



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.

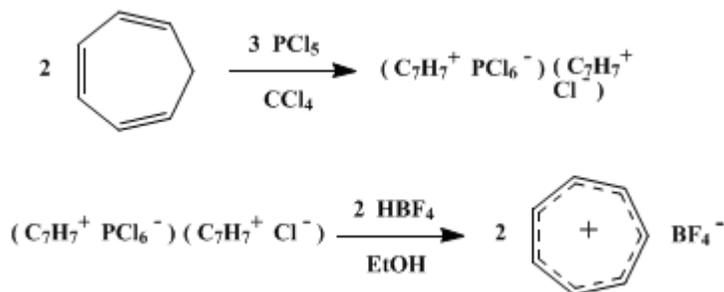
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.1138 (1973); Vol. 43, p.101 (1963).

TROPYLIUM FLUOBORATE

[Cycloheptatrienocarbonium fluoborate]



Submitted by Kenneth Conrow¹

Checked by D. W. Wiley and B. C. McKusick.

1. Procedure

A suspension of 100 g. (0.48 mole, 33% excess) of phosphorus pentachloride in 800 ml. of carbon tetrachloride is prepared in a 1-l. flask equipped with an efficient stirrer and an exit valve for the hydrogen chloride that is evolved (Note 1). Tropilidene (cycloheptatriene; 24.2 g. of 91% material; 0.24 mole) (Note 2) is added all at once, and the mixture is stirred for 3 hours at room temperature (Note 3).

Absolute ethanol (400 ml.) is vigorously stirred in a 1-l. wide-necked Erlenmeyer flask immersed in an ice bath (Note 4). The tropylium hexachlorophosphate-tropylium chloride double salt² is separated from the reaction mixture by suction filtration, washed briefly with fresh carbon tetrachloride, and transferred as rapidly as possible into the cold, well-stirred ethanol (Note 5). The salt dissolves rapidly and exothermally to give a reddish solution. Fifty milliliters (0.39 mole) of 50% aqueous fluoboric acid is added rapidly to the cold stirred solution (Note 6). The dense white precipitate of tropylium fluoborate that forms is separated by suction filtration, washed with a little cold ethanol and with ether, and air-dried at room temperature (Note 7); weight 34–38 g. (80–89%); decomposition point about 200°; $\lambda_{\text{max}}^{0.1N \text{ HCl}}$ 218 m μ (log ϵ 4.70), 274 m μ (log ϵ 3.61). The product is 98–100% pure (Note 8) and (Note 9).

2. Notes

1. The use of a flask just large enough to hold the reaction mixture obviates the necessity for an inert atmosphere, for the evolving hydrogen chloride soon displaces the small amount of air over the reaction mixture.
2. Cycloheptatriene containing 9% toluene is available from the Shell Chemical Company, New York. Less pure cycloheptatriene, obtained by pyrolysis of bicycloheptadiene followed by a crude distillation, has been used successfully in this preparation. The quantity of the tropilidene/toluene mixture is adjusted in accord with its purity as estimated by vapor-phase chromatography on didecyl phthalate.
3. The mixture thickens rapidly. After about an hour, even an efficient stirrer often fails to stir the whole mixture, but after a time the mixture thins again and the reaction is completed without incident.
4. Stirring is most conveniently accomplished with a magnetic stirrer. A large plastic bucket is used to contain the ice used for cooling.
5. Exposure of this salt to the atmosphere causes discoloration that may persist in the final product. A slight discoloration at this stage does not appear to affect the quality of the final product. A rubber dam is helpful on days of high humidity.
6. Use of perchloric acid gives the perchlorate. However, the perchlorate is so dangerously explosive that its use should be avoided.³
7. Additional salt is precipitated by the addition of ether to the ethanolic filtrate, but the quantity is so small that this treatment is not worth while.

8. The product may be crystallized from a large volume of [ethyl acetate](#) or from acetonitrile-ethyl acetate. However, there is little reason to do this, for losses are heavy and the purity, as measured by ultraviolet spectroscopy, is hardly affected.

9. In a variation of this procedure that gives a nearly quantitative yield of good material, the intermediate salt is dissolved in 250 ml. of glacial [acetic acid](#) in a 2-l. beaker, and 100 g. of 50% fluoboric acid is added with stirring. When the evolution of gas has stopped, 1 l. of [ethyl acetate](#) is added to precipitate [tropylium fluoborate](#). The fluoborate is separated by filtration, washed successively with [ethyl acetate](#) and [ether](#), and dried in an oven at 40°.⁴

3. Discussion

This method is a modification of the method originally published by Kursanov and Vol'pin.⁵ Tropylium salts have also been prepared by bromination-dehydrobromination of [tropilidene](#),⁶ and by the hydride-exchange reaction between [tropilidene](#) and triphenylmethyl carbonium ion.⁷

4. Merits of the Preparation

Tropylium salts are starting materials for the preparation of a wide range of substituted tropilidenes. The fluoborate is the salt of choice for work involving the tropylium ion because it is indefinitely stable, non-hygroscopic, and, unlike the perchlorate, non-explosive. Its preparation by this method avoids the use of [triphenyl carbinol](#), which is an unnecessarily expensive reagent in the quantities required for tropylium ion preparation.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 10, 271](#)

References and Notes

1. Department of Chemistry, Kansas State University, Manhattan, Kansas.
2. D. Bryce-Smith and N. A. Perkins, *J. Chem. Soc.*, 1339 (1962).
3. P. G. Ferrini and A. Marxer, *Angew. Chem., Intern. Ed. Engl.*, **1**, 405 (1962).
4. C. V. Wilson, Eastman Kodak Co., private communication.
5. D. N. Kursanov and M. E. Vol'pin, *Doklady Akad. Nauk SSSR*, **113**, 339 (1957) [*C.A.*, **51**, 14572f (1957)].
6. W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **79**, 352 (1957).
7. H. J. Dauben, L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

Appendix

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

fluoboric acid

Cycloheptatrienocarbonium fluoborate

tropylium hexachlorophosphate-tropylium chloride

acetonitrile-ethyl acetate

[ethanol](#) (64-17-5)

hydrogen chloride (7647-01-0)

acetic acid (64-19-7)

Tropilidene (71-43-2)

ethyl acetate (141-78-6)

ether (60-29-7)

phosphorus pentachloride (10026-13-8)

carbon tetrachloride (56-23-5)

toluene (108-88-3)

triphenyl carbinol (76-84-6)

perchloric acid (7601-90-3)

cycloheptatriene (544-25-2)

bicycloheptadiene

Tropylium fluoborate (27081-10-3)

didecyl phthalate (84-77-5)