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Synthesis of Trimethylsily Enynyl Carboxylates via a Silylated Arsonium Ylide

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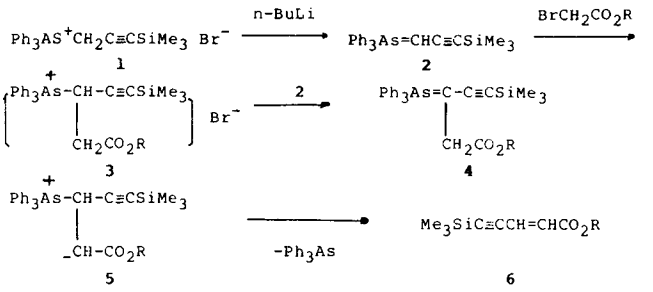
ABSTRACT

Silylated enynyl carboxylic esters can be synthesized with high stereoselectivity by the reaction of 3-trimethylsilyl-2-propynylidenetriphenylarsorane, generated in situ from the corresponding arsonium salt with n-butyllithium and α-bromoacetic esters.

Silylated enynyl carboxylic esters are important intermediates in synthetic organic chemistry, being essential components in the synthesis of some natural products [1] and capable of undergoing a variety of useful synthetic transformations [2]. Boronoeva et al. reported a Wittig reaction of $Me_3SiC{\equiv}CCHO$ with $Ph_3P{=}CHCO_2Et$ to prepare ethyl 5-trimethylsilyl-2-penten-4-ynoate [3]. Some other methods have also appeared in the literature for the preparation of similar compounds [4]. Some of these methods were multistep syntheses and some required starting materials that were not readily available. Thus, it is of much value to develop an efficient method for the preparation of silylated enynyl carboxylic esters with Z-isomer as the predominant product. There are some very interesting natural products containing the endiyne structure that have Z-stereochemistry with respect to the double bond [1].

Recently, we reported a novel double elimination of arsonium salts to prepare 4-trifluoromethyl-2,4-dienyl carboxylic esters [5]. In our continuing investigations to exploit the synthetic utility of this reaction, we found that the reaction of 3-trimethylsilyl-2-propylidenetriphenylarsorane with α-bromoacetic esters could give silylated enynyl carboxylic esters.

The reaction sequence is proposed to be as follows:



Two equivalents of **2** generated from the corresponding arsonium salt **1** were allowed to react with the α-bromoacetic ester to give the product **6**. The reaction mechanism may be similar to that proposed for the preparation of 4-trifluoromethyl-2,4-dienylcarboxylic esters [5], which involves an elimination of triphenylarsine.

It is noteworthy that this reaction gives the E- and Z-isomers in almost equal quantity when the R group in the α-bromoacetic ester is methyl, ethyl, propyl, or butyl and the Z-isomer predominantly when the R group is propenyl or propynyl. The stereoselectivity of this reaction is different from that of the preparation of 4-trifluoromethyl-2,4-dienylcarboxylic esters that gave the E-isomers exclusively [5].

This one-pot synthesis of silylated enynyl carboxylic esters is quite convenient, because it occurs under mild conditions and, in the cases of **6g** and **6h**, gives the Z-isomer with high stereoselectivity. Thus, this reaction provides a new method for the preparation of the title compounds which

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TABLE 1 Preparation of Silylated Enynyl Carboxylates **6**

Product	R	Yield (%)	E:Z[a]
6a	methyl	58	52:48
6b	ethyl	56	50:50
6c	i-propyl	60	48:52
6d	n-butyl	56	52:48
6e	i-butyl	50	50:50
6f	t-butyl	52	52:48
6g	propenyl	46	6:94[b]
6h	propynyl	56	3:97[b]

[a]Isolated yields. The ratios of the E- and Z-isomers were based upon the amounts of isolated products.
[b]The ratios of the E- and Z-isomers were determined by NMR analysis.

could be useful in the synthesis of natural products.

EXPERIMENTAL

All boiling points were uncorrected. The IR spectra of liquid products were obtained as films on a Shimadzu IR-440 spectrometer. The ^{1}H NMR spectra were recorded on a Varian EM-360 (60 MHz) or an XL-200 (200 MHz) spectrometer with $SiMe_4$ (positive for upfield shifts) as external references. Mass spectra were measured on a GC-MS-4021 spectrometer.

GENERAL PROCEDURE

n-Butyllithium (4.0 mmol in 3 mL hexane) was added dropwise over 30 minutes to a stirred suspension of 3-trimethylsilyl-2-propynyltriphenylarsonium bromide (4 mmol) in dry THF (20 mL) at −78°C under nitrogen. The mixture was stirred for 30 minutes at 0°C and cooled to −78°C, and the α-bromoacetic ester (2 mmol) was added. After having been stirred for 2 hours, the product **6** was isolated by column chromatography on silica gel with light petroleum (bp 60–90°C)/ethyl acetate (9:1) as eluant.

E-Methyl 2-Penten-4-ynoate: **6a–E**

bp 50°C/1.5 Torr (Ref. [7], 66°C/0.8 Torr). IR data (film): 2150 (w), 1728 (s), 1620 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$/TMS_{ext}): δ 0.22 (s, 9H), 4.19 (s, 3H), 6.24 (d, 1H, J = 16.0 Hz), 6.74 (d, 1H, J = 16.0 Hz).

Z-Methyl 2-Penten-4-ynoate: **6a–Z**

bp 50°C/1.5 Torr (Ref. [8], 85°C/10.2 Torr). IR data (film): 2140 (w), 1738 (s), 1720 (s), 1610 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$/TMS_{ext}): δ 0.25 (s, 9H), 4.16 (s, 3H), 6.09 (d, 1H, J = 11.6 Hz), 6.17 (d, 1H, J = 11.6 Hz).

E-Ethyl 2-Penten-4-ynoate: **6b–E**

bp 54°C/1.5 Torr (Ref. [9], 75°C/9.2 Torr). IR data (film): 2150 (w), 1720 (s), 1620 (s), cm^{-1}. ^{1}H NMR ($CDCl_3$/TMS_{ext}): δ 0.24 (s, 9H), 1.30 (t, 3H, J = 6.0 Hz), 4.22 (q, 2H, J = 6.0 Hz), 6.19 (d, 1H, J = 16.0 Hz); 6.74 (d, 1H, J = 16.0 Hz).

Z-Ethyl 2-Penten-4-ynoate: **6b–Z**

bp 56°C/1.5 Torr. Anal.: Found: C, 61.04; H, 8.45; $C_{10}H_{16}O_2Si$; Calcd: C, 61.22; H, 8.16%. IR data (film): 2150 (w), 1738 (s), 1720 (s), 1612 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$/TMS_{ext}): δ 0.24 (s, 9H), 1.55 (t, 3H, J = 6.0 Hz), 4.24 (q, 2H, J = 6.0 Hz), 6.07 (d, 1H, J = 11.6 Hz), 6.13 (d, 1H, J = 11.6 Hz). MS m/e: 197 (M^+ +1), 196 (M^+), 181 (M^+ −Me), 167 (M^+ −Et), 151 (M^+ −OEt).

E i-Propyl 2-Penten-4-ynoate: **6C–E**

bp 68°C/1.5 Torr. Anal.: Found: C, 62.85; H, 8.56; $C_{11}H_{18}O_2Si$; Calcd: C, 62.85; H, 8.56%. IR data (film): 2160 (w), 1720 (s), 1620 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$/TMS_{ext}): δ 0.25 (s, 9H), 1.29 (d, 6H, J = 6.0 Hz), 5.12 (hepta, 1H, J = 6.0 Hz), 6.20 (d, 1H, J = 16.0 Hz), 6.53 (d, 1H, J = 16.0 Hz). MS m/e: 221 (M^+ +1), 210 (M^+), 151 [M^+ −(OPr − i)].

Z-i-Propyl 2-Penten-4-ynoate: **6c–Z**

bp 64°C/1.5 Torr. Anal.: Found: C, 62.77; H, 8.53; $C_{11}H_{18}O_2Si$; Calcd.: C, 62.85; H, 8.56%. IR data (film): 2150 (w), 1730 (s), 1712 (s), 1608 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$/TMS_{ext}): δ 0.24 (s, 9H), 1.29 (d, 6H, J = 6.0 Hz), 5.12 (hepta, 1H, J = 6.0 Hz), 6.04 (d, 1H, J = 11.6 Hz), 6.13 (d, 1H, J = 11.6 Hz). MS m/e: 221 (M^+ +1), 210 (M^+), 195 (M^+ −Me), 151 [M^+ −(OPr − i)].

E-n-Butyl 2-Penten-4-ynoate: **6d–E**

bp 78°C/1.5 Torr. Anal.: Found: C, 63.86; H, 8.83; $C_{12}H_{20}O_2Si$; Calcd.: C, 64.28; H, 8.92%. IR data (film): 2140 (w), 1720 (s), 1610 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$/TMS_{ext}): δ 0.22 (s, 9H), 0.95 (t, 3H, J = 6.0 Hz), 1.37–1.48 (m, 2H), 1.61–1.72 (m, 2H), 4.19 (t, 2H, J = 6.0 Hz); 6.23 (d, 1H, J = 16.0 Hz); 6.67 (d, 1H, J = 16.0 Hz). MS m/e: 224 (M^+), 167 [M^+ −(Bu − n)], 151 [M^+ −(OBu − n)].

Z-n-Butyl 2-Penten-4-ynoate: **6d–Z**

bp 76°C/1.5 Torr. Anal.: Found: C, 63.79; H, 8.82; $C_{12}H_{20}O_2Si$; Calcd.: C, 64.28; H, 8.92%. IR data (film): 2140 (w), 1730 (s), 1712 (s), 1608 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$/TMS_{ext}): δ 0.22 (s, 9H), 0.95 (t, 3H, J = 6.0 Hz), 1.37–1.48 (m, 2H), 1.61–1.72 (m, 2H), 4.19 (t, 2H, J = 6.0 Hz), 6.07 (d, 1h, J = 11.6 Hz), 6.17 (d, 1H, J = 11.6 Hz). MS m/e: 224 (M^+), 209

(M^+ −Me), 167 [M^+ −(Bu − n)], 151 [M^+ −(OBu − n)].

E-i-Butyl 2-Penten-4-ynoate: **6e–E**

bp 76°C/1.5 Torr. Anal.: Found: C, 64.79; H, 8.84; $C_{12}H_{20}O_2Si$; Calcd.: C, 64.28; H, 8.92%, IR data (film): 2140 (w), 1720 (s), 1610 (s) cm^{-1}. ^1H NMR ($CDCl_3/TMS_{ext}$): δ 0.24 (s, 9H), 0.89 (t, 3H, J = 6.0 Hz), 1.23 (d, 3H, J = 6.0 Hz), 1.64–1.68 (m, 2H), 4.89–4.98 (m, 1H), 6.26 (d, 1H, J = 16.0 Hz), 6.73 (d, 1H, J = 16.0 Hz). MS m/e: 225 (M^+ + 1), 224 (M^+), 151 [M^+ − (OBu − i)].

Z-i-Butyl 2-Penten-4-ynoate: **6e–Z**

bp 76°C/1.5 Torr. Anal.: Found: C, 63.78; H, 8.87; $C_{12}H_{20}O_2Si$; Calcd: C, 64.28; H, 8.92%. IR data (film): 2140 (w), 1730 (s), 1712 (s), 1608 (s) cm^{-1}. ^1H NMR ($CDCl_3/TMS_{ext}$): δ 0.21 (s, 9H), 0.93 (t, 3H, J = 6.0 Hz), 1.27 (t, 3H, J = 6.0 Hz), 1.64–1.68 (m, 2H), 4.89–4.98 (m, 1H), 6.14 (d, 1H, J = 11.6 Hz), 6.14 (d, 1H, J = 11.6 Hz). MS *m/e*: 225 (M^+ + 1), 224 (M^+), 151 [M^+ − (OBu − i)].

E-t-Butyl 2-Penten-4-ynoate: **6f–E**

bp 72°C/1.5 Torr. Anal.: Found: C, 63.34; H, 8.95; $C_{12}H_{20}O_2Si$; Calcd: C, 64.28; H, 8.92%. IR data (film): 2150 (w), 1718 (s), 1619 (s) cm^{-1}. ^1H NMR ($CDCl_3/TMS_{ext}$): δ 0.25 (s, 9H), 1.58 (s, 9H), 6.18 (d, 1H, J = 16.0 Hz), 6.64 (d, 1H, J = 16.0 Hz). MS *m/e*: 225 (M^+ + 1), 224 (M^+), 151 [M^+ − (OBu − t)].

Z-t-Butyl Penten-4-ynoate: **6f–Z**

bp 72°C/1.5 Torr. Anal.: Found: C, 36.99; H, 8.82; $C_{12}H_{20}O_2Si$; Calcd: C, 64.28; H, 8.92%. IR data (film): 2150 (w), 1730 (s), 1718 (s), 1610 (s) cm^{-1}. ^1H NMR ($CDCl_3/TMS_{ext}$): δ 0.24 (s, 9H), 1.49 (s, 9H), 5.97 (d, 1H, J = 11.6 Hz), 6.07 (d, 1H, J = 11.6 Hz). MS *m/e*: 225 (M^+ + 1), 224 (M^+), 151 [M^+ − (OBu − t)].

Propenyl 2-Penten-4-ynoate: **6g**

bp 68°C/1.5 Torr. Anal.: Found: C, 63.58; H, 7.37; $C_{12}H_{20}O_2Si$; Calcd: C, 63.46; H, 7.68%. IR data (film): 2140 (w), 1734 (s), 1648 (s), 1608 (s) cm^{-1}. ^1H NMR ($CDCl_3/TMS_{ext}$): δ 0.24 (E + Z) (s, 9H), 4.69 (E + Z) (d, 2H, J = 5.6 Hz), 5.25 (E + Z) (dd, 1H, J = 10.4 Hz, J = 1.5 Hz), 5.37 (E + Z) (dd, 1H, J = 17.2 Hz, J = 1.5 Hz) 5.87–6.03 (E + Z) (m, 1H), 6.10 (Z) (d, 0.94H, J = 11.6 Hz), 6.18 (Z) (d, 0.94H, J = 11.6 Hz), 6.25 (E) (d, 0.06H, J = 16.0 Hz), 6.69 (E) (d, 0.06H, J = 16.0 Hz). MS *m/e*: 208 (M^+), 193 (M^+ $-CH_3$), 167 (M^+ $-C_3H_6$), 151 (M^+ $-OC_3H_6$).

Propynyl 2-Penten-4-ynoate: **6h**

bp 62°C/1.5 Torr. Anal.: Found: C, 63.68; H, 6.97; $C_{11}H_{14}O_2Si$; Calcd: C, 64.07; H, 6.79%. IR data (film): 2140 (w), 1740 (s), 1720 (s), 1608 (s) cm^{-1}. ^1H NMR ($CDCl_3/TMS_{ext}$): δ 0.27 (E + Z) (s, 9H), 2.49 (E + Z) (t, 1H, J = 1.6 Hz), 4.78 (E + Z) (d, 2H, J = 1.6 Hz), 6.11 (Z) (d, 0.97H, J = 11.6 Hz), 6.22 (Z) (d, 0.97H, J = 11.6 Hz), 6.25 (E) (d, 0.03H, J = 16.0 Hz), 6.70 (E) (d, 0.03H, J = 16.0 Hz). MS *m/e*: 206 (M^+), 191 (M^+ $-CH_3$), 167 (M^+ $-C_3H_3$), 151 (M^+ $-OC_3H_3$).

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