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Synthesis of terminal trimethylsilyl enynes via a silylated arsonium ylide

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Abstract

The reaction of 3-(trimethylsilyl)-2-propynylidenetriphenylarsorane, generated in situ from the corresponding arsonium salt and n-butyllithium, with ketones gave terminal trimethylsilyl enynes in 72–100% yields. The stereochemical study revealed that the structure of the substrate displayed a profound effect, especially when a bulky t-butyl group was adjacent to the carbonyl group; in this case the *E*-isomer was formed exclusively. The corresponding phosphorane did not react with t-butyl methyl ketone and reacted with other ketones in much lower yields.

Introduction

Some natural products with terminal enyne groups have attracted much attention in terms of their biological properties [1] and they are also important intermediates for the synthesis of naturally occurring polyacetylenic compounds [2]. Corey et al. [3] reported that 3-(trimethylsilyl)-2-propynylidenetriphenylphosphorane reacts with aldehydes to give terminal trimethylsilyl enynes in 54–80% yields, but no reactions with ketones were disclosed. Arsonium ylides bearing an electron-withdrawing substituent at the alkylidene moiety have been found to be more effective than the corresponding phosphonium ylides and are able to react with aldehydes as well as ketones and give moderate to excellent yields [4]. To the best of our knowledge, no report on silyl-2-propynylidenetriphenylarsorane has ever appeared. Here we report on the synthesis of terminal trimethylsilyl enynes by the reaction of 3-(trimethylsilyl)-2-propynylidenetriphenylarsorane with ketones to give products in good to excellent yields. Their stereochemical results are described.

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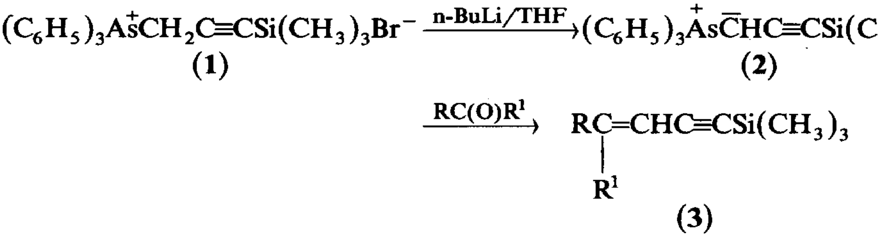
Results and discussion

The reaction of 3-(trimethylsilyl)-2-propynylidenetriphenylarsorane, generated in situ from the corresponding arsonium salt and n-butyllithium, with ketones gave terminal trimethylsilyl enynes in 72–100% yields (eq. 1).



$$\underset{(1)}{(C_6H_5)_3\overset{+}{As}CH_2C{\equiv}CSi(CH_3)_3Br^-} \xrightarrow{n\text{-}BuLi/THF} \underset{(2)}{(C_6H_5)_3\overset{+}{As}\overset{-}{C}HC{\equiv}CSi(CH_3)_3} \xrightarrow{RC(O)R^1} \underset{(3)}{R\underset{R^1}{\underset{|}{C}}{=}CHC{\equiv}CSi(CH_3)_3} \qquad (1)$$

3-(Trimethylsilyl)-2-propynyltriphenylarsonium bromide (**1**) was readily prepared from triphenylarsine and 3-bromo-1-(trimethylsilyl)-1-propyne in acetonitrile at 50–60 °C under nitrogen for 48 h in 97% yield.

The results are listed in Table 1.

The results of the stereochemical study show that a mixture of *E*- and *Z*-isomer generally was obtained. But the structure of the substrate showed a profound effect, especially when a bulky t-butyl group was adjacent to the carbonyl group, which led

Table 1

Synthesis of terminal trimethylsilyl enynes (**3**)

Compound	R	R^1	Yield (%)	Ratio[a] *E*/*Z*
3a	$-(CH_2)_5-$		80	
3b	$-(CH_2)_4-$		83	
3c	CH_3	C_2H_5	86	61/39
3d	CH_3	n-C_3H_7	100	53/47
3e	CH_3	n-C_7H_{15}	91	49/51
3f	$-(CH_2)_4-\underset{CH_3}{\underset{\vert}{CH}}-$		95	83/17
3g	CH_3	t-C_4H_9	72	100/0

[a] The ratios of *E*- and *Z*-isomer were estimated on the basis of ^1H NMR spectra and GLC.

Table 2

Comparison from the reaction of arsorane and phosphorane with ketones

R	R^1	Yield (%)	
		Arsorane	Phosphorane
$-(CH_2)_5-$		80	56[a]
$-(CH_2)_4-\underset{CH_3}{\underset{\vert}{CH}}-$		95	21
CH_3	t-Bu	72	0

[a] In ref. 5, the yield was claimed to be 71%, with the microanalysis not consistent with calculated value well.

to the exclusive formation of *E*-isomer. The corresponding phosphorane did not react with t-butyl methyl ketone and reacted with other ketones in much lower yields. The results are listed in Table 2.

These results show that the arsonium ylides are indeed more reactive than the corresponding phosphonium ylides.

Our method involves a one-pot reaction only, the conditions are mild, and the yields are good to excellent. The structures of all products were deduced from their MS, IR and ^{1}H NMR spectra. All microanalyses were consistent with calculated values.

Experimental

All boiling points were uncorrected. Infrared spectra of the solid products (as KCl disks) and those of the liquid products (as films) were recorded on a Shimadzu RI-440 Spectrometer. ^{1}H NMR spectra (chemical shifts in ppm from TMS) and mass spectra were recorded on an EM-360 Spectrometer (at 60 MHz) and a Finnigan GC-MC 4021 mass spectrometer, respectively.

Preparation of 3-(trimethylsilyl)-2-propynyltriphenylarsonium bromide (1)

A solution of triphenylarsine (0.918 g, 3 mmol) and 3-bromo-1-trimethylsilyl-1-propyne (0.600 g, 3 mmol) in dry acetonitrile (1.2 ml) was stirred at 50–60 ° C under nitrogen for 48 h. The solid was collected by suction to give **1** which was recrystallized from chloroform/dry ether; yield, 1.44 g (97%); m.p. 190 ° C (dec.).

Analysis: Found: C, 57.91; H, 5.22; Br, 16.75. $C_{24}H_{26}AsBrSi$ calc: C, 57.96; H, 5.27; Br, 17.07%. Selected IR data (KCl): 2200w, 1250s, 850s cm^{-1}. ^{1}H NMR ($CDCl_3/TMS_{ext.}$): 0.00(s,9H); 5.20(s,2H); 7.50–8.10(m,15H) ppm. MS *m/e*: 306[$(C_6H_5)_3As^+$], 111($CH_2C{\equiv}CTMS^+$), 73($SiMe_3^+$).

Preparation of terminal trimethylsilyl enynes (3). General procedure

n-Butyllithium (4.0 mmol in 2.6 ml of hexane) was added dropwise with stirring over 0.5 h to a suspension of arsonium bromide **1** (1.99 g, 4.0 mmol) in dry tetrahydrofuran (18 ml) at −70 ° C under nitrogen. The reaction mixture was warmed to −10 ° C, stirred during 0.5 h, recooled to −70 ° C. Ketones (3.00 mmol) in tetrahydrofuran (20 ml) were slowly added and the mixture was stirred for a further 0.5 h. It was then warmed to 20 ° C and stirred for 1 h. The precipitate which formed was collected by suction and washed with dry ether to give triphenylarsine oxide. Evaporation of the solvent gave a residue which when purified by column chromatography, on silica gel eluting with petroleum ether (b.p. 60–90 ° C), gave the product **3**.

3a: yield: 80%; b.p. 83–84°C/3 torr (Lit. data [5], 84–85°C/3 torr). Analysis: Found: C, 74.77; H, 10.25; $C_{12}H_{20}Si$ calc: C, 74.92; H, 10.48%. Selected IR data (film): 2150w, 1625s, 1250s, 850s cm^{-1}. ^{1}H NMR ($CDCl_3/TMS_{ext.}$): 0.00(s,9H); 1.30–1.70(m,6H); 1.90–2.40(m,4H); 5.03(s,1H). MS *m/e*: 192(M^+), 177(M^+-CH_3), 73($SiMe_3^+$).

3b: yield: 83%; b.p. 52–54°C/1.5 torr. Analysis: Found: C, 74.10; H, 10.37; $C_{11}H_{18}Si$ calc: C, 74.08; H, 10.17%. Selected IR data (film): 2150w, 1625s, 1250s, 850s cm^{-1}. ^{1}H NMR ($CDCl_3/TMS_{ext.}$): 0.14(s,9H); 1.50–1.90(m,4H); 2.10–2.60(m,4H); 5.30(s,1H). MS *m/e*: 178(M^+), 163(M^+-CH_3), 73($SiMe_3^+$).

3c: yield: 86%; b.p. 32–35 °C/0.3 torr. Analysis: Found: C, 72.17; H, 11.21; $C_{10}H_{18}Si$ calc: C, 72.21; H, 10.91%. Selected IR data (film): 2150w, 1620s, 1250s, 850s cm^{-1}. ^1H NMR ($CDCl_3/TMS_{ext.}$): 0.10(s,9H); 1.06(t,3H, J 7.0 Hz); 1.80(Z) + 1.90(E) (s,3H); 1.93–2.51(m,2H); 5.20(s,1H). MS m/e: 166(M^+), 151($M^+ - CH_3$), 73($SiMe_3{}^+$).

3d: yield: 100%; b.p. 54–56 °C/1.5 torr. Analysis: Found: C, 73.33; H, 11.44; $C_{11}H_{20}Si$ calc: C, 73.25; H, 11.18%. Selected IR data (film): 2150w, 1620s, 1250s, 850s cm^{-1}. ^1H NMR ($CDCl_3/TMS_{ext.}$): 0.20(s,9H); 0.78–1.60(m,5H); 1.80(Z) + 1.87(E) (s,3H); 1.90–2.50(m,2H); 5.25(s,1H). MS m/e: 180(M^+), 165($M^+ - CH_3$), 73($SiMe_3{}^+$).

3e: yield: 91%; b.p. 64–65 °C/0.4 torr. Analysis: Found: C, 76.37; H, 12.15; $C_{15}H_{28}Si$ calc: C, 76.19; H, 11.93%. Selected IR data (film): 2150w, 1625s, 1260s, 860s cm^{-1}. ^1H NMR ($CDCl_3/TMS_{ext.}$): 0.13(s,9H); 0.60–1.60(m,13H); 1.73(Z) + 1.80(E) (s,3H); 1.83–2.33(m,2H); 5.13(s,1H). MS m/e: 236(M^+), 221($M^+ - CH_3$), 73($SiMe_3{}^+$).

3f: yield: 95%; b.p. 123–124 °C/12 torr. Analysis: Found: C, 75.73; H, 10.65: $C_{13}H_{22}Si$ calc: C, 75.65; H, 10.74%. Selected IR data (film): 2150w, 1610s, 1250s, 850s cm^{-1}. ^1H NMR ($CDCl_3/TMS_{ext.}$/200 MHz): 0.14(s,9H); 0.98(E) + 1.07(Z) (d,3H); 1.30–2.30(m,8H); 2.80–2.92(E) + 3.10–3.22(Z) (m,1H); 5.16(Z) + 5.20(E) (s,1H). MS m/e: 206(M^+), 191($M^+ - CH_3$), 73($SiMe_3{}^+$).

3g: yield: 72%; b.p. 50–52 °C/0.4 torr. Analysis: Found: C, 73.66; H, 11.01; $C_{12}H_{22}Si$ calc: C, 74.15; H, 11.41%. Selected IR data (film): 2150w, 1610s, 1240s, 850s cm^{-1}. ^1H NMR ($CDCl_3/TMS_{ext.}$/200 MHz): 0.12(s,9H); 0.97(s,9H); 1.87(d,3H, J 1 Hz); 5.34(q,1H, J 1 Hz). MS m/e: 194(M^+), 179($M^+ - CH_3$), 73($SiMe_3{}^+$).

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