The Preparation of Unsymmetrical Diacetylenes from Alkenynyl Triflates

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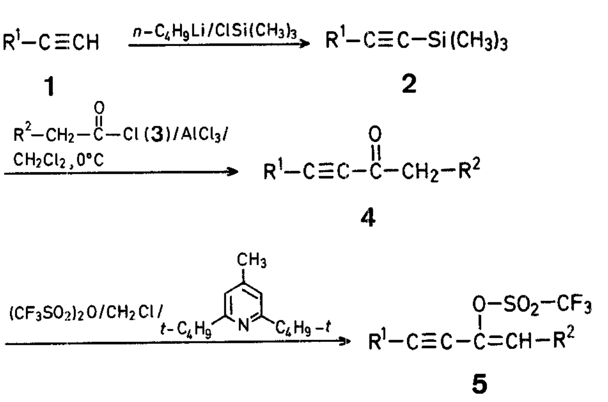
Alkenynyl triflates **5** (alkynylvinyl trifluoromethanesulfonates) are readily converted into unsymmetrical diacetylenes **6** in good yields by the base-initiated elimination of trifluoromethanesulfonic acid.

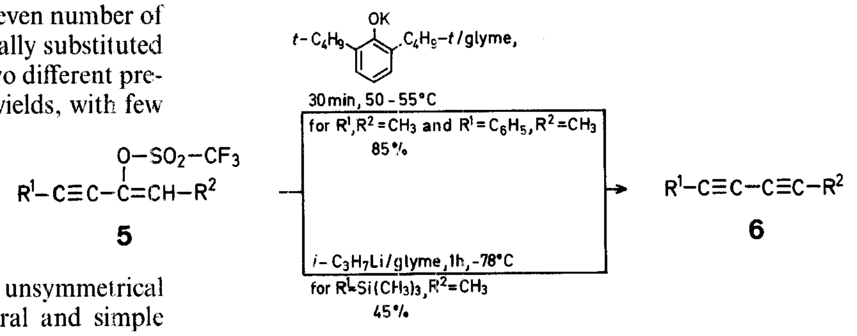
Conjugated diacetylenes are of considerable interest and are usually prepared by various oxidative couplings of terminal alkynes[1]. The coupling of a terminal alkyne with bromoacetylene in the presence of copper(I) ion and a simple amine, as formulated by Cadiot and Chodkiewiz[1] constitutes the best method yet devised for preparing unsymmetrical polyacetylenes containing an even or odd number of triple bonds. These reactions work well for symmetrically substituted diacetylenes or polyacetylenes with an even number of triple bonds. The formation of unsymmetrically substituted diacetylenes requires the cross coupling of two different precursor alkynes *ipso facto*, resulting in poor yields, with few alternative methods of preparation of such unsymmetrical diacetylenes[2]. We now report a new, general and simple method for the preparation of unsymmetrical diacetylenes.



Scheme **A**

Substituted ethynylvinyl trifluoromethanesulfonates (triflates) **5** can be easily made in overall yields of 70–90% by adoption of previously reported[3] methods (Scheme **A**). Specificially, treatment of a terminal alkyne **1** with *n*-butyllithium followed by addition of chlorotrimethylsilane affords silylalkynes **2** in greater than 95% yield. Acylation[4] of **2** with an acid chloride **3** in the presence of aluminium chloride gives ketones **4** in 70–90% yields. Enolization of these ketones in the presence of a hindered amine base and trifluoromethanesulfonic anhydride gives enyne triflate **5** isolated in 60–80% yield.

Subsequent treatment of these triflates with an appropriate base in glyme results in the elimination of trifluoromethanesulfonic acid and formation of the desired alkynes **6** (Scheme **B**).



Scheme **B**

Thus reaction of triflate **5** with potassium 2,6-di-*t*-butylphenoxide[5] in glyme under argon gave an 80–85% yield of pure diynes **6a** and **6b**. Similarly use of lithium diisopropylamide as base gave a 45–50% yield of pure **6c** along with 30–35% recovered starting triflate. The spectral data of **6** (Table) are consistent with the proposed structures and in accord with related literature data[6]. Particularly significant are the well characterized mass spectra and the characteristic infrared spectra.

It is evident from the forgoing that this procedure affords a ready means of preparing unsymmetrical as well as symmetrical diynes in good yield in a simple manner.

Table. Diynes **6a–c** prepared

Product No.	R^1	R^2	Yield [%]	b.p. [°C]/torr		I.R. (neat) ν [cm^{-1}]	^{1}H-N.M.R. (CDCl$_3$/TMS) δ [ppm]	M.S. *m/e* (rel. intensity, %)
				found	reported			
6a	CH_3	CH_3	85	–[b]	–[a]	–	2.0 (s, CH_3)	79 (M^+ + 1, 9.8); 78 (M^+, 100); 77 (M^+ − H, 24.3); 28 ($C_2H_4^+$, 63)
6b	C_6H_5	CH_3	85	80–83°/0.5	54–56°/0.2	2250, 2170 (C≡C)	1.92 (s, 3H, CH_3); 7.1–7.44 (m, 5H, C_6H_5)	141 (M^+ + 1, 11.4); 140 (M^+, 88); 139 (M^+ − H, 100); 63.0 (M^+ − C_6H_5, 8.9); 28 ($C_2H_4^+$, 40.3)
6c	$Si(CH_3)_3$	CH_3	45	–[b]	–[a]	2240, 2110 (C≡C), 850 (Si—C)	0.22 [s, 9H, $Si(CH_3)_3$]; 1.94 [s, 3H, C—CH_3]	137 (M^+ + 1, 1.9); 136 (M^+, 14.5); 121 (M^+ − CH_3, 100); 73 [$(H_3C)_3Si^+$, 2.9]; 28 ($C_2H_4^+$, 75.9)

[a] Physical data are not reported in the original literature[6].

[b] Purified by column chromatography.

All solvents and reagents employed were ACS reagent grade and were purified and dried prior to use. Alkynylvinyl triflates, **4**[3], and potassium 2,6-di-*t*-butylphenoxide[5] were prepared as previously reported.

Diacetylenes 6a and 6b; General Procedure:

Into flame-dried, argon-flushed flask containing a solution of triflate **5a** or **5b** (1.0 mmol) in glyme (50 ml) is added a 0.12 molar solution of potassium 2,6-di-*t*-butylphenoxide[5] (10.3 ml, 1.03 mmol) over a 30 min period. The solution is stirred at 50–55 °C and monitored for unreacted triflate by means of T.L.C. (eluent: 10% dichloromethane in pentane). After 30 min no triflate remains and the solution is concentrated. Extraction of the residue with pentane (2 × 30 ml), followed by column chromatography on silica gel (hexane as eluent) gives an 80–85% yield of pure diynes **5a** and **5b** as colorless and yellow oils, respectively (Table).

1,3-Pentadiynyl-trimethylsilane (6c):

This compound is prepared in a manner similar to **6a** and **6b** except that lithium diisopropylamide prepared from *n*-butyllithium and diisopropylamine is used as the base and the reaction is carried out at −78 °C. At the end of 1 h, 5% ammonium chloride solution (20 ml) is added and the mixture is extracted with pentane (2 × 30 ml). Evaporation of pentane and chromatography of the residue on silica gel using hexane as eluent gives **6c** as a pale yellow oil; yield: 45% (Table). The starting triflate is recovered in 30–35% yield.

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[2] For two recent alternative methods, see:
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[5] Brown, H.C., Nambu, H., Rogic, M.M. *J. Am. Chem. Soc.* **1969**, *91*, 6852.

[6] The diynes **6a–c** prepared herein are known in literature, but have been only partially characterized.
For **6a**, see: Kloster-Jensen, E., Tabachi, R. *Tetrahedron Lett.* **1972**, 4023.
For **6b**, see: Ref.[2a].
For **6c**, see: Holmes, A.B., Jones, G.E. *Tetrahedron Lett.* **1980**, *21*, 3111; **1982**, *23*, 3203.