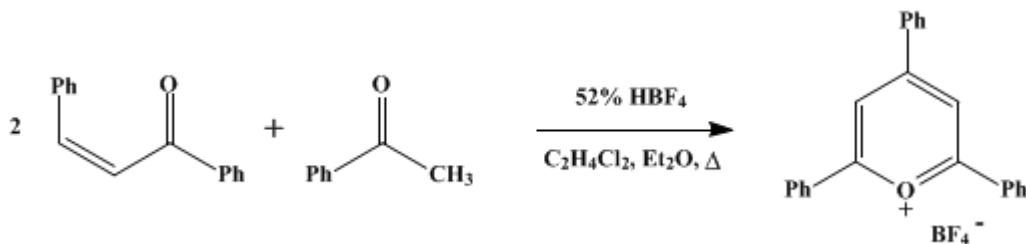


2,4,6-TRIPHENYLPYRYLIUM TETRAFLUOROBORATE

[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)