

A Novel and Stereodefined Synthesis of (*E*)- β -Ethoxycarbonylvinylsilanes: Regio- and Stereo-controlled Hydroethoxycarbonylation of Silylacetylenes by Palladium(II) Catalysis

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[PdCl₂(dppf)]–SnCl₂·2H₂O catalysed hydroethoxycarbonylation of silylacetylenes **1** provided a novel and convenient synthesis of (*E*)- β -ethoxycarbonylvinylsilanes **2**. The reactions, carried out under mild conditions (90 °C, 20 kg cm⁻²) gave the products **2** in excellent yields. This procedure tolerated the presence of chloro or ethoxycarbonyl substituents separated from the carbon–carbon triple bond in silylacetylene **1**. α -Trimethylsilylmethylene- γ -butyrolactones **11**, with an alkoxy-carbonyl substituted vinylsilane moiety, were obtained in excellent yields by the reaction of tetrahydropyranyl ethers of 4-trimethylsilylbut-3-yn-1-ols **10**. A reasonable mechanism for the regio- and stereo-controlled hydroethoxycarbonylation is described.

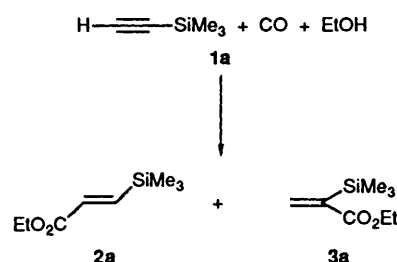
Of a wide variety of organosilicon compounds currently available for organic synthesis,¹ vinylsilanes have attracted much attention for their synthetic utility, their electrophilic substitution providing useful procedures for stereoselective syntheses.² The addition of a Grignard reagent or organolithium reagent to a vinylsilane gives an α -metallated organosilane.³ The condensation of this α -silylcarbanion with carbonyl compounds gave β -hydroxysilanes.⁴ 1,2-Elimination of β -hydroxysilanes is utilized for the stereodefined synthesis of alkenes.⁵ The coupling reaction of vinylsilanes with vinyl or aryl iodides in the presence of fluoride ion and a catalytic amount of a palladium complex provides a novel method for chemo- and stereo-selective C–C bond formation.⁶

Vinylsilanes bearing a carbonyl functionality on one of the vinylic carbons have potential as synthetic intermediates, containing as they do the vinylsilane and α,β -unsaturated carbonyl functionalities adjacent to the same double bond; much effort has been directed towards the synthesis of such compounds.⁷ However, the regio- and stereo-controlled introduction of a carbonyl functionality onto one of the vinylic carbons in such vinylsilanes is still a challenging problem.

Transition metal complex-catalysed carbonylation is useful for introducing a carbonyl function into organic compounds *via* the insertion of carbon monoxide into carbon–metal bonds.⁸ Earlier, we demonstrated the selective synthesis of α - or β -silyl esters by the highly regioselective carbonylation of vinylsilanes⁹ and we have now extended this study to silylacetylenes. Here we report a general method for the synthesis of (*E*)- β -ethoxycarbonylvinylsilanes by regio- and stereo-controlled hydroethoxycarbonylation of easily accessible silylacetylenes.¹⁰

Results and Discussion

The hydroethoxycarbonylation of trimethylsilylacetylene **1a** gave ethyl (*E*)-3-trimethylsilylprop-2-enoate **2a** and ethyl 2-trimethylsilylprop-2-enoate **3a** (Scheme 1). A series of reactions were performed in order to determine conditions for high regio- and stereo-selectivity (Table 1). The reaction proceeded at 90 °C under an initial pressure of 20 kg cm⁻² of carbon monoxide. The *trans* stereochemistry of **2a** was confirmed by the large coupling constant (18.80 Hz) observed for the vinyl proton in the ¹H NMR spectra. The stereochemistry of **2a** showed that this hydroethoxycarbonylation proceeded in a *syn* manner. The [PdCl₂(dppf)]–SnCl₂·2H₂O catalyst system was most effective for the formation of **2a** (Table 1, entry 9). Although



Scheme 1 Conditions: under CO (20 kg cm⁻²) at 90 °C for 15 h

Table 1 Pd^{II}-catalysed hydroesterification of trimethylsilylacetylene **1a**^a

Entry	Catalyst	Solvent	Yield of 2a + 3a (%) ^b	2a ^b	3a ^b
1	[PdCl ₂ (PPh ₃) ₂]	EtOH	59	86	14
2	[PdCl ₂ (PPh ₃) ₂] + 5SnCl ₂	EtOH	70	97	3
3 ^c	[PdCl ₂ (PPh ₃) ₂] + 5SnCl ₂	Benzene	80	95	5
4 ^c	[PdCl ₂ (PPh ₃) ₂] + 5SnCl ₂	MeCN	69	82	18
5 ^d	[PdCl ₂ (dppe)] + 5SnCl ₂	EtOH	0	—	—
6 ^e	[PdCl ₂ (dppb)]	EtOH	0	—	—
7	[PdCl ₂ (dppb)] + 5SnCl ₂	EtOH	5	100	0
8 ^f	[PdCl ₂ (dppf)]	EtOH	46	98	2
9	[PdCl ₂ (dppf)] + 5SnCl ₂	EtOH	85	99	1

^a A mixture of trimethylsilylacetylene **1a** (5 mmol), catalyst (0.05 mmol), SnCl₂·2H₂O (0.25 mmol), EtOH (10 cm³) was heated at 90 °C for 15 h under CO (P_{initial} = 20 kg cm⁻²). ^b Determined by GLC. ^c EtOH (25 mmol) and solvent (10 cm³) were used. ^d dppe = 1,2-bis(diphenylphosphino)ethane. ^e dppb = 1,4-bis(diphenylphosphino)butane. ^f dppf = 1,1'-bis(diphenylphosphino)ferrocene.

the addition of SnCl₂·2H₂O to the reaction mixture increased the yield of **2a** (Table 1, entries 1, 2, 8 and 9), no reaction occurred when [PdCl₂(dppe)]–SnCl₂·2H₂O or [PdCl₂(dppb)] was used (Table 1, entries 5 and 6). In general, the carbonylation of acetylene is much less selective. For example, both the dicarbonylation and monocarbonylation products are usually obtained. Both regio- and stereo-isomers are formed.¹¹ It should be noted that the reaction catalysed by [PdCl₂(dppf)]–SnCl₂·2H₂O is highly regio- and stereo-selective and, furthermore, that polymerization or oligomerization of **1a**, usually observed in the carbonylation of acetylenes, was not observed.

Table 2 Pd^{II}-catalysed stereodefined synthesis of (*E*)-β-ethoxycarbonylvinylnsilanes **2**^a

Entry	R	Substrate	Product	Yield (%) ^b
1	Bu	1b	2b	78
2	Oct	1c	2c	91
3	C-C ₆ H ₁₂	1d	2d	85
4	Ph	1e	2e	88
5	ClCH ₂ CH ₂ CH ₂	1f	2f	82
6	(EtO ₂ C) ₂ CH(CH ₂) ₃	1g	2g	90
7	EtO ₂ C	1h	2h	22
8	Me ₃ Si	1i	2i	0

^a A mixture of silylacetylene **1** (5 mmol), [PdCl₂(dppf)] (0.1 mmol), SnCl₂·2H₂O (0.5 mmol) and EtOH (10 cm³) was heated at 90 °C for 15 h under CO (P_{initial} = 20 kg cm⁻²). ^b Isolated yields.

On the basis of these observations, several silylacetylenes were subjected to [PdCl₂(dppf)]-SnCl₂·2H₂O catalysed hydroethoxycarbonylation at 90 °C under an initial pressure of 20 kg cm⁻² of carbon monoxide (Scheme 2); results are summarized in

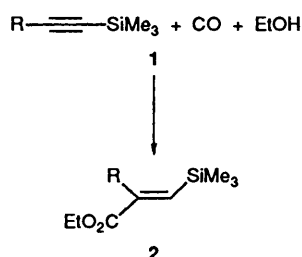
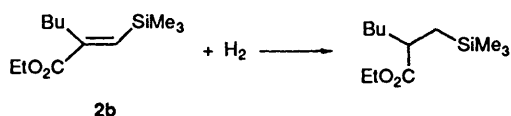
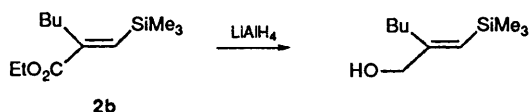
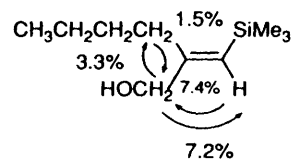
**Scheme 2** Reagents and Conditions: [PdCl₂(dppf)]-SnCl₂·2H₂O, under CO (20 kg cm⁻²) at 90 °C for 15 h

Table 2. This hydroethoxycarbonylation of a silylacetylene, to give as the sole product (*E*)-β-ethoxycarbonylvinylnsilanes **2**, has considerable synthetic scope in spite of the possible formation of both regio- and stereo-isomers. The yields of **2** were excellent, except for entries 7 and 8, Table 2. The regio- and stereochemistry of the hydroethoxycarbonylation was examined as follows. Hydrogenation of **2b** gave ethyl 2-(trimethylsilyl-methyl)hexanoate (Scheme 3) whilst its reduction (Scheme 4)

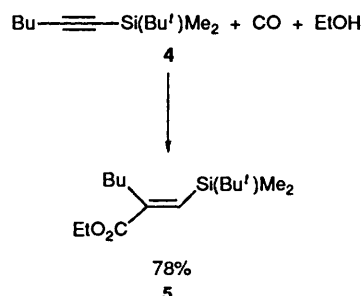
**Scheme 3** Reagents and conditions: Pd/C, MeOH under H₂ (5 kg cm⁻²) at room temperature for 72 h**Scheme 4**

provided an allyl alcohol a difference NOE experiment upon which confirmed the *E* orientation of **2b** (Fig. 1). The silylacetylenes substituted by both a primary or a secondary alkyl group and a phenyl group afforded the corresponding vinylnsilanes in excellent yields (Table 2, entries 1-4). Despite the possible [PdCl₂(dppf)]-catalysed reduction¹² of the carbon-chlorine bond the silylacetylene **1f** afforded the corresponding product in excellent yield (Table 2, entry 5). Silylacetylene bearing an ethoxycarbonyl group separated from the carbon-carbon triple bond was hydroethoxycarbonylated to give **2g** in excellent yield (Table 2, entry 6). In contrast, the silylacetylene **1h**, in which the triple bond is substituted by an ethoxycarbonyl

**Fig. 1** NOE data for the allyl alcohol

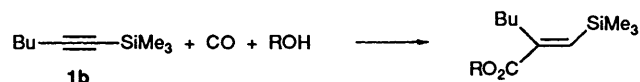
group, gave the corresponding product in low yield (Table 2, entry 7). Attempts to increase the yield of **2h** failed. The strong deactivating effect of an ethoxycarbonyl group was observed. A similar deactivating effect of a polar substituent such as an alkoxy carbonyl group or a cyano group on acetylenes in a carbonylation was reported by Heck.¹³ The presence of an ethoxycarbonyl group attached to a carbon-carbon triple bond did not alter the regiochemistry of this hydroethoxycarbonylation, *i.e.* the ethoxycarbonyl group was introduced at the β-position to the vinylic carbons in the vinylnsilane like the hydroethoxycarbonylation of **1a-g**. Steric hindrance in bis-(trimethylsilyl)acetylene **1i** prevented its hydroethoxycarbonylation even at elevated temperatures in the presence of the [PdCl₂(dppf)]-SnCl₂·2H₂O (Table 2, entry 8), starting material being recovered.

Silylacetylenes with a bulkier organosilyl substituent, **4**, are less reactive (Scheme 5) and a relatively high temperature

**Scheme 5** Reagents and conditions: [PdCl₂(dppf)]-SnCl₂·2H₂O, under CO (20 kg cm⁻²) at 120 °C for 15 h

compared with that for **1a-g** was necessary to obtain the vinylnsilane **5** in high yield.

Although alcohols other than ethanol employed for this hydroalkoxycarbonylation (Scheme 6) gave the corresponding

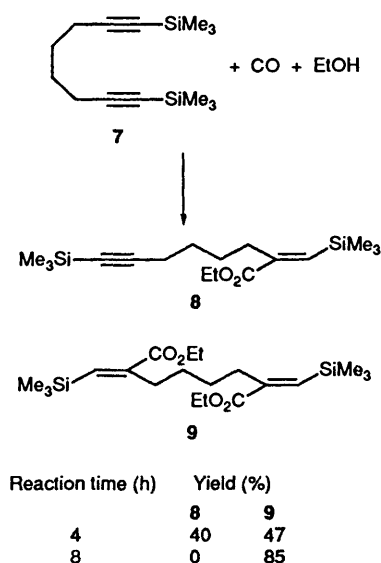


R =	Product	Yield
Et	2b	78%
Me	6a	49%
Bu	6b	56%

Scheme 6 Reagents and conditions: [PdCl₂(dppf)]-SnCl₂·2H₂O, under CO (20 kg cm⁻²) at 90 °C for 15 h

(*E*)-β-alkoxycarbonylvinylnsilanes, the highest product yield was obtained with the latter. 2,2,2-Trifluoroethanol and butan-2-ol failed to react.

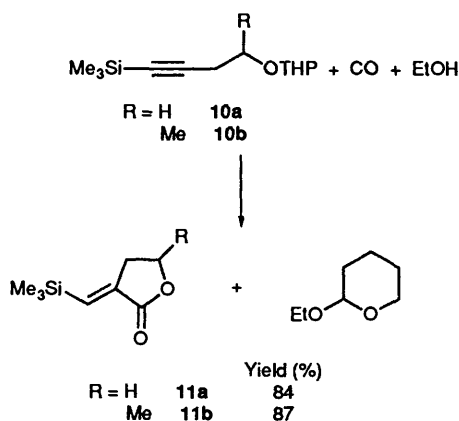
The α,ω-bis(trimethylsilyl)diyne **7** was smoothly hydroethoxycarbonylated at 90 °C under an initial pressure of 20 kg cm⁻² of carbon monoxide in the presence of [PdCl₂(dppf)]-SnCl₂·2H₂O (Scheme 7). Although it has been reported that a Pd^{II} complex catalysed the cyclization of an α,ω-diyne,¹⁴ in our work hydroethoxycarbonylation proceeded selectively, the ethoxycarbonyl group being introduced at the β-position to the vinylic carbons in the vinylnsilanes and the stereochemistry of the carbon-carbon double bond being *E*. Compound **9**, with both of triple bonds were hydroethoxycarbonylated, was obtained exclusively from the reaction after 8 h. We could not obtain **8**,



Scheme 7 Reagents and conditions: $[\text{PdCl}_2(\text{dppf})]\text{-SnCl}_2\cdot 2\text{H}_2\text{O}$ under CO (20 kg cm^{-2})

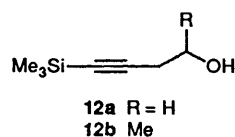
with one of the triple bonds being ethoxycarbonylated, as a single product, even when the reaction was carried out at lower temperature.

α -Trimethylsilylmethylene- γ -butyrolactones **11** were obtained in excellent yields from the hydroalkoxycarbonylation of the tetrahydropyranyl ether of 4-trimethylsilylbut-3-yn-1-ols **10** (Scheme 8). The reactions proceeded under similar conditions



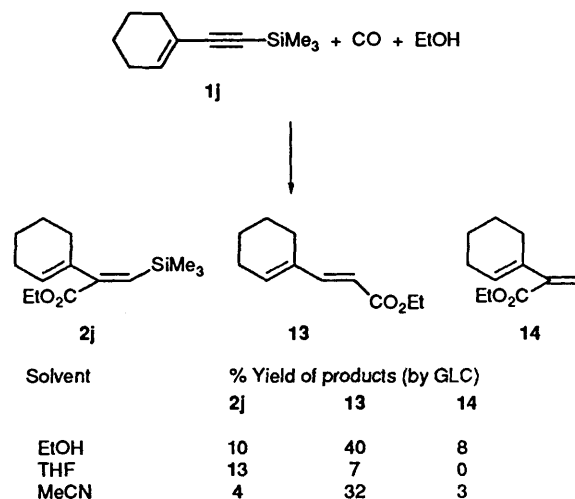
Scheme 8 Reagents and conditions: $[\text{PdCl}_2(\text{dppf})]\text{-SnCl}_2\cdot 2\text{H}_2\text{O}$, under CO (20 kg cm^{-2}) at 90°C for 15 h

to that of **1a-g**, i.e. at 90°C under an initial pressure of 20 kg cm^{-2} of carbon monoxide. The carbonyl carbon was substituted at the β -position to vinylic carbons in the vinylsilane moiety of lactone **11**. The stereochemistry of the carbon-carbon double bond in **11** was *E*. The regio- and stereo-chemistry of the hydroalkoxycarbonylation of **10** was the same as that of **1a-h**, **4** and **7**. Pd-catalysed intramolecular hydroethoxycarbonylation of but-3-yn-1-ols has been reported¹⁵ to give five-membered ring lactones, a reaction which proceeds *via* intramolecular hydroalkoxycarbonylation of the alcohol **12** generated by the deprotection of ether **10**. In fact, the alcohol **12a** was obtained quantitatively from the reaction of **10a** in the presence of a



catalytic amount of $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$ under an argon atmosphere. Similar $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$ -mediated deprotection of acetals has been reported.¹⁶ Since α -methylene- γ -butyrolactone is an important sesquiterpene building block with biological activity,¹⁷ the Si-containing analogues should be of interest both synthetically and biologically.

A conjugated trimethylsilyl enyne **1j**, less easily hydroethoxycarbonylated (Scheme 9), gave the vinylsilane **2j** and the esters



Scheme 9 Reagents and conditions: $[\text{PdCl}_2(\text{dppf})]\text{-SnCl}_2\cdot 2\text{H}_2\text{O}$ under CO (20 kg cm^{-2}) at 90°C for 15 h

13 and **14**; the latter had no trimethylsilyl substituent. No such desilylation products were obtained from the reaction of **1a-h**, **4**, **7** or **10**. Also the yield of the expected vinylsilane **2j** was quite low compared with that of **2a-g**, **5** and **9**. In order to improve the yield of the vinylsilane **2j** we investigated the reaction of a conjugated trimethylsilyl enyne **1j** in detail; results are summarized in Table 3. The $[\text{PdCl}_2(\text{PPh}_3)_2]\text{-SnCl}_2\cdot 2\text{H}_2\text{O}$ system was more effective than $[\text{PdCl}_2(\text{dppf})]\text{-SnCl}_2\cdot 2\text{H}_2\text{O}$ (Table 3, entry 3). The yield of **2j** was markedly affected by the ratio of phosphorus ligand to palladium, e.g. a P/Pd ratio of 3 gave the best yield (Table 3, entry 4); the reaction in THF also gave the best yield of **2j** (Table 3, entry 4-8).

The formation of esters **13** and **14** requires some discussion. In the $[\text{PdCl}_2(\text{dppf})]\text{-SnCl}_2\cdot 2\text{H}_2\text{O}$ catalysed hydroethoxycarbonylation of **1j** a small amount of cyclohexenylacetylene was found. Since it seemed possible that the esters **13** and **14** were produced by the hydroethoxycarbonylation of cyclohexenylacetylene formed by the desilylation of **1j**, cyclohexenylacetylene was subjected to $[\text{PdCl}_2(\text{dppf})]\text{-SnCl}_2\cdot 2\text{H}_2\text{O}$ catalysed hydroesterification under similar conditions. A 75:25 mixture of **13** and **14** was indeed obtained (72%).

The most plausible reaction mechanism for this hydroethoxycarbonylation is shown in Scheme 10 where hydro-

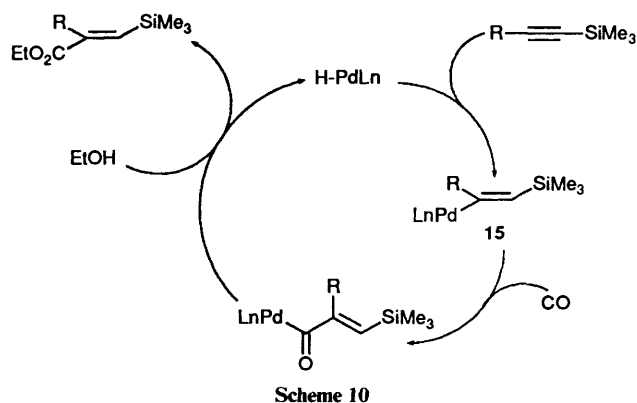


Table 3 Pd^{II} catalysed hydroesterification of cyclohexenyltrimethylsilylacetylene **1j**^a

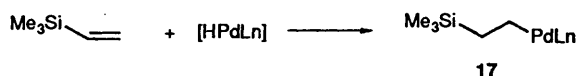
Entry	Catalyst	P/Pd	Solvent	Conv. ^b (%)	Yield of products (%) ^b		
					2j	13	14
1	[PdCl ₂ (PhCN) ₂]	0	THF	92	0	1	0
2	[PdCl ₂ (PhCN) ₂] + PPh ₃	1	THF	41	3	6	3
3	[PdCl ₂ (PPh ₃) ₂]	2	THF	88	49	17	5
4	[PdCl ₂ (PPh ₃) ₂] + PPh ₃	3	THF	97	68	7	2
5	[PdCl ₂ (PPh ₃) ₂] + PPh ₃	3	EtOH	54	28	7	3
6	[PdCl ₂ (PPh ₃) ₂] + PPh ₃	3	Dioxane	54	13	1	0
7	[PdCl ₂ (PPh ₃) ₂] + PPh ₃	3	MeCN	49	8	7	6
8	[PdCl ₂ (PPh ₃) ₂] + PPh ₃	3	Benzene	21	7	2	1
9	[PdCl ₂ (PPh ₃) ₂] + 2PPh ₃	4	THF	82	60	7	3
10	[PdCl ₂ (PPh ₃) ₂] + 3PPh ₃	5	THF	77	53	5	2
11 ^c	[PdCl ₂ (dppf)] + PPh ₃	3	THF	59	49	4	0
12	[PdCl ₂ (dppf)] + 2PPh ₃	4	THF	37	34	3	0
13	[PdCl ₂ (dppf)] + dppf	4	THF	34	32	2	0
14 ^d	[PdCl ₂ (dppe)]	2	THF	30	2	1	0
15 ^d	[PdCl ₂ (dppb)]	2	THF	10	0	0	0

^a A mixture of cyclohexenyltrimethylsilylacetylene **1j** (5 mmol), catalyst (0.1 mmol), SnCl₂·2H₂O (0.5 mmol), EtOH (25 mmol) and solvent (10 cm³) was heated at 90 °C for 15 h under CO (P_{initial} = 20 kg cm⁻²). ^b Determined by GLC. ^c dppf = 1,1-bis(diphenylphosphino)ferrocene. ^d dppe = 1,2-bis(diphenylphosphino)ethane. ^e dppb = 1,4-bis(diphenylphosphino)butane.

palladation of silylacetylene affords the alkenyl-Pd complex.¹⁸ It seems likely that steric repulsion between the trimethylsilyl substituent and the palladium ligands leads to a preference for formation of **15** rather than **16**; a similar steric effect of a

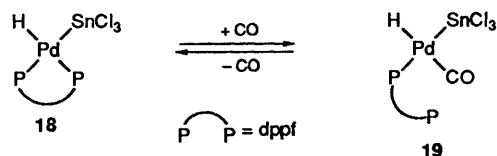


trimethylsilyl substituent has been reported earlier by us.⁹ Thus, the Pd^{II}-catalysed hydroethoxycarbonylation and hydrocarboxylation of vinylsilanes in a highly β -regioselective fashion is explicable in terms of the preferred formation of complex **17** as an initial intermediate (Scheme 11). Insertion of carbon

**Scheme 11**

monoxide into the carbon-palladium bond leads to an acylpalladium species which upon subsequent nucleophilic attack by ethanol yields the corresponding products.

As described above, the addition of SnCl₂·2H₂O as co-catalyst increased the yield and the selectivity for **2a** (Table 1, entries 1, 2, 8 and 9). The insertion of added SnCl₂ into the Pd-Cl bond formed a SnCl₃⁻ ligand on palladium.^{18b,19} SnCl₃⁻ ligand plays important roles. First, the high *trans* effect²⁰ of this ligand facilitates the coordination of carbon monoxide by dissociation of one of the phosphino groups from the metal (Scheme 12) and

**Scheme 12**

second, the SnCl₃⁻ ligand stabilizes five-coordination in complexes.²¹ Since insertion of acetylene into a Pd-H bond in **19** involves a five-coordinate intermediate, this insertion reaction would be promoted by a SnCl₃⁻ ligand. Besides these electronic effects, it also shows a steric effect. The combined steric bulk of the phosphine ligand and SnCl₃⁻ ligand on palladium is responsible

for the formation of **15**, the less hindered complex, in preference to **16**^{19,22} (Table 1, entries 1 and 2).

In conclusion, the hydroethoxycarbonylation of silylacetylenes catalysed by PdCl₂(dppf) combined with SnCl₂·2H₂O gave (*E*)- β -ethoxycarbonylvinylnsilanes in good to excellent yields. The present reaction provides a novel and straightforward method for the stereodefined preparation of vinylsilanes bearing a functional group on one of the vinylic carbons.

Experimental

B.p.s and m.p.s are uncorrected. ¹H NMR and ¹³C NMR spectra were recorded on a JEOL EX-270 instrument in CDCl₃ solutions using Me₄Si as an internal standard. *J* Values are given in Hz. IR spectra were recorded on JASCO IR 810 instrument in neat liquid films except **8**. The IR spectrum of **8** was obtained from KBr pellet. GC analyses were performed with a Shimadzu GC-14A gas chromatograph. Elemental analyses were performed at the Microanalytical Centre of Kyoto university and the analytical centre of Perkin-Elmer Japan. All reagents were dried and purified before use by the usual procedures. Carbon monoxide (>99.9%) was used as received without further purification. [PdCl₂(PhCN)₂] and [PdCl₂(PPh₃)₂] were prepared by literature methods.^{23,24} [PdCl₂(dppe)], [PdCl₂(dppb)] and [PdCl₂(dppf)] were prepared by the reaction of [PdCl₂(PhCN)₂] with the corresponding phosphine. Silylacetylenes (**1b-f**, **j**, **4**, **7**) were prepared by a literature method from the corresponding terminal acetylenes and chlorosilanes.²⁵ Silylacetylene (**1g**) was prepared by the reaction of diethyl sodiomalonate with **1f**. Silylacetylenes (**1a**, **h**, **i**) were purchased. Silylacetylene (**10a**, **10b**) were prepared from the corresponding tetrahydropyranyl ether of but-3-yn-1-ols and chlorotrimethylsilane.

General Procedure for the Hydroethoxycarbonylation of Silylacetylenes.—A mixture of EtOH (10 cm³), silylacetylene (5 mmol), Pd^{II} complex (0.05 or 0.1 mmol), and SnCl₂·2H₂O (0.25 or 0.5 mmol) was placed in a 50 cm³ stainless steel autoclave equipped with a glass liner and a magnetic stirring bar. The reactor was sealed, flushed with carbon monoxide, and then pressurized with carbon monoxide to 20 kg cm⁻². The reaction mixture was then heated and stirred at the temperatures and for the times shown in the Tables. The reaction was terminated by rapid cooling. The products were isolated by distillations under reduced pressure or column chromatography.

Ethyl (E)-3-(trimethylsilyl)prop-2-enoate 2a. B.p. 70–71 °C/10 mmHg (Found: C, 55.6; H, 9.1. Calc. for $C_8H_{16}SiO_2$: C, 55.77; H, 9.36%); δ_H (CDCl₃; 270 MHz) 0.13 [9 H, s, Si(CH₃)₃], 1.29 (3 H, t, *J* 7.25, OCH₂CH₃), 4.20 (2 H, q, *J* 7.25, OCH₂CH₃), 6.23 [1 H, d, *J* 18.80, =CH(SiMe₃)] and 7.24 [1 H, d, *J* 18.80, =CH(CO₂Et)]; δ_C (CDCl₃; 67.8 MHz) –2.0 [Si(CH₃)₃], 14.1 (OCH₂CH₃), 60.3 (OCH₂CH₃), 133.9 [=CH(SiMe₃)], 149.3 [=CH(CO₂Et)] and 165.8 (C=O); ν_{max}/cm^{-1} 1720.

Ethyl 2-(trimethylsilyl)prop-2-enoate 3a. B.p. 70–71 °C/10 mmHg δ_H (CDCl₃; 270 MHz) 0.18 [9 H, s, Si(CH₃)₃], 1.30 (3 H, t, *J* 7.26, OCH₂CH₃), 4.20 (2 H, q, *J* 7.26, OCH₂CH₃), 6.00 (1 H, d, *J* 2.97, =CH₂), 6.79 (1 H, d, *J* 2.97, =CH₂); δ_C (CDCl₃; 67.8 MHz) –1.5 [Si(CH₃)₃], 14.0 (OCH₂CH₃), 60.2 (OCH₂CH₃), 138.9 (=CH₂), 144.3 [=C(SiMe₃)CO₂Et] and 169.1 (C=O); ν_{max}/cm^{-1} 1720.

Ethyl (E)-2-butyl-3-trimethylsilylprop-2-enoate 2b. B.p. 86–87 °C/4 mmHg (Found: C, 62.9; H, 10.8. Calc. for $C_{12}H_{24}SiO_2$: C, 63.10; H, 10.59%); δ_H (CDCl₃; 270 MHz) 0.17 [9 H, s, Si(CH₃)₃], 0.92 (3 H, t, *J* 7.26, CH₃CH₂CH₂), 1.30 (3 H, t, *J* 7.26, OCH₂CH₃), 1.34–1.44 (4 H, m, CH₃CH₂CH₂), 2.38 [2 H, t, *J* 7.59, CH₂(EtO₂C)C=], 4.19 (2 H, q, *J* 7.26, OCH₂CH₃), 6.77 [1 H, s, =CH(SiMe₃)]; δ_C (CDCl₃; 67.8 MHz) –0.4 [Si(CH₃)₃], 13.9 (OCH₂CH₃), 14.2 (CH₂CH₂CH₂CH₃), 22.9 (CH₂CH₂CH₃), 31.9 (CH₂CH₂CH₃), 32.3 [CH₂(EtO₂C)C=], 60.6 (OCH₂CH₃), 140.2 [=CH(SiMe₃)], 148.2 [CH₂(EtO₂C)C=] and 167.4 (C=O, ³J_{C-O,H} 9.8); ν_{max}/cm^{-1} 1715.

Hydrogenation of 1b.—A mixture of **1b** (1 mmol), 5 wt% Pd/C(80 mg), and EtOH (5 cm³) was placed in a 50 cm³ stainless steel autoclave equipped with a glass liner and a magnetic stirring bar. The reactor was sealed, flushed with hydrogen, and then pressurized with hydrogen to 5 kg cm⁻². The mixture was stirred at room temperature for 72 h after which the catalyst was filtered off, and the solvent evaporated under reduced pressure to give the product (0.220 g, 97%).

Ethyl 2-(trimethylsilylmethyl)hexanoate. δ_H (CDCl₃; 270 MHz) –0.05 [9 H, s, Si(CH₃)₃], 0.64 (1 H, dd, *J* 14.85, 5.61, SiCH₂CHCO₂Et), 0.83 (3 H, t, *J* 7.26, CH₂CH₂CH₃), 0.90 (1 H, dd, *J* 14.85, 9.24, SiCH₂CHCO₂Et), 1.16–1.28 (4 H, m, CH₂CH₂CH₃), 1.21 (3 H, t, *J* 7.26, OCH₂CH₃), 1.30–1.44 [1 H, m, CH(CH₂CH₂CH₂CH₃)CO₂Et], 1.51–1.65 [1 H, m, CH(CH₂CH₂CH₂CH₃)CO₂Et], 2.29–2.40 [1 H, m, CH(CH₂CH₂CH₂CH₃)CO₂Et], 4.06 (2 H, qd, *J* 7.26, 1.32, OCH₂CH₃); δ_C (CDCl₃; 67.8 MHz) –1.3 [Si(CH₃)₃], 13.9 (CH₂CH₂CH₂CH₃), 14.2 (OCH₂CH₃), 20.0 (SiCH₂CHCO₂Et), 22.5 (CH₂CH₂CH₃), 29.5 (CH₂CH₂CH₃), 35.7 [CH(CO₂Et)CH₂CH₂CH₂CH₃], 41.3 (CHCO₂Et), 59.9 (OCH₂CH₃) and 177.1 (C=O); ν_{max}/cm^{-1} 1730.

Reduction of 2b by LiAlH₄.—LiAlH₄ (0.109 g) in Et₂O (1.2 cm³) was added to anhydrous AlCl₃ (78 mg) in Et₂O (6 cm³) at 0 °C under argon. After the reaction mixture had been stirred for 15 min at 0 °C, **1b** (0.194 g) in Et₂O (0.5 cm³) was added to it. The reaction mixture was then stirred for 30 min at 0 °C before being poured into cold dilute acid and extracted with Et₂O (10 cm³ × 3). The extract was dried (MgSO₄) and evaporated to yield the product (0.160 g, 100%).

(E)-2-Butyl-3-trimethylsilylprop-2-en-1-ol. δ_H (CDCl₃; 270 MHz) 0.12 [9 H, s, Si(CH₃)₃], 0.92 (3 H, t, *J* 6.93, CH₂CH₂CH₃), 1.26–1.44 (4 H, m, CH₂CH₂CH₃), 1.81 (1 H, br, OH), 2.15 [2 H, t, *J* 6.60, CH₂CH₂(HOCH₂)C=], 4.07 (2 H, d, *J* 1.32, CH₂OH) 5.49 [1 H, t, *J* 1.32, C=CH(SiMe₃)]; δ_C (CDCl₃; 67.8 MHz) 0.2 [Si(CH₃)₃], 14.0 (CH₃CH₂), 23.1 (CH₃CH₂CH₂), 31.6 (CH₃CH₂CH₂), 33.2 [CH₂(HOCH₂)C=], 67.0 (CH₂OH), 121.3 [C=CH(SiMe₃)] and 158.0 [CH₂C(CH₂OH)=]; ν_{max}/cm^{-1} 3330.

Ethyl (E)-2-octyl-3-trimethylsilylprop-2-enoate 2c. B.p. 116–117 °C/2 mmHg (Found: C, 67.6; H, 11.6. Calc. for $C_{16}H_{32}SiO_2$: C, 67.55; H, 11.34%); δ_H (CDCl₃; 270 MHz) 0.17 [9 H, s,

Si(CH₃)₃], 0.88 (3 H, t, *J* 6.60, CH₃CH₂CH₂), 1.24–1.55 (12 H, m, CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₂), 1.30 (3 H, t, *J* 7.26, OCH₂CH₃), 2.37 [2 H, t, *J* 6.93, CH₂(EtO₂C)C=], 4.19 (2 H, q, *J* 7.26, OCH₂CH₃) and 6.77 [1 H, s, =CH(SiMe₃)]; δ_H (CDCl₃; 67.8 MHz) –0.3 [Si(CH₃)₃], 14.1 (CH₂CH₂CH₂CH₃), 14.2 (OCH₂CH₃), 22.7 (CH₂), 29.2 (CH₂), 29.4 (CH₂), 29.9 (CH₂), 30.1 (CH₂), 31.8 (CH₂), 32.2 [CH₂(EtO₂C)C=], 140.2 [=CH(SiMe₃)], 148.3 [CH₂(EtO₂C)C=] and 167.4 (C=O, ³J_{C-O,H} 9.8); ν_{max}/cm^{-1} 1715.

Ethyl (E)-2-cyclohexyl-3-trimethylsilylprop-2-enoate 2d. B.p. 92–92 °C/2 mmHg (Found: C, 66.4; H, 10.6. Calc. for $C_{14}H_{26}SiO_2$: C, 66.09; H, 10.30%); δ_H (CDCl₃; 270 MHz) 0.18 [9 H, s, Si(CH₃)₃], 1.31 (3 H, t, *J* 7.26, OCH₂CH₃), 1.21–1.26 [2 H, m, -(CH₂)₅-], 1.53–1.89 [8 H, m, -(CH₂)₅-], 2.40 [1 H, tt, *J* 11.87, 3.30, (CH₂)CHC=], 4.18 (2 H, q, *J* 7.26, OCH₂CH₃) and 6.57 [1 H, s, =CH(SiMe₃)]; δ_C (CDCl₃; 67.8 MHz) –0.3 [Si(CH₃)₃], 25.8 (CH₂), 26.7 (CH₂), 31.0 (CH₂), 45.0 [CH(EtO₂C)C=], 60.2 (OCH₂CH₃), 139.3 [=CH(SiMe₃)], 153.3 [CH₂(EtO₂C)C=] and 167.4 (C=O, ³J_{C-O,H} 9.8); ν_{max}/cm^{-1} 1710.

Ethyl (E)-2-phenyl-3-trimethylsilylprop-2-enoate 2e. B.p. 122–124 °C/3 mmHg (Found: C, 67.9; H, 8.2. Calc. for $C_{14}H_{20}SiO_2$: C, 67.70; H, 8.11%); δ_H (CDCl₃; 270 MHz) –0.12 [9 H, s, Si(CH₃)₃], 1.25 (3 H, t, *J* 7.26, OCH₂CH₃), 4.20 (2 H, q, *J* 7.26, OCH₂CH₃), 7.17–7.23 and 7.29–7.34 [6 H, m, phenyl and =CH(SiMe₃)]; δ_C (CDCl₃; 67.8 MHz) –0.8 [Si(CH₃)₃], 14.2 (OCH₂CH₃), 61.1 (OCH₂CH₃), 127.58 (phenyl), 127.62 (phenyl), 129.3 (phenyl), 138.3 (phenyl), 144.9 [=CH(SiMe₃)], 147.9 [Ph(EtO₂C)C=] and 166.8 (C=O, ³J_{C-O,H} 9.8); ν_{max}/cm^{-1} 1720.

Ethyl (E)-2-(3-chloropropyl)-3-trimethylsilylprop-2-enoate 2f. B.p. 91–92 °C/2 mmHg (Found: C, 53.3; H, 8.8; Cl, 14.5. Calc. for $C_{11}H_{21}ClSiO_2$: C, 53.10; H, 8.51; Cl, 14.25%); δ_H (CDCl₃; 270 MHz) 0.20 [9 H, s, Si(CH₃)₃], 1.31 (3 H, t, *J* 7.26, OCH₂CH₃), 1.87–1.98 (2 H, m, ClCH₂CH₂), 2.54 [2 H, m, CH₂(EtO₂C)C=], 3.57 (2 H, t, *J* 6.59, ClCH₂), 4.20 (2 H, q, *J* 7.26, OCH₂CH₃), 6.89 [1 H, s, =CH(SiMe₃)]; δ_C (CDCl₃; 67.8 MHz) –0.4 [Si(CH₃)₃], 14.2 (OCH₂CH₃), 29.7 (CH₂CH₂CH₂), 32.7 [CH₂(EtO₂C)C=], 44.9 (ClCH₂), 60.8 (OCH₂CH₃), 142.2 [=CH(SiMe₃)], 146.1 [CH₂(EtO₂C)C=] and 166.9 (C=O, ³J_{C-O,H} 9.7); ν_{max}/cm^{-1} 1710.

Ethyl (E)-2-[4,4-(diethoxycarbonyl)butyl]-3-trimethylsilylprop-2-enoate 2g. B.p. 160–163 °C/2 mmHg (Found: C, 57.8; H, 8.9. Calc. for $C_{18}H_{32}SiO_6$: C, 58.03; H, 8.66%); δ_H (CDCl₃; 270 MHz) 0.18 [9 H, s, Si(CH₃)₃], 1.26 (6 H, t, *J* 7.26, OCH₂CH₃), 1.30 (3 H, t, *J* 7.26, OCH₂CH₃), 1.41–1.53 (2 H, m, CH₂CH₂CH₂), 1.93 [2 H, q, *J* 7.59, (EtO₂C)₂CHCH₂], 2.41 [2 H, t, *J* 7.59, CH₂(EtO₂C)C=], 3.32 [1 H, t, *J* 7.59, (EtO₂C)₂CHCH₂], 4.19 (6 H, q, *J* 7.26, OCH₂CH₃), 6.83 [1 H, s, =CH(SiMe₃)]; δ_C (CDCl₃; 67.8 MHz) –0.4 [Si(CH₃)₃], 14.0 (OCH₂CH₃), 14.2 (OCH₂CH₃), 27.7 (CH₂CH₂CH₂), 28.8 (CH₂CH₂CH₂), 31.7 [CH₂(EtO₂C)C=], 51.9 [(EtO₂C)₂C], 60.7, (OCH₂CH₃), 61.2 (OCH₂CH₃), 141.4 [=CH(SiMe₃)], 147.2 [CH₂(EtO₂C)C=], 167.0 (C=O, ³J_{C-O,H} 11.0) and 169.3 (C=O); ν_{max}/cm^{-1} 1750, 1735 and 1710.

Ethyl 2-ethoxycarbonyl-3-trimethylsilylprop-2-enoate 2h. After the reaction had been terminated, the solvent was evaporated under reduced pressure. The residue was chromatographed (silica gel; hexane–EtOAc, 15:1) to give a colourless oil (0.268 g) (Found: C, 54.2; H, 8.45. Calc. for $C_{11}H_{20}SiO_4$: C, 54.07; H, 8.25%); δ_H (CDCl₃; 270 MHz) 0.18 [9 H, s, Si(CH₃)₃], 1.31 (3 H, t, *J* 7.26, OCH₂CH₃), 1.34 (3 H, t, *J* 7.26, OCH₂CH₃), 4.25 (2 H, q, *J* 7.26, OCH₂CH₃), 4.28 (2 H, q, *J* 7.26, OCH₂CH₃), 7.20 [1 H, s, =CH(SiMe₃)]; δ_C (CDCl₃; 67.8 MHz) –1.4 [Si(CH₃)₃], 13.98 (OCH₂CH₃), 14.02 (OCH₂CH₃), 61.26 (OCH₂CH₃), 61.44 (OCH₂CH₃), 140.6 [(EtO₂C)₂C=], 149.8 [=CH(SiMe₃)], 163.9 (C=O, ³J_{C-O,H} 11.0) and 166.3 (C=O, ³J_{C-O,H} 13.4); ν_{max}/cm^{-1} 1750.

Ethyl (E)-2-cyclohex-1-enyl-3-trimethylsilylprop-2-enoate 2j. B.p. 94 °C/2 mmHg (Found: C, 66.6; H, 9.85. Calc. for $C_{14}H_{24}SiO_2$: C, 66.61; H, 9.58%; δ_H (CDCl₃; 270 MHz) 0.12 [9 H, s, Si(CH₃)₃], 1.29 (3 H, t, *J* 7.26, OCH₂CH₃), 1.61–1.69 (4 H, m, CH₂), 2.07–2.13 (4 H, m, CH₂), 4.18 (2 H, q, *J* 7.26, OCH₂CH₃), 5.54–5.57 (1 H, m, CH₂CH=) and 6.80 [1 H, s, =CH(SiMe₃)]; δ_C (CDCl₃; 67.8 MHz) –0.2 [Si(CH₃)₃], 14.2 (OCH₂CH₃), 21.7 (CH₂), 22.4 (CH₂), 25.1 (CH₂), 28.6 (CH₂), 60.7 (OCH₂CH₃), 127.1 (vinyl), 137.1 (vinyl), 141.8 [=CH(SiMe₃)], 150.8 [(EtO₂C)C=] and 166.9 (C=O, $^3J_{C-O,H}$ 8.6); ν_{max}/cm^{-1} 1710.

Ethyl (E)-2-butyl-3-(tert-butyl dimethylsilyl)prop-2-enoate 5. B.p. 104–105 °C/1 mmHg (Found: C, 66.6; H, 11.3. Calc. for $C_{15}H_{30}SiO_2$: C, 66.61; H, 11.18%; δ_H (CDCl₃; 270 MHz) 0.14 [6 H, s, Si(CH₃)₂(Bu^t)], 0.92 [12 H, s, C(CH₃)₃ and CH₃CH₂CH₂], 1.30 (3 H, t, *J* 7.26, OCH₂CH₃), 1.36–1.41 (4 H, m, CH₃CH₂CH₂), 2.38 [2 H, t, *J* 7.26, CH₂(EtO₂C)C=], 4.20 (2 H, q, *J* 7.26, OCH₂CH₃), 6.80 [1 H, s, =CH(SiMe₃)]; δ_C (CDCl₃; 67.8 MHz) –4.6 [Si(CH₃)₂(Bu^t)], 13.9 (CH₃CH₂CH₂), 14.2 (OCH₂CH₃), 16.9 [C(CH₃)₃], 23.0 (CH₃CH₂CH₂), 26.4 [C(CH₃)₃], 32.1 (CH₃CH₂CH₂), 32.3 [CH₂(EtO₂C)C=], 60.6 (OCH₂CH₃), 137.6 [=CH(SiMe₃)], 149.1 [CH₂(EtO₂C)C=] and 167.45 (C=O, $^3J_{C-O,H}$ 9.8); ν_{max}/cm^{-1} 1710.

Methyl (E)-2-butyl-3-trimethylsilylprop-2-enoate 6a. B.p. 67–70 °C/8 mmHg; δ_H (CDCl₃; 270 MHz) 0.17 [9 H, s, Si(CH₃)₃], 0.92 (3 H, t, *J* 7.26, CH₃CH₂CH₂), 1.28–1.46 (4 H, m, CH₃CH₂CH₂), 2.38 [2 H, t, *J* 7.59, CH₂(MeO₂C)C=], 3.74 (3 H, s, OCH₃) and 6.79 [1 H, s, =CH(SiMe₃)]; δ_C (CDCl₃; 67.8 MHz) –0.4 [Si(CH₃)₃], 13.9 (CH₂CH₂CH₂CH₃), 22.9 (CH₂CH₂CH₃), 31.9 (CH₂CH₂CH₃), 32.3 [CH₂(EtO₂C)C=], 51.8 (OCH₃), 140.7 [=CH(SiMe₃)], 147.9 [CH₂(EtO₂C)C=] and 167.9 (C=O); ν_{max}/cm^{-1} 1720.

Butyl (E)-2-butyl-3-trimethylsilylprop-2-enoate 6b. B.p. 89–92 °C/2 mmHg (Found: C, 65.6; H, 10.9. Calc. for $C_{14}H_{28}SiO_2$: C, 65.57; H, 11.00%; δ_H (CDCl₃; 270 MHz) 0.18 [9 H, s, Si(CH₃)₃], 0.92 (3 H, t, *J* 7.26, CH₃), 0.95 (3 H, t, *J* 7.26, CH₃), 1.32–1.49 (6 H, m, CH₂), 1.67 (2 H, quintet, *J* 6.60, OCH₂CH₂CH₂CH₃), 2.38 [2 H, t, *J* 8.57, CH₂(BuO₂C)C=], 4.14 (2 H, t, *J* 6.60, OCH₂CH₂CH₂CH₃) and 6.78 [1 H, s, =CH(SiMe₃)]; δ_C (CDCl₃; 67.8 MHz) –0.4 [Si(CH₃)₃], 13.7 (CH₃), 13.9 (CH₃), 19.2 (CH₂CH₂CH₃), 22.9 (CH₂CH₂CH₃), 30.7 (CH₂CH₂CH₃), 31.9 (CH₂CH₂CH₃), 32.3 [CH₂(EtO₂C)C=], 64.5 (OCH₂CH₃), 140.2 [=CH(SiMe₃)], 148.2 [CH₂(EtO₂C)C=] and 167.5 (C=O); ν_{max}/cm^{-1} 1710.

Ethyl (E)-2-(6-trimethylsilylhex-5-ynyl)-3-trimethylsilylprop-2-enoate 8. The hydroethoxycarbonylation of **6** (0.688 g, 2.75 mmol) was carried out according to the general procedure at 90 °C for 4 h. After termination of the reaction, the solvent was evaporated under reduced pressure. The residue was chromatographed (silica gel; hexane EtOAc, 100/1) to give **7** as a colourless oil (0.267 g) (Found: C, 62.5; H, 10.2. Calc. for $C_{17}H_{32}Si_2O_2$: C, 62.90; H, 9.94%; δ_H (CDCl₃; 270 MHz) 0.13 [9 H, s, Si(CH₃)₃], 0.18 [9 H, s, Si(CH₃)₃], 1.30 (3 H, t, *J* 7.25, OCH₂CH₃), 1.51–1.56 (4 H, m, CH₂CH₂CH₂CH₂), 2.24 (2 H, t, *J* 6.60, CCH₂), 2.39 [2 H, t, *J* 7.59, CH₂(EtO₂C)C=], 4.19 (2 H, q, *J* 7.25, OCH₂CH₃) and 6.81 [1 H, s, =CH(SiMe₃)]; δ_C (CDCl₃; 67.8 MHz) –0.3 [Si(CH₃)₃], 0.1 [Si(CH₃)₃], 14.2 (OCH₂CH₃), 19.7 (CCH₂), 28.95 (CH₂CH₂CH₂), 29.35 (CH₂CH₂CH₂), 31.7 [CH₂(EtO₂C)C=], 60.7 (OCH₂CH₃), 84.4 (alkyne), 107.2 (alkyne) 140.8 [=CH(SiMe₃)], 147.6 [CH₂(EtO₂C)C=] and 167.3 (C=O); ν_{max}/cm^{-1} 1710.

Diethyl (1E,7E)-1,8-bis(trimethylsilyl)octa-1,7-diene-2,7-dicarboxylate 9. M.p. 46–48 °C (Found: C, 60.0; H, 9.8. Calc. for $C_{20}H_{38}Si_2O_4$: C, 60.25; H, 9.61%; δ_H (CDCl₃; 270 MHz) 0.17 [18 H, s, Si(CH₃)₃], 1.30 (6 H, t, *J* 7.26, OCH₂CH₃), 1.48–1.51 (4 H, m, CH₂), 2.39 [4 H, m, CH₂(EtO₂C)C=], 4.19 (4 H, q, *J* 7.26, OCH₂CH₃) and 6.80 [2 H, s, =CH(SiMe₃)]; δ_C (CDCl₃; 67.8 MHz) –0.4 [Si(CH₃)₃], 14.2 (OCH₂CH₃), 30.3 (CH₂),

32.0 [CH₂(EtO₂C)C=], 60.6 (OCH₂CH₃), 140.6 [=CH(SiMe₃)], 147.8 [CH₂(EtO₂C)C=] and 167.2 (C=O, $^3J_{C-O,H}$ 9.8); ν_{max}/cm^{-1} 1700.

(E)-2-Trimethylsilylmethylene- γ -butyrolactone 11a. B.p. 111 °C/3 mmHg (Found: C, 56.4; H, 8.15. Calc. for $C_8H_{14}SiO_2$: C, 56.43; H, 8.29%; δ_H (CDCl₃; 270 MHz) 0.20 [9 H, s, Si(CH₃)₃], 2.97 (2 H, td, *J* 7.26, 2.97, CH₂C=), 4.38 (2 H, t, *J* 7.26, OCH₂) and 6.94 [1 H, t, *J* 2.97, =CH(SiMe₃)]; δ_C (CDCl₃; 67.8 MHz) –1.4 [Si(CH₃)₃], 27.2 (=CCH₂), 65.0 (OCH₂), 138.85 [CH₂C=], 138.94 [=CH(SiMe₃)] and 170.5 (C=O, $^3J_{C-O,H}$ 9.8); ν_{max}/cm^{-1} 1760.

(E)-2-Trimethylsilylmethylene-4-methyl- γ -butyrolactone 11b. B.p. 104–107 °C/4 mmHg (Found: C, 58.7; H, 8.5. Calc. for $C_9H_{16}SiO_2$: C, 58.65; H, 8.75%; δ_H (CDCl₃; 270 MHz) 0.19 [9 H, s, Si(CH₃)₃], 1.42 (3 H, d, *J* 6.27, CHCH₃), 2.50 (1 H, ddd, *J* 17.15, 5.94, 2.97, =CCH₂), 3.10 (1 H, ddd, *J* 17.15, 7.59, 2.64, =CCH₂), 4.59–4.71 [1 H, m, C(CH₃)HO] and 6.88–6.91 [1 H, m, =CH(SiMe₃)]; δ_C (CDCl₃; 67.8 MHz) –1.6 [Si(CH₃)₃], 21.9 (CHCH₃), 35.0 (=CCH₂), 73.4 (OCHCH₃), 139.0 [=CH(SiMe₃)], 140.2 (CH₂C=) and 169.9 (C=O, $^3J_{C-O,H}$ 9.8); ν_{max}/cm^{-1} 1750.

The Deprotection of Compound 10a.—A mixture of EtOH (10 cm³), **9a** (5 mmol), and SnCl₂·2H₂O (0.5 mmol) was placed in a 50 cm³ stainless steel autoclave equipped with a glass liner and a magnetic stirring bar. The reactor was sealed, flushed with argon and the stirred mixture heated at 90 °C for 15 h. The reaction was terminated by rapid cooling. The solvent was evaporated under reduced pressure and the residue was chromatographed (silica gel; hexane–EtOAc, 2:1) to give a colourless oil (0.498 g).

4-Trimethylsilylbut-3-yn-1-ol 12a. δ_H (CDCl₃; 270 MHz) 0.16 [9 H, s, Si(CH₃)₃], 2.14 (1 H, s, OH), 2.50 (2 H, t, *J* 6.60, OCH₂CH₂) and 3.71 (2 H, t, *J* 6.60, OCH₂CH₂); δ_C (CDCl₃; 67.8 MHz) 0.0 [Si(CH₃)₃], 24.2 (OCH₂CH₂), 60.8 (OCH₂CH₂), 86.8 (alkyne) and 103.4 (alkyne); ν_{max}/cm^{-1} 3350, 2180.

Hydroethoxycarbonylation of Cyclohexenylacetylene.—A mixture of EtOH (10 cm³), cyclohexenylacetylene (0.562 g, 5.3 mmol), [PdCl₂(dppf)] (77 mg, 0.11 mmol), and SnCl₂·2H₂O (120 mg, 0.53 mmol) was placed in a 50 cm³ stainless steel autoclave equipped with a glass liner and a magnetic stirring bar. The reactor was sealed, flushed with carbon monoxide, and then pressurized with carbon monoxide to 20 kg cm⁻². The stirred mixture was heated at 90 °C for 15 h after which the solvent was evaporated under reduced pressure. Chromatography (silica gel) of the residue gave three fractions: an early fraction (hexane–EtOAc, 300:1) gave 0.031 g of ethyl 2-cyclohex-1-enylprop-2-enoate (0.031 g); a middle one (hexane–EtOAc, 100:1) gave a mixture of ethyl 3-cyclohex-1-enylprop-2-enoate and ethyl 2-cyclohex-1-enylprop-2-enoate (0.235 g); and a later one (hexane–EtOAc, 100:1) gave 0.425 g of ethyl 3-cyclohex-1-enylprop-2-enoate.

Ethyl (E)-3-cyclohex-1-enylprop-2-enoate 13. (Found: C, 73.0; H, 9.1. Calc. for $C_{11}H_{16}O_2$: C, 73.3; H, 8.95%; δ_H (CDCl₃; 270 MHz) 1.30 (6 H, t, *J* 7.25, OCH₂CH₃), 1.57–1.74 (4 H, m, CH₂), 2.12–2.28 (4 H, m, CH₂), 4.20 (2 H, q, *J* 7.26, OCH₂CH₃), 5.76 (1 H, dd, *J* 15.84, 0.66, CH=CHCO₂Et), 6.16 (1 H, m, CH₂CH=) and 7.28 (d, 1 H, *J* 15.84, CH=CHCO₂Et); δ_C (CDCl₃; 67.8 MHz) 14.3 (OCH₂CH₃), 22.00 (CH₂), 22.03 (CH₂), 24.0 (CH₂), 26.4 (CH₂), 60.0 (OCH₂CH₃), 114.5 (vinyl), 134.8 (vinyl), 138.6 (vinyl), 148.0 (vinyl) and 166.8 (C=O); ν_{max}/cm^{-1} 1710.

Ethyl 2-cyclohex-1-enylprop-2-enoate 14. δ_H (CDCl₃; 270 MHz) 1.32 (3 H, t, *J* 7.25, OCH₂CH₃), 1.55–1.74 (4 H, m, CH₂), 2.08–2.18 (4 H, m, CH₂), 4.24 (2 H, q, *J* 7.26, OCH₂CH₃), 5.46 (1 H, d, *J* 0.66, =CH₂), 5.69 (1 H, s, =CH₂) and 5.98–6.01 (1 H, m, CH₂CH=C); δ_C (CDCl₃; 67.8 MHz) 14.2 (OCH₂CH₃), 21.8 (CH₂), 22.5 (CH₂), 25.6 (CH₂), 26.3 (CH₂), 60.7 (OCH₂CH₃),

118.7 (vinyl), 128.7 (vinyl), 133.3 (vinyl), 143.8 (vinyl) and 168.1 (C=O); $\nu_{\max}/\text{cm}^{-1}$ 1710.

Acknowledgements

We are grateful for financial supports from a Grant-in-aid for Science Research (03750621) from the Ministry of Education, Science and Culture of Japan and grants in support of the promotion of research at Yokohama City University.

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Paper 3/00183K

Received 11th January 1993

Accepted 28th January 1993