

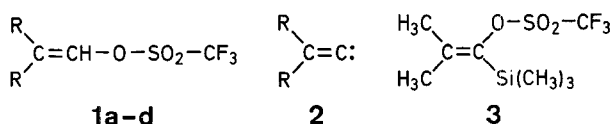
COMMUNICATIONS

Single-Step Improved Synthesis of Primary and Other Vinyl Trifluoromethanesulfonates

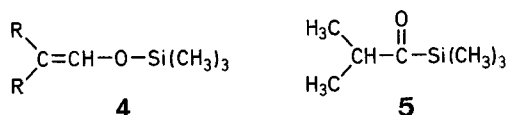
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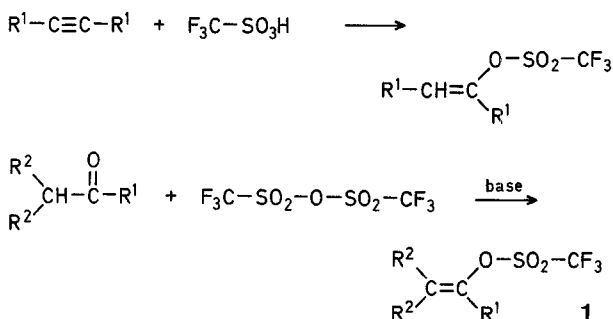
Primary vinyl triflates **1** serve as premier progenitors of alkylidene-carbenes **2**, via potassium *t*-butoxide-initiated α -elimination¹. Similarly, fluoride-initiated elimination of silylvinyl triflate **3** leads quantitatively to carbene **2** under very mild conditions².



However, the full synthetic application of alkylidene-carbenes has been impeded¹ by the modest yields of these precursors by current procedures. To date, primary vinyl triflates **1a-d** have been prepared from aldehydes in a two-step procedure³, involving silyl enol ethers **4**, in 28–56% overall yields and the yield of silylvinyl triflate **3** from the precursor ketone **5** was only 30–35%.

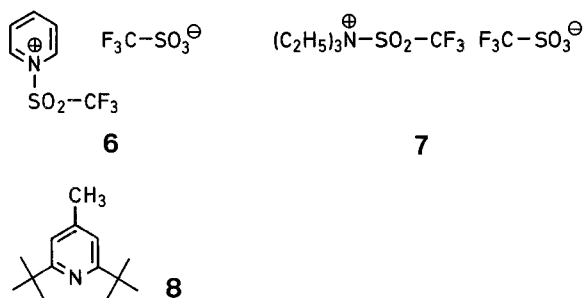


We report here a much improved single-step procedure for the preparation of these key compounds **1a-d** as well as related vinyl triflates **1e-h**. Vinyl triflates (**1**, 1-alkenyl triflates) have generally been made via electrophilic addition of trifluoromethanesulfonic acid to alkynes⁴ or by interaction of enolizable ketones with triflic anhydride in the presence of a base such as pyridine or triethylamine⁵.



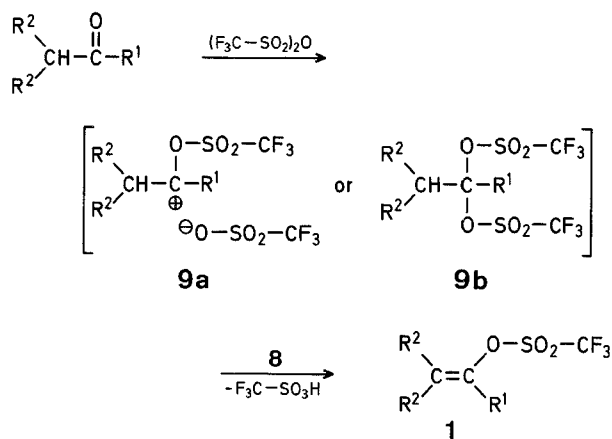
Because of Markovnikov's rule, the former procedure is inapplicable to the preparation of primary vinyl triflates **1a-d** and use of aldehydes in the second procedure results mostly in tar with very little or no triflate. Furthermore, use of common amine bases results in heterogeneous reaction conditions with highly colored reaction mixtures⁵ where the triflating agent is most likely the amine salt **6** or **7** rather than the anhydride itself.

- New or improved synthetic methods
- Key intermediates
- with full experimental and analytical data




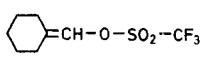
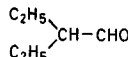
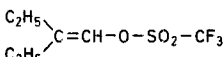
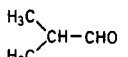
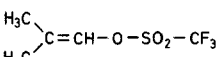
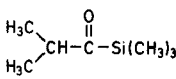
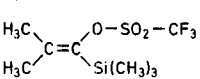

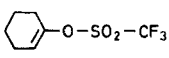
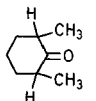
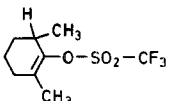
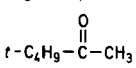
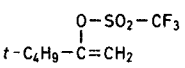
In contrast, use of the readily available⁶, sterically hindered, and non-nucleophilic 2,6-di-*t*-butyl-4-methylpyridine (**8**) as base results in clear, clean, homogeneous reaction conditions and significantly improved yields. More important, use of this base allows the *direct* conversion of aldehydes to primary vinyl triflates (**1a-d**) in yields greater than 80%, and the conversion of silyl ketone **5** to 2,2-dimethyl-1-trimethylsilylvinyl triflate (**1e**) in 75–80% yield as summarized in the Table.

It is known⁷ that pyridine rings containing the 2,6-di-*t*-butyl functionality enable such bases to distinguish between Brønsted (protic) and Lewis acids due to steric crowding in the region of the N-atom. Hence, unlike less hindered or unhindered bases, the hindered pyridine **8** does not react with triflic anhydride to give salts analogous to **6** and **7** that precipitate out of solution, and as a consequence the sulfonating agent under these conditions is the anhydride itself. Sulfonation under these conditions most likely proceeds via *gem*-diesters **9** either in their ionic (**9a**) or covalent form (**9b**) with subsequent loss of triflic acid with the aid of hindered base **8**.



Analogous *gem*-diesters are known^{8,9} to be intermediates in the reaction of carbonyl compounds with carboxylic anhydrides and in particular with trifluoroacetic anhydride. Furthermore, carbonyl compounds containing electron-withdrawing groups on the α -carbon, such as dibromoacetaldehyde or ω -trimethylsilyloxyacetophenone, do not give vinyl triflates under these conditions and can be recovered unchanged even under forcing (100 °C, neat reagents) con-

Table. 1-Alkenyl Triflates **1** from Enolizable Aldehydes or Ketones and Triflic Anhydride in the Presence of 2,6-Di-*t*-butyl-4-methylpyridine (**8**)

Starting Carbonyl Compound	Reaction conditions	Product 1	Yield ^a [%]		b.p. [°C] / torr		Reference
			obtained	reported	found	reported	
a 	CH ₂ Cl ₂ , reflux, 1h		85	50	85–86/19	83–86/18	3
b 	CH ₂ Cl ₂ , reflux, 4h		89	50	78–79/45	78–80/45	3
c H ₃ C–(CH ₂) ₃ –CHO	ClCH ₂ –CH ₂ Cl, reflux, 2h	H ₃ C–CH ₂ –CH ₂ –CH=CH–O–SO ₂ –CF ₃	81	28	72–73/50	71–73/48	3
d 	ClCH ₂ –CH ₂ Cl, reflux, 1h		80 ^b	44	65–66/70	63–66/72	3
e 	CH ₂ Cl ₂ , r.t., 10h		78	35	52–53/1.8	40–41/0.9	2
f 	CH ₂ Cl ₂ , r.t., 12h		76	38	75–76/15	75–78/15	5
g 	CH ₂ Cl ₂ , reflux, 6 days		88	54	64–66/4	52–54/0.25	5
h 	CH ₂ Cl ₂ , r.t., 4 days		73	40	59–60/29	42–45/17	15

^a Yield of isolated product.

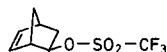
^b Yield determined by ¹H-N.M.R. analysis. Yield of isolated product: 40–45 % due to loss during distillation of solvent.

ditions¹⁰. Moreover, *gem*-ditriflates **10** and **11** have recently been isolated from the interaction of the corresponding ketones with triflic anhydride¹¹.

F₃C–SO₂–O



10



11

In summary, we have developed a general, simple, high-yield procedure for the direct conversion of aldehydes into 1-alkenyl triflates (**1**). As seen in the Table, this procedure is superior to previous ones and applicable to the conversion of other carbonyl compounds such as **5**, as well as ordinary ketones, to the corresponding 1-alkenyl triflates¹², or nonaflates¹³.

1-Alkenyl Triflates (**1**); General Procedure:

Into a 250 ml round-bottom flask, equipped with a reflux condenser and a stirrer, are added dry solvent (either dichloromethane or 1,2-dichloroethane, see Table; 100 ml), freshly distilled aldehyde (30 mmol), triflic anhydride (5.67 g, 32 mmol), and 2,6-di-*t*-butyl-4-methylpyridine (**8**; 6.77 g, 33 mmol). The solution is either stirred at room temperature or refluxed as shown in the Table. In all cases, the reaction mixture stays homogeneous, clean, and clear throughout with some precipitation of 2,6-di-*t*-butyl-4-methylpyridinium triflate¹⁴ towards the end of the reaction. After the appropriate reaction time (best determined by G.L.C. monitoring for unreacted carbonyl compound), the solvent is removed on a rotary evaporator and the residue combined with pentane (150 ml). The solid pyridinium triflate is filtered off and washed with additional pentane (25 ml). The pentane solution is washed with cold 1 molar hydrochloric acid (1 × 150 ml) and with saturated sodium chloride solution (1 × 50 ml), and is dried with anhydrous potassium carbonate. The solution is filtered, the solvent distilled off, and the residual product distilled in vacuo to give the pure products **1**; yields: 73–89%.

This investigation was supported by Public Health Service Research Grants 2R01 CA 16903-03 and 04 from the National Cancer Institute.

Received: September 4, 1979

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