ml. of dry ether. A brown viscous solid separates. The mixture is stirred for 15 minutes and then stirred and heated under reflux on a steam bath for 30 minutes. The solvent is removed by decantation, and the viscous solid is washed with 500 ml. of benzene. The addition product is then hydrolyzed with 100 ml. of water containing 5 ml. of concentrated hydrochloric acid.

The hydrolysis mixture is transferred to a 1-l. round-bottomed flask fitted with a reflux condenser, and 500 ml. of concentrated hydrochloric acid is added (Note 5). The mixture is heated on a steam bath for 1.5–2 hours. The flask is cooled in an ice bath; the crystals are collected on a sintered-glass funnel and washed with 200 ml. of ice-cold concentrated hydrochloric acid and then with 200 ml. of ice-cold dry ether. The crude product weighs 50–56 g. The product is dissolved in a mixture of 50 ml. of water and 150 ml. of concentrated hydrochloric acid by boiling under reflux. The tetraphenylarsonium chloride hydrochloride separates when the solution is cooled in an ice bath. The white needles are collected on a sintered-glass funnel and washed with 50 ml. of ice-cold concentrated hydrochloric acid and then with 200 ml. of ice-cold dry ether. The yield of tetraphenylarsonium chloride hydrochloride melting at 204–208° with decomposition is 42–45 g. (74–80%).

2. Notes

1. If the addition of the arsenic trichloride-chlorobenzene mixture is too rapid, the reaction becomes vigorous and must be moderated with a cooling bath.
2. Before being discarded, the residue should be treated with ethanol to destroy unreacted sodium.
3. If crude triphenylarsine is used, the final product is difficult to purify
4. Triphenylarsine oxide is partly converted to the dihydroxide when heated with water. However, it is not hygroscopic under ordinary conditions.[3]
5. The hydrolysis product consists mainly of tetraphenylarsonium bromide, which is converted to tetraphenylarsonium chloride hydrochloride by crystallization from concentrated hydrochloric acid.

3. Discussion

Triphenylarsine has been prepared by the action of arsenic triiodide[4] or arsenic trichloride[5] on phenylmagnesium bromide and by the action of sodium and arsenic trichloride on chlorobenzene[6] or bromobenzene.[7] The method described here is essentially that of Pope and Turner.[6]

Triphenylarsine oxide has been prepared by the action of sodium hydroxide on triphenylarsine dibromide,[8] by the action of potassium permanganate on triphenylarsine,[9] and by the action of hydrogen peroxide on triphenylarsine.[10] The method described here is essentially that of Vaughan and Tarbell.[10]

Tetraphenylarsonium chloride hydrochloride has been prepared by the action of phenylmagnesium bromide on triphenylarsine oxide.[11] The method described here is essentially that of Blicke and Monroe.[11]

References and Notes

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2. *Org. Syntheses Coll. Vol.* **1**, 252 (1941).
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4. Burrows and Turner, *J. Chem. Soc.*, **117**, 1373 (1920).
5. Pfeiffer and Pietsch, *Ber.*, **37**, 4621 (1904).
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7. Michaelis, *Ann.*, **321**, 160 (1902).
8. Philips, *Ber.*, **19**, 1031 (1886).
9. Blicke and Safir, *J. Am. Chem. Soc.*, **63**, 575 (1941).
10. Vaughan and Tarbell, *J. Am. Chem. Soc.*, **67**, 144 (1945).
11. Blicke and Monroe, *J. Am. Chem. Soc.*, **57**, 720 (1935).

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

arsenic trichloride-chlorobenzene

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

ether (60-29-7)

sodium hydroxide (1310-73-2)

magnesium (7439-95-4)

potassium permanganate (7722-64-7)

acetone (67-64-1)

chlorobenzene (108-90-7)

sodium (13966-32-0)

bromobenzene (108-86-1)

hydrogen peroxide (7722-84-1)

Phenylmagnesium bromide (100-58-3)

Tetraphenylarsonium chloride hydrochloride,
Arsonium chloride, tetraphenyl-, hydrochloride (123334-18-9)

arsenic trichloride (7784-34-1)

Triphenylarsine (603-32-7)

Triphenylarsine oxide (1153-05-5)

tetraphenylarsonium bromide

arsenic triiodide (7784-45-4)

triphenylarsine dibromide