



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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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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1,2,3-TRIPHENYLCYCLOPROPENIUM BROMIDE

[Cyclopropenylum, triphenyl-, bromide]



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1. Procedure

1,2,3-Triphenylcyclopropenium bromide. A flame-dried, 500-mL, three-necked, round-bottomed flask, equipped with a magnetic stirring bar and a reflux condenser fitted with an argon inlet vented through a mineral oil bubbler, glass stopper, and rubber septum, is flushed with argon and charged with a solution of diphenylacetylene (3.92 g, 0.022 mol) (Note 1) and potassium tert-butoxide (9.97 g, 0.089 mol) in dry benzene (100 mL) (Note 2). Efficient magnetic stirring is initiated, and 5.8 mL of α,α -dichlorotoluene (7.2 g, 0.045 mol) (Note 3) is added dropwise over \sim 5 min via a syringe under argon (Note 4). The reaction mixture is then heated under reflux for 3 hr during which time the precipitate dissolves (Note 5). After the reaction mixture is cooled to room temperature, 100 mL of water is added to remove inorganic salts. The organic layer is separated and the aqueous layer is extracted with portions of ether (2×50 -mL). The organic layers are combined, dried over magnesium sulfate, and filtered. The filtrate is saturated with anhydrous hydrogen bromide (Note 6), whereupon a light yellow precipitate forms that is collected to afford 6.8–7.2 g (89–93%) of essentially pure triphenylcyclopropenium bromide (Note 7). The material prepared in this manner provides a satisfactory elemental analysis,² but it can be further purified by recrystallization from acetonitrile, if desired.

2. Notes

1. Diphenylacetylene, potassium tert-butoxide, and α,α -dichlorotoluene were purchased from Aldrich Chemical Company, Inc. and used without further purification.
2. Benzene is obtained from the Fisher Scientific Company and purified by distillation from CaH_2 .
3. An excess of α,α -dichlorotoluene and potassium tert-butoxide is necessary to ensure high conversion of diphenylacetylene. When 1 equiv of α,α -dichlorotoluene and 2 equiv of potassium tert-butoxide are used, only 60% conversion of diphenylacetylene is achieved and the remainder is recovered during the workup. Nonetheless, the yield corrected for recovered diphenylacetylene is still more than 90%.
4. The reaction mixture is observed to bubble, fume, become brown in color, and deposit a precipitate. When the reaction is carried out in the air rather than under argon, the conversion is only 50%.
5. Slightly lower conversion is consistently realized when the reflux period is shortened to 1 hr.
6. When the usual preparative procedure was interrupted before the addition of water, and the inorganic material was removed by filtration, concentration of the solution and addition of dry hexane caused crystallization of 1,2,3-triphenylcyclopropenyl tert-butyl ether as white prisms.² The checkers did not observe reprecipitation of the salts upon cooling the reaction mixture.
7. The crude product is quite pure and has the following spectral characteristics: ^1H NMR (300 MHz, CD_3NO_2) δ : 7.99 (t, 6 H, $J = 8$), 8.12 (t, 3 H, $J = 8$), 8.71 (d, 6 H, $J = 8$); ^{13}C NMR (75 MHz, CD_3NO_2) δ : 119.65, 130.18, 135.40, 138.18, 155.26; IR (CHCl_3) cm^{-1} : 3382, 1712, 1594, 1505, 1410. On heating it decomposes without a defined melting point.

Waste Disposal Information

All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

3. Discussion

This is the procedure first reported in 1961.² It involves generation of phenylchlorocarbene, or more likely a related carbenoid, which adds to the acetylene to form triphenylcyclopropenium chloride. This chloride reacts with tert-butoxide ion to form the covalent tert-butyl ether, which can be isolated. With water, this ether hydrolyzes to bis(triphenylcyclopropenyl) ether, but either of these compounds is converted to the ionic bromide salt with HBr.

According to this procedure, with proper choice of reaction conditions, a sizeable amount of diphenylacetylene can be converted quantitatively to triphenylcyclopropenium bromide in a few hours. The reaction is of wide generality and can be applied to p-anisylphenylacetylene and to di-p-anisylacetylene, or with p-anisal chloride instead of α,α -dichlorotoluene, to prepare p-methoxy derivatives of the title compound.² Since the initial preparation of this derivative of the cyclopropenyl cation by a less efficient procedure,³ many aryl-, alkyl- and heteroatom-substituted derivatives of this simplest cyclic aromatic system have been synthesized,^{4 5 6} including the parent cyclopropenyl cation itself.⁷ They have been used for various physical studies,⁸ and for the preparation of derivatives such as covalent cyclopropenes and metal coordination complexes.^{9,10}

The cyclopropenyl cation is the simplest aromatic system, and thus of some theoretical interest. In addition, the chemistry of cyclopropene derivatives is full of interesting rearrangements to other novel structures,¹¹ reflecting the great strain energy of the cyclopropene ring.

References and Notes

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Appendix

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

CaH₂

acetylene (74-86-2)

Benzene (71-43-2)

ether (60-29-7)

acetonitrile (75-05-8)

hydrogen bromide,
HBr (10035-10-6)

α,α -dichlorotoluene (98-87-3)

magnesium sulfate (7487-88-9)

Diphenylacetylene (501-65-5)

hexane (110-54-3)

argon (7440-37-1)

phenylchlorocarbene

potassium tert-butoxide (865-47-4)

1,2,3-TRIPHENYLCYCLOPROPENIUM BROMIDE (4919-51-1)

Cyclopropenylium, triphenyl-, bromide,
Triphenylcyclopropenium bromide (4919-51-1)

1,2,3-triphenylcyclopropenyl tert-butyl ether

triphenylcyclopropenium chloride (58090-78-1)

tert-butyl ether (6163-66-2)

bis(triphenylcyclopropenyl) ether

p-anisylphenylacetylene

di-p-anisylacetylene

p-anisal chloride