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.

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PHENYL(TRICHLOROMETHYL)MERCURY

$$C_6H_5HgCl \quad + \quad Cl_3C{-}CO_2Na \xrightarrow{\text{DME, }\Delta} C_6H_5HgCCl_3$$

Submitted by Ted J. Logan[1]
Checked by William E. Parham and John R. Potoski.

1. Procedure

Into a 250-ml. round-bottomed flask equipped with a magnetic stirrer and reflux condenser fitted with a drying tube containing Drierite® are placed 150 ml. of dimethoxyethane (Note 1), 27.8 g. (0.15 mole) of sodium trichloroacetate (Note 2), and 31.3 g. (0.1 mole) of phenylmercuric chloride. The stirred mixture (Note 3) is heated to reflux (~85°) by use of a heating mantle. Carbon dioxide evolution, which begins shortly after heating is begun. is accompanied by the appearance of a precipitate of sodium chloride. The reactants are heated at the reflux temperature until no more carbon dioxide evolution is obvious (~1 hour), then cooled to room temperature and poured into 500 ml. of water. The resulting mixture, consisting of a dense oil layer, a solid, and an aqueous layer, is extracted with four 50-ml. portions of diethyl ether. The combined ether layers are then washed with two 50-ml. portions of water, dried over anhydrous magnesium sulfate, filtered, and the solvent removed using a rotary evaporator. The resulting white solid, which weighs 44.8 g., is dissolved in 130 ml. of hot chloroform and fractionally crystallized. The first three fractions weigh 2.3 g. and are recovered phenylmercuric chloride. Successive reduction of solvent volume and further fractional crystallization provides 25.6 g. of product (65% yield), m.p. 110° (Note 4) and (Note 5).

2. Notes

1. The 1,2-dimethoxyethane (monoglyme) was purchased from Matheson Coleman and Bell and purified by distillation from lithium aluminum hydride. The use of unpurified solvent had little effect on the yield of product.
2. Sodium trichloroacetate may be purchased from the Dow Chemical Company (96.4% pure by Cl analysis) or prepared by neutralizing trichloroacetic acid (Matheson Coleman and Bell) with aqueous sodium hydroxide to the phenolphthalein end point. The product is dried under vacuum for 12 hours, sieved, then dried an additional 12 hours under vacuum, all at room temperature. The salt prepared by this method and used in this preparation was 98.5% pure, based on chlorine analysis, and can be stored indefinitely without decomposition. The submitter has obtained nearly identical yields of phenyltrichloromethylmercury from the commercial and from the prepared salts.
3. If all the reactants are stirred for several minutes at room temperature, they dissolve to give a turbid solution. Stirring while heating then becomes unnecessary, except to promote more even heating, since the refluxing solvent and carbon dioxide evolution keep the precipitated sodium chloride in suspension.
4. Purity of the product was ascertained by quantitative X-ray fluorescence analysis for chlorine and mercury, which showed satisfactory agreement with calculated values. Compounds containing both mercury and chlorine are difficult to analyze by classical "wet" analytical procedures.
5. Yields as high as 77% have been obtained by this procedure. It is difficult to recover all the product from the mother liquor. The use of a 1:1 ratio of sodium trichloroacetate and phenylmercuric chloride gave yields of 39–45%, while a 1.25:1 ratio gave a 61% yield of product.

3. Discussion

This procedure is essentially identical with that previously published by the submitter.[2]

The pyrolysis of sodium trichloroacetate in 1,2-dimethoxyethane was originally described by Wagner.[3] Razuvaev later adapted this procedure to the synthesis of organomercurials, including the title compound.[4]

Phenyl(trichloromethyl)mercury has also been prepared by the reaction of phenylmercuric bromide with sodium methoxide and ethyl trichloroacetate[5] (62–71% yield); of phenylmercuric chloride with potassium *t*-butoxide and chloroform[6] (75% yield); of phenylmagnesium bromide with trichloromethylmercuric bromide[7] (24% yield); of trichloromethylmercuric bromide with diphenyldichlorotin (49%); and of trichloromethylmercuric bromide with phenylmagnesium bromide[8] (no yield given).

4. Merits of the Preparation

The main advantages of this procedure are simplicity of apparatus and technique, availability of reactants, ease of product isolation in good yield, and purity of product. The submitter has also used this method successfully for the preparation of trichloromethylmercuric chloride (from mercuric chloride), bis-(trichloromethyl)mercury (from a 2:1 ratio of sodium trichloroacetate to mercuric chloride or mercuric acetate), and trichloromethylmercuric bromide (from mercuric bromide).

Phenyl(trihalomethyl)mercurials, including the title compound, can be thermally decomposed in the presence of olefins to yield the corresponding dichlorocyclopropane derivatives.[2,9,10,11] Olefins such as tetrachloroethylene and ethylene, which give exceptionally low yields of dichlorocyclopropanes when treated with other reagents for generating dichlorocarbene ($:CCl_2$), give reasonable yields of dichlorocyclopropanes when heated with phenyltrichloromethylmercurials.[12]

These mercurials have also been employed in the preparation of dihalomethyl derivatives of carbon, silicon, and germanium,[13] in the conversion of carboxylic acids to dichloromethyl esters,[14] in the deoxygenation of pyridine N-oxide,[5] in the synthesis of diarylcyclopropenones from diaryl acetylenes,[15] and in numerous other applications. Leading references to these applications may be found in a recent review on the use of phenyl (trihalomethyl)mercury compounds as divalent carbon transfer reagents.[16]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 874
- Org. Syn. Coll. Vol. 6, 142

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References and Notes

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

1,2-dimethoxyethane (monoglyme)

ether,
diethyl ether (60-29-7)

sodium hydroxide (1310-73-2)

chloroform (67-66-3)

sodium chloride (7647-14-5)

mercuric acetate (1600-27-7)

mercury (7439-97-6)

carbon dioxide (124-38-9)

sodium methoxide (124-41-4)

carbon (7782-42-5)

chlorine (7782-50-5)

ethylene (9002-88-4)

mercuric chloride (7487-94-7)

Phenylmagnesium bromide (100-58-3)

phenylmercuric bromide

phenolphthalein (77-09-8)

magnesium sulfate (7487-88-9)

trichloroacetic acid (76-03-9)

tetrachloroethylene (127-18-4)

mercuric bromide (7789-47-1)

lithium aluminum hydride (16853-85-3)

phenylmercuric chloride

trichloromethylmercuric bromide

diphenyldichlorotin (1135-99-5)

trichloromethylmercuric chloride

bis-(trichloromethyl)mercury

germanium

1,2-dimethoxyethane (110-71-4)

dimethoxyethane (534-15-6)

ethyl trichloroacetate (515-84-4)

Pyridine N-oxide (694-59-7)

silicon

sodium trichloroacetate (650-51-1)

Phenyl(trichloromethyl)mercury, phenyltrichloromethylmercury (3294-57-3)

potassium t-butoxide (865-47-4)