Organic Syntheses

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.

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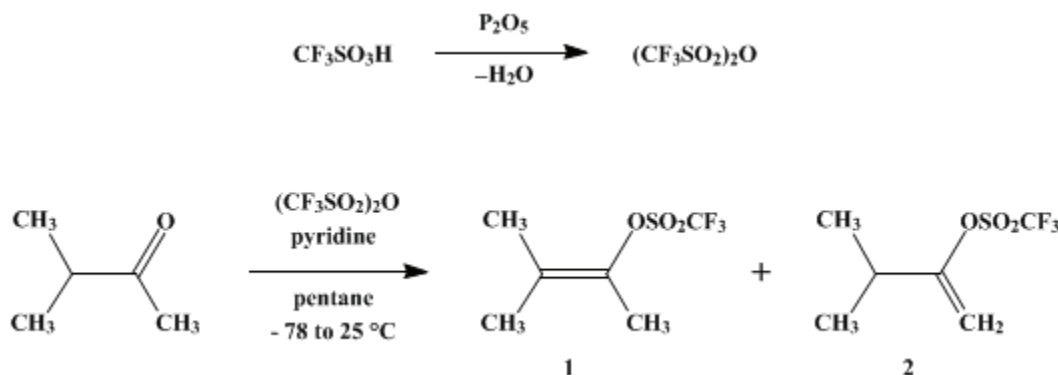
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

PREPARATION OF VINYL TRIFLUOROMETHANESULFONATES: 3-METHYL-2-BUTEN-2-YL TRIFLATE

[Methanesulfonic acid, trifluoro-, 1,2-dimethyl-1-propenyl ester]

$$CF_3SO_3H \xrightarrow[-H_2O]{P_2O_5} (CF_3SO_2)_2O$$

Submitted by Peter J. Stang[1] and Thomas E. Dueber.
Checked by Wayne Jaeger and Herbert O. House.

1. Procedure

A. *Trifluoromethanesulfonic anhydride.* A dry, 100-ml., round-bottomed flask is charged with 36.3 g. (0.242 mole) of trifluoromethanesulfonic acid (Note 1) and 27.3 g. (0.192 mole) of phosphorus pentoxide (Note 2). The flask is stoppered and allowed to stand at room temperature for at least 3 hours. During this period the reaction mixture changes from a slurry to a solid mass. The flask is fitted with a short-path distilling head and heated first with a stream of hot air from a heat gun and then with the flame from a small burner. The flask is heated until no more trifluoromethanesulfonic anhydride distills, b.p. 82–115°, yielding 28.4–31.2 g. (83–91%) of the anhydride, a colorless liquid. Although this product is sufficiently pure for use in the next step, the remaining acid may be removed from the anhydride by the following procedure. A slurry of 3.2 g. of phosphorus pentoxide in 31.2 g. of the crude anhydride is stirred at room temperature in a stoppered flask for 18 hours. After the reaction flask has been fitted with a short-path distilling head, it is heated with an oil bath, yielding 0.7 g. of forerun, b.p. 74–81°, followed by 27.9 g. of the pure trifluoromethanesulfonic acid anhydride, b.p. 81–84° (Note 3).

B. 3-*Methyl-2-buten-2-yl triflate.* A solution of 2.58 g. (0.0300 mole) of 3-methyl-2-butanone (Note 4) and 2.78 g. (0.0352 mole) of anhydrous pyridine (Note 5) in 10 ml. of anhydrous *n*-pentane (Note 6) is placed in a dry, 50-ml. Erlenmeyer flask, and the flask is stoppered with a rubber septum. After the solution has been cooled in an acetone–dry ice cooling bath, 9.72 g. (5.80 ml., 0.0395 mole) of trifluoromethanesulfonic anhydride is added with a hypodermic syringe, dropwise and with swirling over 2–3 minutes. The resulting mixture, from which a white solid separates initially, is allowed to warm to room temperature over 22–24 hours. During this period the reaction mixture becomes red in color (Note 7), and a viscous, red semisolid separates. The supernatant pentane solution is decanted, and the residual viscous semisolid is washed with two 10-ml. portions of pentane. While the combined pentane solutions are stored over anhydrous potassium carbonate, the remaining red semisolid is dissolved in 5 ml. of saturated aqueous sodium bicarbonate and extracted with three 5-ml. portions of pentane. The combined pentane solutions (including the solid potassium carbonate) are washed rapidly (Note 8) with 5 ml. of cold saturated aqueous sodium hydrogen carbonate and dried over anhydrous potassium carbonate. After the orange pentane solution has been concentrated to a volume of approximately 10 ml. with a rotary evaporator, it is transferred to a small distilling apparatus. The remaining pentane is removed by distillation at atmospheric pressure (Note 9). The residual liquid is fractionally distilled under reduced pressure, yielding 2.94–2.97 g. (45%) of a colorless, liquid fraction

containing 3-methyl-2-buten-2-yl triflate and a lesser amount of 3-methyl-1-buten-2-yl triflate, b.p. 58–66° (22 mm.), n_D^{25} 1.3832–1.3898 (Note 10). Fractional distillation of this mixture with a 40-cm. spinning band column separated higher boiling fractions, b.p. 45–47° (12 mm.), that contained (Note 10) 98% of the 3-methyl-2-buten-2-yl triflate as a colorless liquid, n_D^{25} 1.3838 (Note 11).

2. Notes

1. Trifluoromethanesulfonic acid, purchased from Eastman Organic Chemicals, was used without purification. Trifluoromethanesulfonic acid in large quantities is available from 3M Company as Fluorocarbon Acid FC-24.

2. The phosphorus pentoxide should be protected from atmospheric moisture by weighing this reagent in a dry, stoppered flask. On a larger scale the yields are better and the reaction easier if the phosphorus pentoxide is premixed with an equal volume of Celite (filter aid).

3. This product exhibits one major GC peak (retention time 2.3 minutes, silicone fluid QF_1 on Chromosorb P) as well as one minor, unidentified, more rapidly eluted impurity. The product has strong IR absorption (CCl_4) at 1470, 1240, and 1130 cm.$^{-1}$.

4. 3-Methyl-2-butanone, purchased from Eastman Organic Chemicals, was used without purification. In general, commercially available ketones may be used without further purification.

5. A reagent grade of pyridine, purchased from Fisher Scientific Company, was dried over anhydrous potassium carbonate, distilled, and collected at 112–113°.

6. A commercial sample of *n*-pentane was distilled from calcium hydride to separate the pure solvent, b.p. 35–36°.

7. The intensity of color developed in the reaction mixture is an approximate indication of the extent of reaction. With reactive triflates a dark, almost tarry-looking mass develops in a few hours, while with the slower forming triflates several days at room temperature may be required for adequate color development. In no case was any product isolated when fairly dark color had not developed in the reaction mixture.

8. Only relatively stable vinyl triflates should be washed with water. More reactive triflates such as α-styryltriflate do not survive washing with water.

9. For the more volatile triflates, removal of the solvent should be accomplished by distillation to minimize loss of the volatile product. Also, care should be taken not to overheat the residual product since overheating can result in decomposition.

10. The fractions from this distillation may be analyzed by GC, employing a column packed with Carbowax 20 *M* suspended on Chromosorb P. The retention times for the various components (minutes) are: pentane (1.6), 3-methyl-2-butanone (4.2), 3-methyl-1-buten-2-yl triflate (6.7), and 3-methyl-2-buten-2-yl triflate (9.5).

11. The pure, more highly substituted olefin, n_D^{25} 1.3840, could also be separated by preparative GC, and the unchanged ketone could be separated from the two triflate isomers by chromatography on a silica gel column with pentane as the eluant. The pure product has IR absorption (CCl_4) at 1700 (enol C=C), 1210 and 1140 cm.$^{-1}$ (SO_2) with end absorption in the UV (heptane, ε 700 at 210 nm) and the following broad singlets in the ^1H NMR spectrum (C_6H_6): δ 1.42 (3H, CH_3), 1.63 (3H, CH_3), and 1.82 (3H, CH_3). The mass spectrum of the product exhibits the following relatively abundant peaks, *m/e* (relative intensity): 218 (M$^+$, 58), 69 (75), 57 (92), 43 (100), 41 (44), and 39 (24).

3. Discussion

Vinyl trifluoromethanesulfonates (triflates) are a new class of compounds, unknown before 1969, that have been used most extensively in solvolytic studies to generate vinyl cations[2,3,4,5,6,7,8,9] and unsaturated carbenes.[10] Three methods have been used to prepare these sulfonic esters. The first, involving the preparation and decomposition of acyltriazines,[11] requires several steps to prepare the acyltriazines and is limited to the preparation of fully substituted vinyl triflates. The second method involves the electrophilic addition of trifluoromethanesulfonic acid to acetylenes[12,13,14] and, consequently, is not applicable to the preparation of trisubstituted vinyl triflates and certain cyclic vinyl triflates. However, this second procedure is relatively simple and often gives purer products in higher yield than the discussed reaction with ketones. Table I lists vinyl triflates prepared by this procedure.
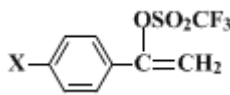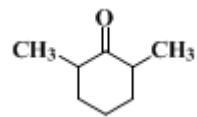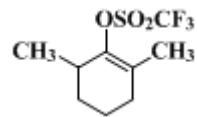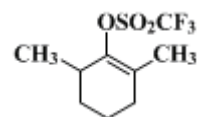
TABLE I

Substrate	Product	b.p.	Yield, %
$CH_3C≡CH$	$CH_2=C(CH_3)OSO_2CF_3$	25–27° (12 mm.)	60–80
$C_2H_5C≡CC_2H_5$	cis and trans $C_2H_5CH=C(C_2H_5)OSO_2CF_3$	68.5–69.5° (25 mm.)	40–60
$(CH_3)_3CC≡CH$	$CH_2=C(OSO_2CF_3)C(CH_3)_3$	45–50° (15 mm.)	40–60
$C_6H_5C≡CH$	$CH_2=C(C_6H_5)OSO_2CF_3$	44–45° (0.3 mm.)	20–60
$CH_3(CH_2)_3C≡CH$	$CH_2=C(OSO_2CF_3)CH_2(CH_2)_2CH_3$	67–69° (15 mm.)	70
$(CH_3)_2CHC≡CH$	$CH_2=C(OSO_2CF_3)CH(CH_3)_2$	37–40° (15 mm.)	62

The third procedure, illustrated by this preparation, involves the reaction of ketones with trifluoromethanesulfonic anhydride in a solvent such as pentane, dichloromethane, or carbon tetrachloride and in the presence of a base such as pyridine, lutidine, or anhydrous sodium carbonate[4,5,6,7,14,15] and, most recently, the sterically hindered, nonnucleophilic 2,6-di-*tert*-butyl-4-methylpyridine.[16] This procedure, which presumably involves either acid- or base-catalyzed enolization of the ketone followed by acylation of the enol with the acid anhydride, has also been used to prepare other vinyl sulfonate esters such as tosylates[8] or methanesulfonates.[9] Vinyl tosylates (but not vinyl triflates) may also be prepared from the ditosylate derivatives of 1,2-diols.[17]

Examples of the use of this procedure to prepare vinyl triflates from ketones are provided in Table II. Often mixtures of *cis* and *trans* isomers as well as the various double bond isomers of vinyl triflates are obtained by this procedure, and the amounts of these isomers produced may vary with the base and solvent used.[18] Also, small amounts of unchanged ketone may contaminate the initial crude product. Consequently, separation procedures such as preparative GC or efficient fractional distillation may be required to obtain a single vinyl triflate isomer.

TABLE II
VINYL TRIFLATES PREPARED FROM KETONES

Ketone	Reaction Conditions	Time, Days	Product	Yield, %
$XC_6H_4COCH_3$ (X = H, 4-Cl, 3-Cl, c-CF_3, 4-NO_2)	CH_2Cl_2, Na_2CO_3	3–21		15–45
	CH_2Cl_2, Na_2CO_3	14		28
	CCl_4, pyridine	5		54
$C_6H_5CH(CH_3)COCH_3$	CCl_4, pyridine	2–4	$C_6H_5C(CH_3)=C(CH_3)OSO_2CF_3$ (cis, 18%; trans, 51%) + $C_6H_5CH(CH_3)C(OSO_2CF_3)=CH_2$ (31%)	53
	CCl_4, P_2O_5	1	$C_6H_5C(CH_3)=C(CH_3)OSO_2CF_3$ (trans, 80%; cis, 20%)	32
	CH_2Cl_2, Na_2CO_3	10	$(CH_3)_2C=C(CH_3)OSO_2CF_3$ (**1**, 70%) + $(CH_3)_2CHC(OSO_2CF_3)=CH_2$ (**2**, 30%)	33

$(CH_3)_2CHCCH_3$ with O double bond (structure shown)

	CCl_4, pyridine	1	**1** (90%) + **2** (10%)	58

This preparation is referenced from:

- Org. Syn. Coll. Vol. 8, 97
- Org. Syn. Coll. Vol. 8, 126
- Org. Syn. Coll. Vol. 8, 306
- Org. Syn. Coll. Vol. 9, 553

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

P_2O_5

α-styryltriflate

potassium carbonate (584-08-7)

sodium bicarbonate,
sodium hydrogen carbonate (144-55-8)

sodium carbonate,
Na_2CO_3 (497-19-8)

carbon tetrachloride,
CCl_4 (56-23-5)

pyridine (110-86-1)

lutidine (583-61-9)

Pentane,
n-PENTANE (109-66-0)

dichloromethane,
CH_2Cl_2 (75-09-2)

3-methyl-2-butanone (563-80-4)

calcium hydride (7789-78-8)

trifluoromethanesulfonic acid (1493-13-6)

Trifluoromethanesulfonic anhydride,
trifluoromethanesulfonic acid anhydride (358-23-6)

3-Methyl-2-buten-2-yl triflate,
Methanesulfonic acid, trifluoro-, 1,2-dimethyl-1-propenyl ester (28143-80-8)

3-methyl-1-buten-2-yl triflate

vinyl triflate

phosphorus pentoxide (1314-56-3)

2,6-Di-tert-butyl-4-methylpyridine (38222-83-2)