



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

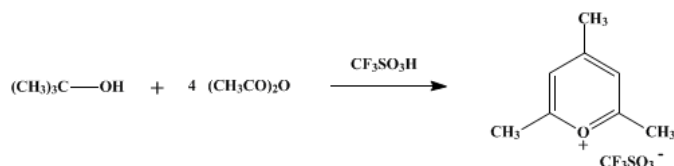
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

2,4,6-TRIMETHYLPYRYLIUM TRIFLUOROMETHANESULFONATE



Submitted by A. T. Balaban and A. J. Boulton¹.
Checked by Dorothy G. McMahan and Henry E. Baumgarten.

1. Procedure

In a 150-ml. Erlenmeyer flask are mixed 18 ml. (19.4 g., 192 mmol.) of acetic anhydride and 3.2 ml. (2.5 g., 34 mmol.) of anhydrous *t*-butyl alcohol. Two to three drops of trifluoromethanesulfonic acid (Note 1) is added and the mixture is swirled rapidly until the initial esterification reaction is complete (temperature stops rising). Further trifluoromethanesulfonic acid (total acid: 3.0 ml., 5.0 g. (33 mmol.)) is added in 0.1–0.2-ml. portions, over 10 minutes, with swirling and pausing between each addition until the temperature begins to fall. At the end of the addition the temperature is 60–70° (Note 2), and the solution is brown in color. It is allowed to stand for a further 5 minutes and then is cooled in ice. Anhydrous ether (100 ml.) is added, whereupon the pyrylium salt separates. The mixture is filtered with suction using a sintered glass funnel and the crude product is washed with a further 50 ml. of dry ether (Note 3), giving 3.6–3.8 g. (40–42%) of mustard colored to pale brown plates, m.p. 116–118° (Note 4).

The crude product is recrystallized from dioxane-acetic acid (7:1) or chloroform-carbon tetrachloride (2:1). The crystal form is very variable; needles, plates, or prisms may be formed, depending on the rate of formation, and the temperature. After recrystallization the 2,4,6-trimethylpyrylium trifluoromethane sulfonate melts at 119–120° (Note 5).

2. Notes

1. Trifluoromethanesulfonic acid may be obtained from Aldrich Chemical Company or Pierce Chemical Company.
2. If the reaction is conducted at a lower temperature (*ca.* 20°), a lighter solution and a more nearly pure product result, but the yield is much reduced (1–2 g., 11–22%). Allowing the temperature to rise above 70° gives a darker brown mixture, but with no improvement in yield.
3. The washing ether should be added before the crystals are exposed to the air, and the ether and crystals should be stirred to ensure thorough mixing. Otherwise a troublesome tar may separate. The product should be isolated within 2–3 hours of its precipitation, or it will be accompanied by black impurities which are slowly deposited by the mother liquor, and are difficult to remove.
4. The checkers observed a variable range of melting points for the crude product, as broad as 108–113° and as sharp as 116–117°.
5. The checkers used chloroform-carbon tetrachloride for recrystallization and found that about 500 ml. of this mixture was required to dissolve the crude product and give a green colored solution. Their final yield after two recrystallizations was 3.2–3.4 g. (36–38%), m.p. 118–119°.

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3. Discussion

Although more expensive in materials, and so suitable mainly for small-scale work, the product does not have the explosive hazard of the corresponding perchlorate.² This advantage is shared with the tetrafluoroborate,³ which, however, requires more acetic anhydride and may give poorer yields. The trifluoromethanesulfonate salt is also more soluble in organic solvents than the perchlorate or tetrafluoroborate (1 g. dissolves in 7 ml. of chloroform at 20°, and in 3 ml. at *ca.* 35°; it is also very soluble in alcohols and dichloromethane). For the usefulness of 2,4,6-trimethylpyrylium salts in general, see the notes pertaining to the perchlorate.²

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 1112

References and Notes

1. Institute of Atomic Physics, Bucharest, Rumania.
2. A. T. Balaban and C. D. Nenitzescu, this volume, p. 1106; K. Hafner and H. Kaiser, this volume, p. 1108.
3. A. T. Balaban and A. J. Boulton, this volume, p. 1112.

Appendix

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

chloroform-carbon tetrachloride

2,4,6-trimethylpyrylium trifluoromethane sulfonate

acetic acid (64-19-7)

ether (60-29-7)

acetic anhydride (108-24-7)

chloroform (67-66-3)

carbon tetrachloride (56-23-5)

dichloromethane (75-09-2)

dioxane (123-91-1)

t-butyl alcohol (75-65-0)

2,4,6-Trimethylpyrylium trifluoromethanesulfonate (40927-60-4)

trifluoromethanesulfonic acid (1493-13-6)

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