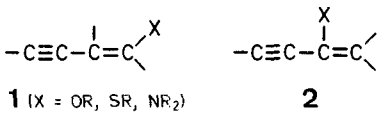
Synthesis of 1-(Ethynyl)-vinyl Trifluoromethanesulfonates

Peter J. Stang*, Thomas E. Fisk

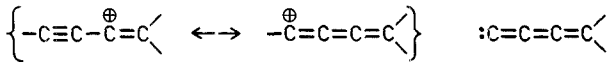
Chemistry Department, The University of Utah, Salt Lake City, Utah 84112, U.S.A.

The syntheses and reactions of 2-(ethynyl)-vinyl compounds **1** are a well established part of diacetylene derivative chemistry[1]. In contrast, the chemistry of the isomeric 1-(ethynyl)-vinyl compounds **2** is virtually unknown, presumably due to the lack of appropriate synthetic methodology. To the best of our knowledge there are few known compounds of type **2**.

Appropriately functionalized enynes of type **2** would be desirable for several reasons. They can serve as precursors for the direct solvolytic generation of α-(ethynyl)-vinyl cations **3** which are the only remaining unknown members of the family of stabilized vinyl cations[2]. They can be utilized as progenitors for extended unsaturated carbenes **4**[3,4]. Finally, they may possess interesting biological properties such as antimycotic activity characteristic of many similarly functionalized acetylenes[5]. Hence we wish to report a convenient and general synthesis of 1-(ethynyl)-vinyl trifluoromethanesulfonates (triflates) **7**, an important class of functionalized enynes of type **2**.

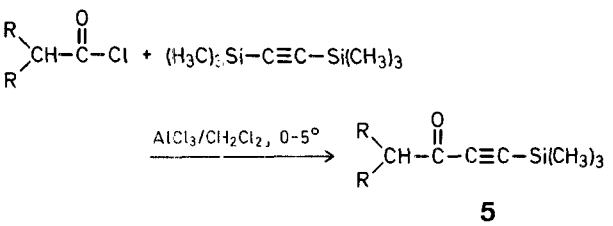


1 (X = OR, SR, NR_2) **2**

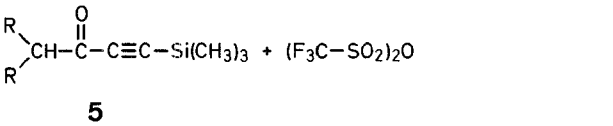


3 **4**

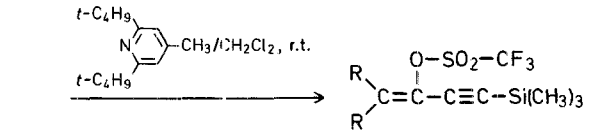
Reaction of bis[trimethylsilyl]acetylene with the appropriate acyl halides under Friedel-Crafts conditions[6] gave monoacyl trimethylsilylacetylenes **5** in good yields. Reaction of acylalkynes **5** with triflic anhydride in dichloromethane in the presence of 2,6-di-*t*-butyl-4-methylpyridine[7] gave the enyne sulfonate esters **6**. Use of the readily available, sterically hindered, non-nucleophilic 2,6-di-*t*-butyl-4-methylpyridine, rather than pyridine or other bases employed in the standard[8] preparation of vinyl triflates, was essential for the success of this key step. Treatment of **5** with triflic anhydride under the standard conditions[8] gave, in addition to unreacted starting ketones, tarring and very low yields or no product **6**. In contrast, use of the hindered base, which acts only as a proton acceptor and is incapable of reacting with the starting triflic anhydride, resulted in homogeneous, clear reaction conditions and good product yields. Desilylation



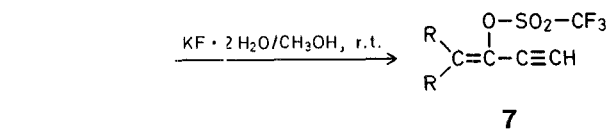
5



5



6



7

of **6** to 1-(ethynyl)-vinyl triflates **7** was accomplished nearly quantitatively by reaction with excess potassium fluoride dihydrate in methanol. The more common reagent, hydrox-

0039-7881/79/0632-0438 $ 03.00

Table. Preparation and Properties of Ketones **5** and Vinyl Triflates **6** and **7**

Compound	R	Reaction Time	Yield [%]	m.p. or b.p./torr (Lit. m.p. or b.p./torr)	Molecular Formula	^{1}H-N.M.R. (CCl_4) δ [ppm]	I.R. (neat) ν_{max} [cm^{-1}]
5a	H	3 h	78	55–58°/14 (62–64°/28)[10]	$C_7H_{12}OSi$ (140.3)	0.20 (s, 9H); 2.20 (s, 3H)	2155 (C≡C); 1680 (C=O); 1260 [$Si(CH_3)_3$]
5b	CH_3	3 h	86	74–76/14 (78.2–81.8°/17)[10]	$C_9H_{16}OSi$ (168.3)	0.25 (s, 9H); 1.80 (d, 6H; J = 7 Hz); 2.60 (m, 1H, J = 7 Hz)	2155 (C≡C); 1678 (C=O); 1259 [$Si(CH_3)_3$]
5c	C_6H_5	3 h	80	43–45°	$C_{19}H_{20}OSi$ (292.4)	0.13 (s, 9H); 5.13 (s, 1H); 7.25 (s, 10H)	2158 (C≡C); 1670 (C=O); 1258 [$Si(CH_3)_3$]
6a	H	24 h	90	77–79°/14	$C_8H_{11}F_3O_3SSi$ (272.3)	0.17 (s, 9H); 4.95 (m, 2H)	1630 (C=C); 1433, 1220, 1150 (OSO_2CF_3)
6b	CH_3	15 h	89	61–67°/1.4	$C_{10}H_{15}F_3O_3SSi$ (300.4)	0.17 (s, 9H); 1.82 (s, 3H)	2160 (C≡C); 1655 (C=C); 1428, 1220, 1152 (OSO_2CF_3)
6c	C_6H_5	7 days, 5 days[a]	56, 64[a]	42–44°	$C_{20}H_{19}F_3O_3SSi$ (424.5)	0.13 (s, 9H); 7.13 (m, 10H)	2158 (C≡C); 1600 (C=C); 1425, 1215, 1145 (OSO_2CF_3)
7a	H	30 min	98	45–47°/30	$C_5H_2F_3O_3S$ (199.1)	3.18 (s, 1H); 5.52 (m, 2H)	2127 (C≡C); 1632 (C=C); 1430, 1220, 1445 (OSO_2CF_3)
7b	CH_3	30 min	95	69–71°/17	$C_7H_6F_3O_3S$ (227.2)	1.95 (s, 3H); 2.00 (s, 3H); 3.32 (s, 1H)	2118 (C≡C); 1657 (C=C); 1435, 1220, 1147 (OSO_2CF_3)
7c	C_6H_5	30 min	90	45–47°	$C_{17}H_{10}F_3O_3S$ (351.3)	3.13 (s, 1H); 7.23 (m, 10H)	2108 (C≡C); 1603 (C=C); 1425, 1220, 1145 (OSO_2CF_3)

[a] Using dimethylaminopyridine as base.

ide in methanol, resulted in rapid sulfur-oxygen bond cleavage of the triflates **6** with reformation of the starting ketones **5** rather than the desired desilylation. Such nucleophilic attack upon the sulfur of sulfonate esters is well established[9] but the preferential attack of hydroxide (or methoxide) on sulfur rather than silicon is somewhat surprising. Both the 1-(trimethylsilylethynyl)-vinyl **6** and the 1-(ethynyl)-vinyl triflates **7** were obtained G.L.C. pure by passage through an unactivated silica gel column with pentane as eluent.

In summary, we have developed a simple, general, and high yield synthesis of 1-(trimethylsilylethynyl)-vinyl **6** and 1-(ethynyl)-vinyl triflates **7**, a new class of derivatized enynes, whose chemistry is being actively investigated and will be reported on in future papers.

Trimethylsilylethynyl Ketones 5; General Procedure:
Into a 250 ml Erlenmeyer flask with a magnetic stirring bar is added commercial bis[trimethylsilyl]acetylene (29 mmol) and the appropriate acyl chloride (29 mmol) dissolved in dichloromethane (100 ml). With the contents stirred under an argon atmosphere and cooled to 0–5° with an ice/water bath, commercial anhydrous aluminum trichloride (29 mmol) is added all at once. The solution immediately becomes colored. After 3 h stirring at 0–5°, the solution is poured into a mixture of 10% aqueous hydrochloric acid (50 ml) and ice (50 ml). The aqueous layer is extracted with diethyl ether (4 × 50 ml) and the combined organic phase is washed with saturated sodium hydrogen carbonate, followed by brine, and then dried over anhydrous magnesium sulfate. Removal of the solvent and vacuum distillation gives the product ketones summarized in the Table.

1-(Trimethylsilylethynyl)-vinyl Triflates 6; General Procedure:
Into a 500 ml Erlenmeyer flask maintained under argon and equipped with a magnetic stirring bar are added sequentially 2,6-di-*t*-butyl-4-methylpyridine[7] (31 mmol; 25% excess) dissolved in dichloromethane (250 ml), triflic anhydride[8] (37.5 mmol; 50% excess), and the appropriate ketone **5** (25 mmol). The clear mixture is stirred at room temperature and monitored by G.L.C. or T.L.C. until no ketone remains (see Table). Formation of the diphenyl compound (**6c**) could be speeded up by use of 4-dimethylaminopyridine (5 days vs 7 days) rather than the 2,6-di-*t*-butyl-4-methylpyridine as base. The dichloromethane is removed using a rotary evaporator and pentane (200 ml) is added to the brown residue. The pyridinium triflate salt is filtered and the pentane solution washed with cold aqueous 10% hydrochloric acid, saturated sodium hydrogen carbonate, followed with saturated sodium chloride (3 × 50 ml each), and then dried over anhydrous magnesium sulfate. The pentane is removed and the residual oil eluted on a silica gel column (30 × 2 cm) with pentane. Pure vinyl triflates **6** are eluted in the first 250 ml portion of pentane. Removal of pentane gives the products listed in the Table. The hindered base may be recovered by addition of the pyridinium triflate (combined from several reactions) to a stirring two phase mixture of 50% aqueous sodium hydroxide and pentane. The free base is recovered from the pentane phase in greater than 95% yield and may be repurified by elution with pentane through an unactivated silica gel column.

1-(Ethynyl)-vinyl Triflates 7; General Procedure:
Into a 250 ml Erlenmeyer flask, equipped with a magnetic stirring bar, is added commercial $KF \cdot 2H_2O$ (45 mmol; 300% excess) dissolved in methanol (150 ml) followed by triflate **6** (15 mmol). After stirring for 30 minutes at room temperature, water (50 ml) is added and the entire mixture extracted with pentane (4 × 50 ml). The combined pentane phase is washed with brine and then dried over anhydrous magnesium sulfate. Removal of the pentane and elution of the remaining oil through a silica gel column with pentane gives, after evaporation of the solvent, the product vinyl triflates listed in the Table. 1-(Ethynyl)-vinyl triflates **7** turn

brown overnight at room temperature but remain clear for several days at 0° or in dilute pentane solution at room temperature.

Financial support by the NSF (CHE 78-03596) and the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

Received: February 2, 1979

[1] M. F. Shostakovskii, A. V. Bogdanova, *Khimiia Diatsetilena*, Izdatel'stvo Nauka, Moscow, 1971.
The Chemistry of Diacetylenes, Keter Publishing House Jerusalem Ltd., 1974.
[2] P. J. Stang, Z. Rappoport, M. Hanack, L. R. Subramanian, *Vinyl Cations*, Academic Press, New York, 1979.
M. Hanack, *Angew. Chem.* **90**, 346 (1978); *Angew. Chem. Int. Ed. Engl.* **17**, 333 (1978).
[3] For a review on unsaturated carbenes see: P. J. Stang, *Chem. Rev.* **78**, 383 (1978).
[4] P. J. Stang, T. E. Fisk, *J. Am. Chem. Soc.*, submitted.
[5] O. G. Yashina, L. I. Vereshchagin, *Usp. Khim.* **47**, 557 (1978); *Russ. Chem. Rev.* (Engl. Transl.) **47**, 307 (1978).
[6] R. M. Walton, F. Waugh, *J. Organometal. Chem.* **37**, 45 (1972); L. Birkofer, A. Ritter, H. Uhlenbrauck, *Chem. Ber.* **96**, 3280 (1963).
[7] A. G. Anderson, P. J. Stang, *J. Org. Chem.* **41**, 3034 (1976); *Org. Synth.*, submitted.
[8] P. J. Stang, T. E. Dueber, *Org. Synth.* **54**, 79 (1974).
[9] L. R. Subramanian et al., *J. Org. Chem.* **41**, 4099 (1976).
R. H. Summerville et al., *J. Am. Chem. Soc.* **96**, 1100 (1974).
C. A. Bunton, Y. F. Frei, *J. Chem. Soc.* **1951**, 1872.
[10] M. W. Logue, G. L. Moore, *J. Org. Chem.* **40**, 131 (1975).

0039–7881/79/0632–0440 $ 03.00