



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.

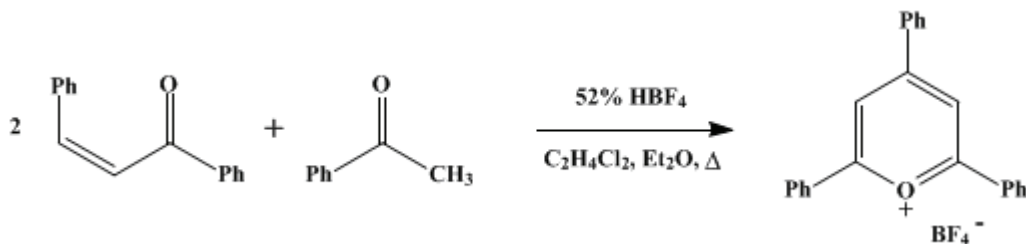
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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.1135 (1973); Vol. 49, p.121 (1969).

2,4,6-TRIPHENYLPYRYLIUM TETRAFLUOROBORATE

[Pyrilium tetrafluoroborate, 2,4,6-triphenyl-]



Submitted by K. Dimroth, C. Reichardt, and K. Vogel¹.
Checked by Saul Cerkofsky and Richard E. Benson.

1. Procedure

In a 1-l. four-necked flask (or a three-necked flask with a Y-tube connector) equipped with a mechanical stirrer, a reflux condenser, a dropping funnel, and a thermometer are placed 208 g. (1.00 mole) of **benzalacetophenone** (Note 1), 60 g. (58.5 ml., 0.50 mole) of **acetophenone**, and 350 ml. of **1,2-dichloroethane**. The contents of the flask are warmed to 70–75°, and 160 ml. of a 52% ethereal solution of fluoboric acid (Note 2) is added from the funnel with stirring during 30 minutes. With the first addition the mixture becomes orange; subsequently the color changes to brownish yellow. After the addition is completed, the mixture is stirred and heated under reflux for 1 hour (Note 3). The fluorescent mixture is allowed to stand overnight in a refrigerator. The crystalline product that separates is collected on a Buchner funnel and washed well with **ether**. By addition of 250 ml. of **ether** (Note 4) to the mother liquor an additional quantity of **2,4,6-triphenylpyrylium tetrafluoroborate** is obtained. A total yield of 125–135 g. (63–68%) of yellow crystals results; m.p. 218–225° (Note 5). The product can be recrystallized from 650–700 ml. of **1,2-dichloroethane**, when it separates in the form of yellow needles, m.p. 251–257° (Note 6). The yield of product dried at 80° (10 mm.) for 3 hours is 102.5–107 g. (52–54%) (Note 6).

2. Notes

1. The preparation of **benzalacetophenone** is described in *Org. Syntheses, Coll. Vol. 1*, 78 (1941).
2. Ethereal fluoboric acid can be prepared as follows: 19 ml. (19 g., 0.95 mole) of anhydrous **hydrofluoric acid**, b.p. 19.4° (760 mm.) [*Caution! Hydrofluoric acid in contact with the skin produces extremely painful burns. It is therefore necessary to use every precaution to protect exposed parts of the body, especially the hands and eyes. Cf. Org. Syntheses, Coll. Vol. 2, 295 (1943). Note 3; this volume, p. 136, Note 1*] is added in small portions with shaking or stirring to 126 ml. (142 g., 1.00 mole) of distilled **boron trifluoride etherate**, b.p. 126° (760 mm.), contained in a 500-ml. polyethylene flask that is cooled in an ice bath to 0°. The concentration of the resulting yellowish solution of fluoboric acid in **ether** is about 52% by weight (*ca.* 6.6 moles per l.).
3. Some **boron trifluoride** is evolved during the first part of the refluxing; it may be disposed of by absorption in water in a gas trap [cf. *Org. Syntheses, Coll. Vol. 2*, 3 (1943)].
4. The **ether** used for washing the product may be added to the filtrate.
5. The **2,4,6-triphenylpyrylium tetrafluoroborate** resulting from this procedure is sufficiently pure for use in the preparation of **2,4,6-triphenylnitrobenzene**.²
6. It is necessary to dry under reduced pressure in order to remove that portion of the solvent that is tightly held. *Anal.* Calcd. for C₂₃H₁₇BF₄O: C, 69.73; H, 4.33; B, 2.73; F, 19.18. Found: C, 69.38; H, 4.47; B, 3.07; F, 19.51. The n.m.r. spectrum (acetone-d₆) shows a singlet at 9.1 p.p.m. (2 H) and multiplets at 8.6 p.p.m. and 7.9 p.p.m. (15 H) (downfield from internal tetramethylsilane reference).

3. Discussion

The present procedure is an improved modification of that described by Balaban³ for the corresponding perchlorate. 2,4,6-Triphenylpyrylium tetrafluoroborate has also been prepared from the corresponding tetrachloroferrate^{4,5} with fluoboric acid,⁵ from acetophenone and boron trifluoride,⁶ and from acetophenone, benzaldehyde, and boron trifluoride etherate.⁷ Additional methods for the preparation of pyrylium salts have been reviewed.^{5,8,9,10,11,12,13,14}

2,4,6-Triphenylpyrylium tetrafluoroborate is a versatile and useful stable starting material. Its reaction with nitromethane under basic conditions has made 2,4,6-triphenylnitrobenzene easily available.^{2,15} In addition, pyrylium salts are readily converted to a variety of pyridine derivatives^{16,17,18} including alkyl- and arylpyridinium salts,^{17,18} to thiopyrylium salts,¹⁹ and to substituted azulenes.²⁰

The chemistry and transformation of pyrylium salts have been reviewed.^{5,8,9,10,11,21,14}

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 1128](#)

References and Notes

1. Institut für Organische Chemie der Philipps-Universität Marburg (Lahn), Germany.
2. K. Dimroth, A. Berndt, and C. Reichardt, *Org. Syntheses*, this volume, p. 114.
3. A. T. Balaban, *Compt. Rend.*, **256**, 4239 (1963).
4. W. Dilthey, *J. Prakt. Chem.*, [2] **94**, 53 (1916).
5. K. Dimroth, *Angew. Chem.*, **72**, 331 (1960).
6. W. C. Dovey and R. Robinson, *J. Chem. Soc.*, 1389 (1935); R. C. Elderfield and T. P. King, *J. Am. Chem. Soc.*, **76**, 5437 (1954).
7. R. Lombard and J.-P. Stephan, *Bull. Soc. Chim. France*, 1458 (1958).
8. A. T. Balaban and C. D. Nenitzescu, *Rev. Chim. Acad. Rep. Populaire Roumaine*, **6**, 269 (1961); *Acad. Rep. Populare Romine, Studii Cercetari Chim.*, **9**, 251 (1961) [*Chem. Abstr.*, **57**, 8534 (1962)].
9. K. Dimroth and K. H. Wolf, in W. Foerst, "Newer Methods of Preparative Organic Chemistry," Vol. 3, Academic Press, Inc., New York, 1964, p. 357.
10. W. Schroth and G. Fischer, *Z. Chem.*, **4**, 281 (1964).
11. H. Meerwein, in E. Müller, "Methoden der Organischen Chemie (HoubenWeyl)," Vol. 6, Part 3, Georg Thieme Verlag, Stuttgart, 1965, p. 325.
12. G. N. Dorofeenko, S. V. Krivun, V. I. Dulenko, and Yu. A. Zhdanov, *Usp. Khim.*, **34**, 219 (1965); *Russ. Chem. Rev. (English Transl.)*, 88 (1965) [*Chem. Abstr.*, **62**, 12993 (1965)].
13. A. T. Balaban and C. D. Nenitzescu, this volume, p. 1106.
14. A. T. Balaban, W. Schroth, and G. Fischer, in A. R. Katritzky and A. J. Boulton, *Advan. Heterocycl. Chem.*, **10**, 241 (1969).
15. K. Dimroth, G. Neubauer, H. Möllenkamp, and G. Oosterloo, *Ber.*, **90**, 1668 (1957).
16. A. Baeyer, *Ber.*, **43**, 2337 (1910); W. Dilthey, *J. Prakt. Chem.*, [2] **102**, 209 (1921).
17. W. Schneider, W. Döbling, and R. Cordua, *Ber.*, **70**, 1645 (1937); K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Ann.*, **661**, 1 (1963).
18. A. T. Balaban and C. Toma, *Tetrahedron*, Suppl. **7**, 1 (1966); C. Toma and A. T. Balaban, *Tetrahedron*, Suppl. **7**, 9, 27 (1966).
19. R. Wizinger and P. Ulrich, *Helv. Chim. Acta*, **39**, 207 (1956).
20. K. Hafner and H. Kaiser, *Ann.*, **618**, 140 (1958); this volume, p. 1088.
21. A. T. Balaban and C. D. Nenitzescu, *Ann.*, **625**, 74 (1959).

(Registry Number)

fluoboric acid

ether (60-29-7)

1,2-dichloroethane (107-06-2)

hydrofluoric acid (7664-39-3)

Benzalacetophenone (94-41-7)

benzaldehyde (100-52-7)

Acetophenone (98-86-2)

Nitromethane (75-52-5)

boron trifluoride (7637-07-2)

boron trifluoride etherate (109-63-7)

2,4,6-Triphenylnitrobenzene (10368-47-5)

2,4,6-Triphenylpyrylium tetrafluoroborate,
Pyrylium tetrafluoroborate, 2,4,6-triphenyl- (448-61-3)