Simple, Novel Preparation of Unsymmetrical Triacetylenes

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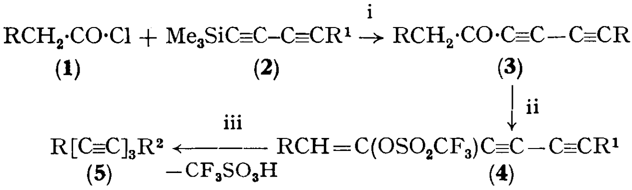
Summary Base-initiated elimination of trifluoromethanesulphonic acid from $\mathrm{RCH{=}C(OSO_2CF_3)C{\equiv}C{-}C{\equiv}CSiMe_3}$ readily affords the unsymmetrical trialkynes $\mathrm{R[C{\equiv}C]_3SiMe_3}$ or $\mathrm{R[C{\equiv}C]_3H}$.

CONJUGATED polyacetylenes are of considerable current interest and are generally made by various oxidative couplings of terminal alkynes.[1] These reactions work best for symmetrically substituted polyacetylenes with an even number of triple bonds; as the formation of unsymmetrically substituted polyalkynes, or polyalkynes with an odd number of triple bonds, requires the cross-coupling of two different precursor alkynes, the oxidative-coupling method gives, *ipso facto*, poor yields. Herein, we report a general, simple, and new method for the preparation of unsymmetrical conjugated triacetylenes.

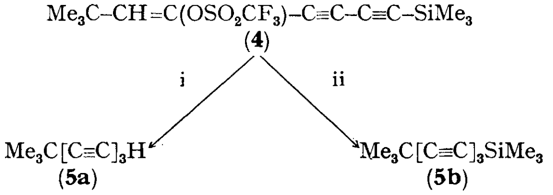


$$\begin{tikzcd} \underset{(1)}{\mathrm{RCH_2{\cdot}CO{\cdot}Cl}} + \underset{(2)}{\mathrm{Me_3SiC{\equiv}C{-}C{\equiv}CR^1}} \arrow[r, "\text{i}"] & \underset{(3)}{\mathrm{RCH_2{\cdot}CO{\cdot}C{\equiv}C{-}C{\equiv}CR^1}} \arrow[d, "\text{ii}"] \\ \underset{(5)}{\mathrm{R[C{\equiv}C]_3R^2}} & \underset{(4)}{\mathrm{RCH{=}C(OSO_2CF_3)C{\equiv}C{-}C{\equiv}CR^1}} \arrow[l, "\text{iii}", "-\mathrm{CF_3SO_3H}"'] \end{tikzcd}$$

$\mathrm{R^1 = SiMe_3}$, alkyl, aryl; $\mathrm{R^2 = SiMe_3}$, alkyl, aryl, H.

SCHEME 1. *Reagents:* i, $\mathrm{AlCl_3}$, $\mathrm{CH_2Cl_2}$; ii, $\mathrm{[CF_3SO_2]_2O}$, $\mathrm{CH_2Cl_2}$, pyridine; iii, base, glyme.

The formation of a variety of substituted 1-(butadiynyl)-vinyl trifluoromethanesulphonates (**4**) (triflates) can be readily accomplished in overall yields of 60—75% as previously reported[2] and shown in Scheme 1. Subsequent treatment of these triflates with an appropriate base in glyme results in the elimination of $\mathrm{CF_3SO_3H}$ and formation of the desired unsymmetrically substituted trialkynes (**5**). The procedure is best illustrated by the synthesis of two new triynes; namely 7,7-dimethylocta-1,3,5-triyne (**5a**)† and 7,7-dimethyl-1-trimethylsilylocta-1,3,5-triyne (**5b**), as shown in Scheme 2.



$$\begin{tikzcd} & \underset{(4)}{\mathrm{Me_3C{-}CH{=}C(OSO_2CF_3){-}C{\equiv}C{-}C{\equiv}C{-}SiMe_3}} \arrow[dl, "\text{i}"'] \arrow[dr, "\text{ii}"] & \\ \underset{(5a)}{\mathrm{Me_3C[C{\equiv}C]_3H}} & & \underset{(5b)}{\mathrm{Me_3C[C{\equiv}C]_3SiMe_3}} \end{tikzcd}$$

SCHEME 2. *Reagents:* i, $\mathrm{2,6\text{-}Bu^t_2C_6H_3OK}$, glyme, 30 min, 50—55 °C; ii, $\mathrm{Pr^i_2NLi}$, glyme, 30 min, 50—55 °C.

Treatment of 1·5 mmol of the ene-diyne (**4**) with 2,6-di-t-butylphenyl oxide[3] in glyme under argon gave, upon concentration of the solvent and column chromatography on

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† This compound has been reported (F. Bohlmann, *Chem. Ber.*, 1953, **86**, 657) as an unstable intermediate without characterization.

TABLE. Summary of spectral data of the triynes (**5**).

	(**5a**)	(**5b**)
ν_{max} (neat) cm^{-1}	3295s(C≡C–H), 2220s(C≡C)	2210s, 2180m, 2110w, 2085s (C≡C), 850s(Si–Me)
δ_H (CCl_4, Me_4Si)	1·28 (9 H, s, Me), 1·95 (1 H, s, C≡CH)	0·20 (9 H, s, SiMe), 1·29 (9 H, s, CMe)
λ_{max} (hexane) nm (log ϵ)	211(4·48), 243(2·87), 254(2·91), 268·5(3·08), 282·5sh(2·90), 302(2·50), 332·5(2·09)	220(5·02), 244sh(3·92), 255(4·16), 267·5(4·35), 278(4·34), 296 (4·38), 332(3·16)
m/z (70 eV) (%)	130(57·1, M^+), 129(14·6, $M^+ - H$), 115(100, M^+–Me), 73(26·7, M^+–Bu), 57(47·3, $C_4H_9^+$)	202(37·6, M^+), 187(100, $M^+ -$Me), 172(10·6, $M^+ -$2Me), 159(20·4, $M^+ -$Pr), 145(23·7, $M^+ -$Bu), 129 (5·8, $M^+ - SiMe_3$), 73(46·2, Me_3Si^+)

silica gel (pentane as eluent), an 85—90% yield of the pure‡ triyne (**5a**). Similar treatment with lithium di-isopropylamide as base, followed by chromatography, gave a 42—47% yield of compound (**5b**) as well as 30—40% of the initial triflate (**4**). The triynes (**5**) were identified by spectroscopy, as shown in the Table.

These spectral data are clearly consistent with the proposed structures and in accord with literature data[4] on analogous triacetylenic compounds, specifically Me[C≡C]$_3$H. Particularly significant are the well characterized mass spectra and the typical i.r. and u.v. spectra.[4]

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‡ Thin layer chromatography showed a single spot and the spectral data indicated a pure compound. However, the triyne (**5a**) is extremely unstable in the pure form at room temperature and a black polymer is formed within minutes. It is best handled and kept in solution and in the cold. Compound (**5b**), as expected (B. F. Coles and D. R. M. Walton, *Synthesis*, 1975, 390; R. Eastmond and D. R. M. Walton, *Chem. Commun.*, 1968, 204), is much more stable.

[1] For recent reviews and references see 'Methoden Org. Chem., Houben-Weyl,' 1977, Vol. 5/2a, pp. 915—962; W. D. Huntsman in 'The Chemistry of the Carbon Carbon Triple Bond,' ed. S. Patai, Wiley-Interscience, London, 1978, pp. 553—620.

[2] P. J. Stang and M. Ladika, *Synthesis*, 1981, 218.

[3] H. C. Brown, H. Nambu, and M. M. Rogic, *J. Am. Chem. Soc.*, 1969, **91**, 6852.

[4] *Inter alia:* A. J. Alexander, H. W. Kroto, M. Maier, and D. R. M. Walton, *J. Mol. Spectrosc.*, 1978, **70**, 84; F. Bohlmann, W. Sucrow, and I. Queck, *Chem. Ber.*, 1964, **97**, 2586; P. Jouve and M. -P. Simonnin, *C.R. Acad. Sci.*, 1963, **257**, 121; J. B. Armitage, C. L. Cook, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1952, 2010; C. L. Cook, E. R. H. Jones, and M. C. Whiting, *ibid.*, 1952, 2883.