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4-Propargyl-2-azetidinone as a Versatile Synthon for the Synthesis of β-Lactam Antibiotics: Hydrostannation and Its Reactivities[1)]

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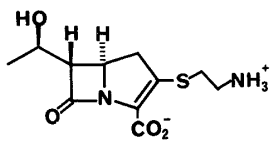
An efficient preparation of 4-propargyl-2-azetidinone (**6**) from 4-phenylsulfonyl-2-azetidinone is described. This compound was converted to the ketones **14** and **16**, which are the key intermediates for the synthesis of carbapenem and carbacephem antibiotics. In this transformation it was found that polar functional groups (β-lactam, OH, *etc.*) control the regiochemistry of hydrostannation of the internal alkyne. The reaction of epoxystannanes with formic acid to give the ketones is also described.

Keywords——β-lactam antibiotic; carbapenem; carbacephem; 4-propargyl-2-azetidinone; hydrostannation; alkenylstannane; epoxystannane; formic acid; neighboring group participation; hydroxy protecting group

Since the discovery of thienamycin (**1**), the carbapenem (**2**) and carbacephem (**3**) skeletons have been key targets for chemists interested in synthetic studies of β-lactam antibiotics.[3)] Many attempts at the synthesis of these skeletons have been reported, of which two methodologies are efficient and have wide applicabilities.

One is the intramolecular carbene insertion reaction into the N–H bond by the decomposition of the diazo β-keto esters (**4a**, **4b**), developed by a Merck group[4)] and the other is the intramolecular Wittig reaction of the keto phosphorane (**5a**, **5b**), first demonstrated by Woodward's group.[5)] For the synthesis of carba-type β-lactam antibiotics using these methods, a suitably oxygenated side chain is required at C-4 on a β-lactam ring. 4-Propargyl-2-azetidinone (**6**) is expected to be a useful "building block" for the synthesis of carba-type



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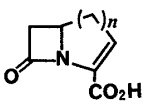
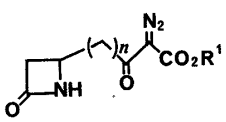
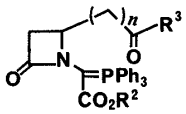


2: $n=1$
3: $n=2$



4a: $n=1$ R^1, R^2 = alkyl
4b: $n=2$ R^3 = alkyl, –S-alkyl



5a: $n=1$
5b: $n=2$

Fig. 1

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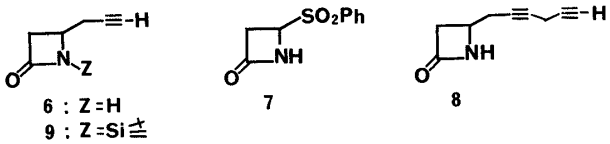

6 : Z=H
9 : Z=Si≡ 7 8

Fig. 2

bicyclic β-lactam antibiotics, because the propargyl group could be further alkylated *via* metal acetylide and transformed to carbonyl compounds.

Therefore, first of all, the preparation of **6** was examined. Then the transformation of **6** to the ketone (**14**) was carried out, to demonstrate the utility of **6**, by employing new methodology for the conversion of internal alkynes to unsymmetrical ketones. This is the full description of that work.[6]

Results and Discussion

Preparation of 4-Propargyl-2-azetidinone (6)

For the preparation of **6**, we attempted the reaction of 4-acetoxy-2-azetidinone with carbanionic reagents such as $LiC\equiv CCH_2Li$, $LiCH_2C\equiv CSi(CH_3)_3$, or $CuCH_2C\equiv CSi(CH_3)_3$. Since no desired product was obtained, the reaction of 4-phenylsulfonyl-2-azetidinone (**7**)[7] with propargylmagnesium bromide was examined.[8] Although the reaction of **7** with propargylmagnesium bromide prepared in tetrahydrofuran (THF) gave the desired product (**6**), the yield was low (41%) and the structure of a by-product proved to be 4-(2,5-hexadiynyl)-2-azetidinone (**8**) (24%). Since the coupling reaction between propargyl bromide and propargylmagnesium bromide in refluxing THF was anticipated (Chart 1),[9] the Grignard reagent prepared in refluxing ether was employed for the reaction with **7**. Because of the low solubility of **7** in ether, THF was added to a cooled (−25 °C) solution of the Grignard reagent. To this, a THF solution of **7** was added at −25 °C (see Experimental). In this reaction, **6** was obtained in 87.4% yield as a sole product. After careful investigation, it was found that at least 2 eq (practically 3 to 5 eq) of the Grignard reagent are necessary to obtain **6** in high yield.[10] This observation suggests that 1 eq of the reagent must be consumed for the abstraction of the amide proton of the β-lactam ring, as pointed out by Hiraoka *et al.*[8]

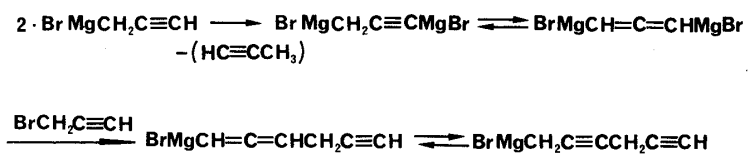

Chart 1

Hydrostannation of Internal Alkynes

Although there are many reports on the hydration of alkynes,[11] the application of the conventional conditions to **10a**, which was prepared by the silylation and subsequent methylation of **6**, resulted in serious decomposition of the β-lactam ring. Therefore we had to develop a new method for the conversion of **10b** into the ketone (**14**).

Recently, it has been reported that the hydrometallation of acetylenes is a useful method for the preparation of vinyl metal compounds. Tri-*n*-butyltin hydride (TBTH) also reacts with acetylenes to give the corresponding alkenylstannanes, which are used as a vinyl halide equivalent and serve as a vinyl lithium.[12] However, the regiochemistry in the hydrostannation of functionalized internal alkynes has not been systematically investigated except in the case where they have strongly electron-withdrawing substituents.[13] Considering the electro-

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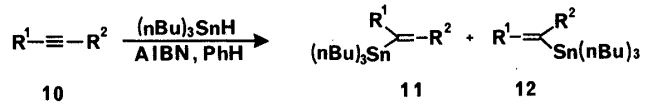
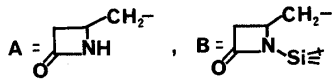
philicity of organostannanes due to the high polarizability of the Sn–C bond together with the availability of *d* orbitals,[13] it is expected that the regiochemistry of the hydrostannation would be controlled by polar (electron-donating) substituents, such as a β-lactam ring, in the vicinity of the triple bond.[14]

The *N*-protected butynyl-2-azetidinone (**10b**) was heated with 2 eq of TBTH in the presence of azobisisobutyronitrile (AIBN) under an argon atmosphere at 92 °C for 1 h to give a mixture of the alkenylstannanes. The alkenylstannanes in which a trialkylstannyl group is placed at the terminal vinyl carbon are generally unstable, whereas the resultant mixture of **11b** and **12b** showed considerable stability and could be separated by the usual chromatographic technique without any decomposition (Table I). As was expected, the major product was found to be **11b** and the minor one to be its regioisomer (**12b**) in a ratio of *ca.* 2 : 1.[15] In the case of **10a**, prepared by the desilylation of **10b**, **11a** was obtained as the major product. These observations cannot be explained in terms of steric hindrance around the triple bond. Therefore, the coordination of the β-lactam ring to the tin atom should control the regioselectivity of these hydrostannation reactions; the unexpected steric requirement can be rationalized in terms of the length of the C–Sn bond (*ca.* 2.2 Å). In contrast with **10a** and **10b**, the hydrostannation of **10c** gave **12c** regioselectively due to the strong coordinating effect of the hydroxy group. The methoxyethoxymethyl (MEM) ether in **10d** also resulted in high selectivity.[16] In the reaction of simpler substrates (**10e**—**g**), the same regioselectivity governed by the oxygen functionalities was observed.[17]



a: R^1 = A, R^2 = CH_3
b: R^1 = B, R^2 = CH_3
c: R^1 = B, R^2 = $CH(OH)CH_3$
d: R^1 = B, R^2 = $CH(OMEM)CH_3$
e: R^1 = $Ph(CH_2)_3$, R^2 = $CH(OH)CH_3$
f: R^1 = $Ph(CH_2)_3$, R^2 = $CH(OCOCH_3)CH_3$
g: R^1 = $Ph(CH_2)_3$, R^2 = $CH(OCH_2Ph)CH_3$



MEM = $CH_2O(CH_2)_2OCH_3$ nBu = *n*-butyl

Chart 2

TABLE I. Regioselective Hydrostannation of Internal Alkynes

Substrate	$(n\text{Bu})_3\text{SnH}$ (eq)	Temp. (°C)	Time (h)	Yield (%)[a]	Ratio (12/11)
10a	1.5	100	0.5	82	0.63
10b	2.0	92	1.0	94	0.33
10c	1.5	103	0.3	91	5.0
10d	10.0	101	2.0	86	4.0
10e	1.5	94	1.0	78	**12** (Exclusively)
10f	1.5	100	1.0	71	7.9
10g	1.4	92	1.5	64	11.8

a) Isolated yield.

Conversion of Alkenylstannanes to Ketones

Firstly, the oxidation of alkenylstannanes with $CrO_3 \cdot 2$ pyridine[18] was attempted, but the alkenylstannanes were fairly stable to oxidation, in contrast with the alkylstannanes.

Since alkenylsilanes can easily be converted to ketones *via* epoxy-silanes,[19] it was expected that alkenylstannanes could be converted to ketones *via* epoxy-stannanes (**13**). The

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alkenylstannanes were reacted with *m*-chloroperbenzoic acid (*m*CPBA) to give a stereomixture of the epoxy-stannanes, which was directly treated with *ca.* 90% formic acid in methylene chloride at room temperature (Chart 3). As shown in Table II, the alkenylstannane (**11b**), which has no oxygen-substituent at the allylic position, gave two products; the more polar product was found to be the desired ketone (**14**), and less polar product was the enol formate (**15**). Since the isolated formate was easily hydrolyzed by treatment with lithium hydroxide in aqueous THF in 89% yield, the ketone (**14**), a key intermediate for the synthesis of carbapenem compounds, was obtained in 63% overall yield from **11b**. On the other hand, the hydroxy-alkenylstannane (**12e**) gave more complex results; the two hydroxy-ketones (**18** and **19**) and also the enones (**20** and **21**) were isolated. Because the participation of the hydroxy group in the ring opening of the epoxy-stannane (*vide infra*) was anticipated, the reaction of the benzyloxy-alkenylstannane (**12g**) was examined. The major product was again the enone (**20**) and the yield of the desired product (**24**) was very low. The acetoxy-alkenylstannane (**12f**) gave the two acetoxyketones (62%) which showed adjacent spots on a silica gel plate. After separation by preparative thin layer chromatography (TLC), it was found that the less polar product was the rearranged acetoxy-ketone (**23**), and the more polar product was the nonrearranged one (**22**). The ratio of **22** and **23** was determined by integration of the methyl proton signals [δ 1.38 ppm (doublet) and 1.06 ppm (triplet) for **22** and **23**] in the proton nuclear magnetic resonance (^{1}H-NMR) spectrum. Since the conversion of **12f** to the acetoxy-ketones could be carried out efficiently, the transformation of **12h** was examined. Similarly, **12h** could be converted to the two acetoxy-ketones (**16** and **17**)[20] in modest yield.

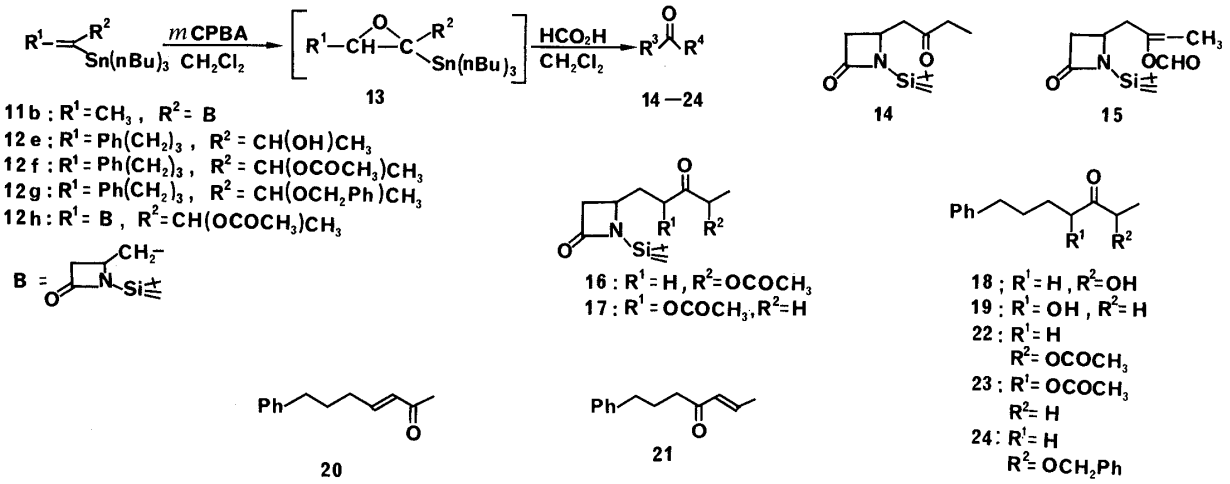

Chart 3

TABLE II. Conversion of Alkenylstannanes to Ketones

Substrate	Product(s), (Yield)[a]	
11b	**14** (31),	**15** (39)
12e	**18** (18),	**19** (21),
	20 (21),	**21** (1)
12f	**22** (32),[b]	**23** (29)[b]
12g	**24** (9),	**20** (36)
12h	**16** (37),	**17** (50)

a) Isolated yield. *b*) Determined by ^{1}H-NMR spectroscopy.

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Mechanism

The reaction courses of the epoxy-stannanes can be conveniently classified in terms of the substituent at the allylic position as shown in Chart 4.

Type I in the Case of 11b——The mechanism for the reaction of epoxy-silane with formic acid is generally explained as follows[13,19]; the protonated epoxy ring opens to afford the β-silyl cation (I) (Chart 5), which is stabilized by the electron-donating effect of silicon-containing groups, and subsequent elimination gives the corresponding ketone. A similar mechanism seems to be applicable to the formation of ketones from alkenylstannanes. However, in this case no rational explanation for the formation of the enol formate is apparent; the conversion from the corresponding ketone under these conditions is highly unlikely. Although formic acid is a weak nucleophile, Magnus and Roy reported the formation of the enol formate in the reaction of an epoxy-silane with anhydrous formic acid.[21] Hence, in the case of the alkenylstannanes as well, the enol formate may be formed by the nucleophilic attack of formic acid, followed by acid-catalyzed dehydroxystannation and partial acid hydrolysis of the enol formate gives the ketone.

Type II in the Case of 12e——Under acidic conditions, the hydroxy-epoxy-stannane (A) would be in equilibrium with B owing to the participation of the neighboring hydroxy group. The nucleophilic attack of formic acid on both A and B would give the hydroxy-ketones (C and D) *via* the enol formates. However the competing intramolecular hydride shift, as represented by paths b and b′, would afford the enones (E and F).

Type III in the Case of 12f and 12h——In the case of acyloxy-alkenylstannanes, the

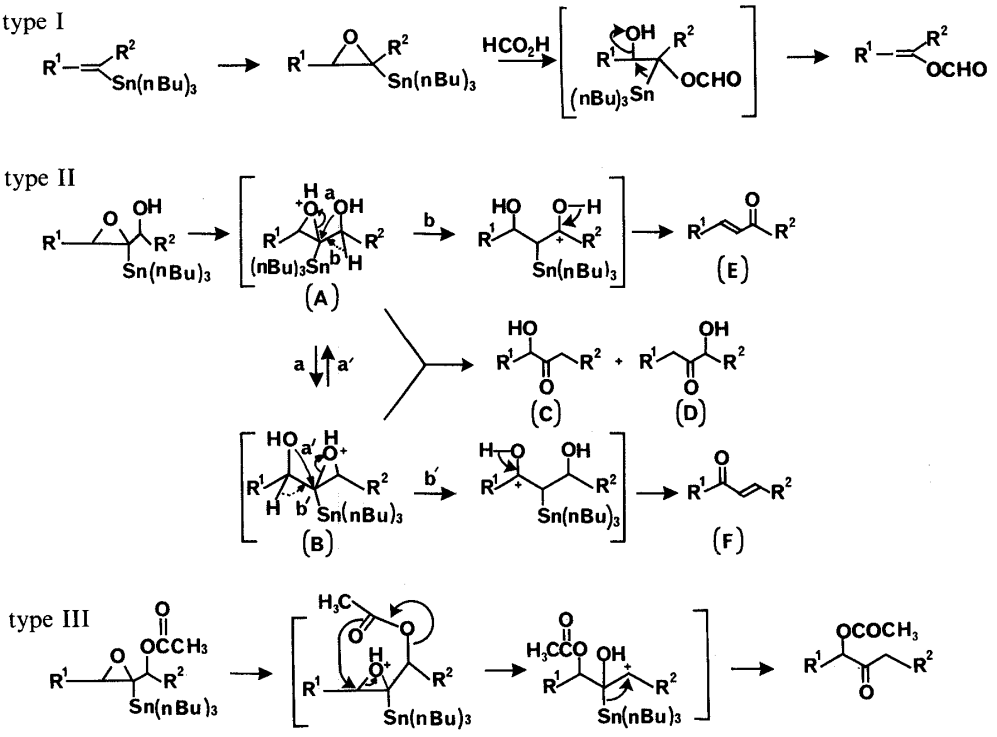

Chart 4

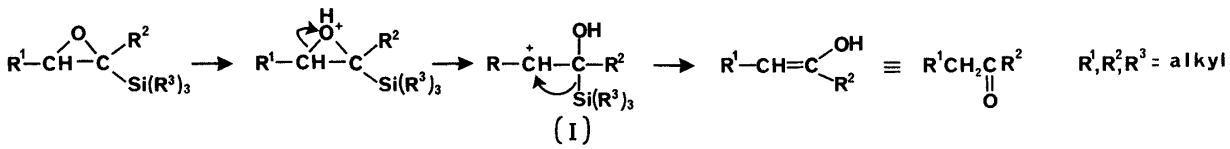

Chart 5

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strong stabilization of the β-cation by the tin atom facilitates the migration of the acyl group by way of the cyclic transition state in the ring opening of the epoxy-stannanes. The resultant β-stannyl cation undergoes spontaneous elimination of the trialkylstannyl group to give acyloxy-ketones. The reaction competes with the type I reaction.

Experimental

Melting points were measured on a Yanagimoto micro melting point apparatus and are uncorrected. Infrared (IR) spectra were measured on a Hitachi 215 grating infrared spectrometer. ^{1}H-NMR spectra were recorded on a Varian EM360A NMR spectrometer or Varian XL-100-12 NMR spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Low-resolution mass spectra (MS) were recorded on a JEOL JMS-D300 mass spectrometer and high-resolution MS on a JEOL JMS-OISG-2 mass spectrometer. TLC was carried out on a silica gel plate (Merck Art 5715) and all *Rf* values refer to a silica gel plate. In general, reactions were carried out under an argon atmosphere unless otherwise mentioned. Reaction products were isolated by extraction with the solvent indicated, followed by washing with brine, drying over anhydrous sodium sulfate or magnesium sulfate, and evaporation of the solvent.

4-Propargyl-2-azetidinone (6)——In a dried two-necked flask, equipped with a stirring bar, a condenser protected by a drying tube, and a rubber cap, were placed 1.15 g (47 mgram atom) of magnesium turnings, 24.9 mg of mercuric chloride and 32 ml of dry ether. To this, 4.22 ml (47 mmol) of propargyl bromide was added at a rate sufficient to allow mild refluxing of the ether. After completion of the vigorous reaction, the mixture was stirred for a further 20 min at room temperature, then cooled to -25 °C, and diluted with 32 ml of THF. A THF (32 ml) solution of 4-phenylsulfonyl-2-azetidinone (2.00 g, 9.5 mmol) was added to the magnesium reagent, and the whole was stirred at -25 °C for 1 h, then warmed to 0 °C, and stirring was continued for a further 4 h. Finally, after stirring of the mixture at room temperature for 30 min, the reaction was quenched by addition of sat. NH_4Cl aq. at 0 °C. The whole was warmed to room temperature, and organic solvents were removed *in vacuo*. The residue was extracted with ethyl acetate (AcOEt). After the usual work-up, the crude product (1.09 g) was purified by silica gel column chromatography (100 g, AcOEt–petr. ether (5 : 1)) to give an oil, 0.90 g (87.4%), which was crystallized in a refrigerator. Recrystallization from ether gave an analytically pure sample. mp 45—46 °C. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3425, 3320, 2995, 2950, 2110, 1750, 1410, 1360, 1298, 1178, 1070, 985. ^{1}H-NMR δ (ppm): 2.07 (1H, t, J=3 Hz), 2.55 (2H, dd, J=6, 3 Hz), 2.78 (1H, ddd, J=14, 3, 3 Hz), 3.12 (1H, ddd, J=14, 5, 3 Hz), 3.83 (1H, ddd, J=12, 5, 3 Hz), 7.17 (1H, br). MS *m/e*: 110, 109 (M^+), 70, 66, 43, 40, 39 (base peak); *m/e*: 109.0526 (Calcd for C_6H_7NO, 109.0527, M^+). *Anal.* Calcd for C_6H_7NO: C, 66.02; H, 6.43; N, 12.84. Found: C, 66.00; H, 6.48; N, 12.90.

4-(2,5-Hexadiynyl)-2-azetidinone (8)——mp 76—76.5 °C (ether–petr. ether). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430, 3325, 3000, 1760, 1345, 1150. ^{1}H-NMR δ (ppm): 2.05 (1H, t, J=2 Hz), 2.43 (4H, br s), 3.05 (1H, ddd, J=14.5, 3, 2 Hz), 3.32 (1H, ddd, J=14.5, 5, 2 Hz), 4.30 (1H, m), 6.54 (1H, br). MS *m/e*: 148 (M^++1), 118, 105, 104, 103, 78, 77 (base peak), 65, 51; *m/e*: 147.0674 (Calcd for C_9H_9NO, 147.0684, M^+). *Anal.* Calcd for C_9H_9NO: C, 73.43; H, 6.12; N, 9.52. Found: C, 73.56; H, 6.21; N, 9.42.

1-*tert*-Butyldimethylsilyl-4-propargyl-2-azetidinone (9)——A mixture of **6** (5.42 g, 50 mmol), imidazole (5.08 g, 75 mmol), *tert*-butyldimethylchlorosilane (11.07 g, 73 mmol), and dimethylformamide (DMF, 6.4 ml) was stirred under an argon atmosphere at room temperature overnight. After evaporation of DMF *in vacuo*, the residue was dissolved in AcOEt. The solution was worked up as usual to give an oil (10.95 g), which was purified by silica gel column chromatography (200 g, AcOEt–petr. ether (1 : 5)). Pure **9** was obtained as a colorless oil (9.50 g, 85.7%), which was crystallized in a refrigerator. mp 32—34 °C. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3330, 2930, 2855, 1730, 1325, 1185, 840. ^{1}H-NMR δ (ppm): 0.21 (3H, s), 0.25 (3H, s), 0.96 (9H, s), 2.05 (1H, t, J=3 Hz), 2.24—2.75 (2H, m), 2.88 (1H, dd, J=16, 3 Hz), 3.14 (1H, dd, J=16, 5 Hz), 3.70 (1H, m). MS *m/e*: 224, 223 (M^+), 166, 124 (base peak), 110, 97; *m/e*: 224.1466 (Calcd for $C_{12}H_{22}NOSi$, 224.1470, M^++1). *Anal.* Calcd for $C_{12}H_{21}NOSi$: C, 64.53; H, 9.49; N, 6.28. Found: C, 64.83; H, 9.34; N, 6.26.

1-*tert*-Butyldimethylsilyl-4-(2-butynyl)-2-azetidinone (10b)——A THF (20 ml) solution of **9** was added over 5 min to a THF solution of lithium diisoporpylamide (LDA) [prepared from diisopropylamine (1.47 ml, 10.49 mmol) and *n*-butyl lithium (*n*-BuLi, 1.55 M in *n*-hexane solution, 6.36 ml, 10.49 mmol) in THF (50 ml) at -78 °C] at -78 °C. The mixture was stirred at the same temperature for 30 min, then 0.66 ml of methyl iodide (10.60 mmol) and 7 ml of hexamethylphosphoramide were added, and the whole was gradually warmed to -40 °C for 1.5 h. After stirring for 10 min without a cooling bath, the reaction was quenched by addition of sat. NH_4Cl aq. at -40 °C, then warmed to room temperature. Extraction with AcOEt (30 ml, 3 times), followed by usual work-up, gave an oil which was purified by silica gel column chromatography (120 g, AcOEt–petr. ether (1 : 5)) to give pure **10b**, 1.97 g (83.2%). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3000, 2940, 2866, 1735, 1185, 1005, 842, 822. ^{1}H-NMR δ (ppm): 0.22 (3H, s), 0.25 (3H, s), 0.96 (9H, s), 1.77 (3H, t, J=3 Hz), 2.29—2.74 (2H, m), 2.86 (1H, dd, J=16, 3 Hz), 3.14 (1H, dd, J=16, 5 Hz), 3.67 (1H, m). MS *m/e*: 238, 237 (M^+), 236, 222, 180, 111, 100; *m/e*: 238.1625 (Calcd for $C_{13}H_{24}NOSi$, 238.1625, M^++1).

4-(2-Butynyl)-2-azetidinone (10a)——A mixture of **10b** (733.5 mg) and 0.5 ml of 10% HCl in 10 ml of methanol was stirred overnight at room temperature. The reaction was quenched by adding sat. $NaHCO_3$ aq. and the mixture

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was concentrated *in vacuo* to give a residue, which was extracted with AcOEt. Usual work-up and silica gel column chromatography (30 g, AcOEt) gave **10a**, 357 mg (93.8%). mp 62.8—64.8 °C (ether–*n*-hexane). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430, 3000, 2950, 1755, 1415, 1365, 1300. ^{1}H-NMR δ (ppm): 1.82 (3H, t, J=2.5 Hz), 2.38—2.61 (2H, m), 2.75 (1H, dd, J=15, 1.5 Hz), 3.10 (1H, dd, J=15, 2 Hz), 3.79 (1H, m), 6.22 (1H, m). MS *m/e*: 124 ($M^+ + 1$), 93, 80 (base peak), 79, 70; *m/e*: 123.0668 (Calcd for C_7H_9NO, 123.0684, M^+). *Anal.* Calcd for C_7H_9NO: C, 68.25; H, 7.37; N, 11.38. Found: C, 68.26; H, 7.37; N, 11.40.

1-*tert*-Butyldimethylsilyl-4-(4-hydroxy-2-pentynyl)-2-azetidinone (10c)——A THF (5 ml) solution of **9** (574 mg, 2.6 mmol) was added to a THF (10 ml) solution of LDA [prepared from 0.44 ml (3.1 mmol) of diisopropylamine and 2 ml of *n*-BuLi (1.55 M *n*-hexane solution, 3.1 mmol)] at −78 °C, and the whole was stirred under these conditions for 20 min. Then, 0.3 ml of freshly distilled acetaldehyde was added to the lithium acetylide solution, and the mixture was stirred under these conditions for 45 min. The reaction was quenched by adding sat. NH_4Cl aq. and the mixture was warmed to room temperature. After evaporation of the THF, the residue was extracted with AcOEt (30 ml, 3 times). Usual work-up and silica gel column chromatography (70 g, AcOEt–petr. ether (1 : 3)) gave pure **10c**, 486 mg (71%) and 98 mg of **9** was recovered. IR ν_{max}^{film} cm^{-1}: 3400, 2925, 2845, 1720, 1325, 1250, 1180, 1085, 1000, 835, 820, 808, 775. ^{1}H-NMR δ (ppm): 0.22 (3H, s), 0.26 (3H, s), 0.98 (9H, s), 1.43 (3H, d, J=6.5 Hz), 2.54 (1H, dd, J=6, 2 Hz), 2.59 (1H, dd, J=4, 2 Hz), 2.87 (1H, dd, J=16, 3 Hz), 3.18 (1H, dd, J=16, 4 Hz), 3.69 (1H, m), 4.50 (1H, br q, J=6.5 Hz). MS *m/e*: 268, 267 (M^+), 250, 210, 168; *m/e*: 268.1756 (Calcd for $C_{14}H_{26}NO_2Si$, 268.1731, $M^+ + 1$).

1-*tert*-Butyldimethylsilyl-4-[4-[(2-methoxyethoxy)methoxy]-2-pentynyl]-2-azetidinone (10d)——A mixture of **10c** (34 mg, 0.13 mmol), 2-methoxyethoxymethyl chloride (60 μl, 0.53 ml) and ethyldiisopropylamine (0.1 ml, 0.57 mmol) in methylene chloride (CH_2Cl_2, 0.5 ml) was stirred at room temperature for 17.5 h. To this mixture, 30 ml of AcOEt and 30 ml of water were added, and the aqueous layer was separated and extracted with AcOEt. Usual work-up of the combined AcOEt layers gave a crude product which was purified by silica gel column chromatography (15 g, AcOEt–petr. ether (1 : 3)) to provide 37 mg of **10d**. IR ν_{max}^{film} cm^{-1}: 2930, 2880, 2230, 1740, 1460, 1320, 1258, 1183, 1108, 1035, 840, 825, 810, 778. ^{1}H-NMR δ (ppm): 0.22 (3H, s), 0.25 (3H, s), 0.97 (9H, s), 1.42 (3H, d, J=7 Hz), 2.48 (1H, ddd, J=16, 6.5, 2 Hz), 2.66 (1H, ddd, J=16, 4, 2 Hz), 2.84 (1H, dd, J=16, 3 Hz), 3.16 (1H, dd, J=16, 5 Hz), 3.40 (3H, s), 3.44—3.84 (5H, m), 4.49 (1H, tq, J=7, 2 Hz), 4.83 (2H, ABq, J=7 Hz). MS *m/e*: 356, 355 (M^+), 340, 298, 280, 268, 250, 224, 222, 192, 142, 133, 115; *m/e*: 356.2267 (Calcd for $C_{18}H_{34}NO_4Si$, 356.2257, $M^+ + 1$).

7-Phenyl-3-heptyn-2-ol (10e)——A THF (10 ml) solution of 5-phenyl-1-pentyne (860 mg, 5.97 mmol) was treated with 4.6 ml of *n*-BuLi (1.55 M hexane solution, 7.13 mmol), and the mixture was stirred at 0 °C for 30 min. Freshly distilled acetaldehyde (0.5 ml) was added to the acetylide solution, stirring was continued for another 20 min, and the reaction was quenched by adding sat. aq. NH_4Cl. Extraction with ether and usual work-up, followed by silica gel column chromatography (50 g, AcOEt–petr. ether (1 : 10—1 : 5)) gave **10e** as a colorless oil, 698 mg (62%). IR ν_{max}^{film} cm^{-1}: 3320, 3090, 3070, 3030, 2980, 2930, 2860, 2240, 1600, 1497, 1330, 1155, 1080, 1010, 890, 745, 700. ^{1}H-NMR δ (ppm): 1.43 (3H, d, J=7 Hz), 1.82 (2H, quint., J=5 Hz), 2.21 (2H, dt, J=5, 2 Hz), 2.73 (2H, t, J=7 Hz), 4.54 (1H, br q, J=7 Hz), 7.24 (5H, m). MS *m/e*: 189, 188 (M^+), 173, 155, 145, 129, 105, 104, 91, 77 (base peak); *m/e*: 188.1195 (Calcd for $C_{13}H_{16}O$, 188.1201, M^+).

2-Acetoxy-7-phenyl-3-heptyne (10f)——In the presence of 4-dimethylaminopyridine (catalytic), **10e** (156 mg, 0.83 mmol) was allowed to react with acetic anhydride (0.16 ml, 1.69 mmol) in pyridine (1 ml) to give **10f**, 169 mg (89%). IR ν_{max}^{film} cm^{-1}: 3030, 2980, 2940, 2885, 1735, 1600, 1448, 1368, 1235, 1166, 1058, 1017, 743, 698. ^{1}H-NMR δ (ppm): 1.48 (3H, d, J=7 Hz), 1.81 (2H, quint.-like, J=6.5 Hz), 2.04 (3H, s), 2.21 (2H, dt, J=6.5, 2 Hz), 2.72 (2H, t, J=8 Hz), 5.50 (1H, tq, J=7, 2 Hz), 7.25 (5H, m). MS *m/e*: 230 (M^+), 229, 188, 170, 155; *m/e*: 230.1369 (Calcd for $C_{15}H_{18}O_2$, 230.1307, M^+).

2-Benzyloxy-7-phenyl-3-heptyne (10g)——Compound **10e** (267 mg, 1.42 mmol) was added to a stirred suspension of sodium hydride (60% dispersion, 85 mg) in DMF (2 ml) at 0 °C. The mixture was stirred at the same temperature for 5 min, then allowed to stand for 10 min without a cooling bath. To this, 0.2 ml (1.68 mmol) of benzyl bromide was added at 0 °C, and the whole was stirred overnight at room temperature. After addition of water, the product was extracted with ether. Usual work-up and silica gel column chromatography (30 g, *n*-hexane–AcOEt (10 : 1)) gave pure **10g**, 358 mg (91%). IR ν_{max}^{film} cm^{-1}: 3090, 3070, 3028, 2938, 2855, 2225, 1600, 1498, 1453, 1370, 1330, 1160, 1110, 1085, 1050, 1028, 740, 698. ^{1}H-NMR δ (ppm): 1.45 (3H, d, J=6 Hz), 1.82 (2H, quint., J=7.5 Hz), 2.24 (2H, t, J=7.5 Hz), 2.73 (2H, t, J=7.5 Hz), 4.25 (1H, q, J=6 Hz), 4.66 (2H, ABq, J=11.5 Hz), 7.12—7.50 (10H, m). MS *m/e*: 279, 278 (M^+), 268, 235, 187, 157, 144, 143, 129, 105, 104, 92, 91; *m/e*: 278.1667 (Calcd for $C_{20}H_{22}O$, 278.1671, M^+).

General Procedure for Hydrostannation——A mixture of an acetylenic compound, tri-*n*-butyltin hydride and AIBN (catalytic) was heated under an argon atmosphere with stirring. After cooling, the products were separated by silica gel column chromatography. The reaction conditions and the yields are shown in Table I. Physical data for alkenylstannanes thus obtained are as follows.

4-(2-Tri-*n*-butylstannyl-2-butenyl)-2-azetidinone (11a)——IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3420, 2950, 2920, 2860, 2840, 1750, 1600, 1410, 1360, 1285, 1175, 1070, 860. ^{1}H-NMR δ (ppm): 0.42—1.10 (15H, m), 1.12—1.66 (12H, m), 1.73 (3H, d, J=7 Hz), 2.27—2.76 (3H, m), 2.99 (1H, ddd, J=14.5, 5, 2 Hz), 3.55 (1H, m), 6.17 (1H, q, J=7 Hz), 6.32 (1H, br s). MS *m/e*: 415 (M^+ for ^{120}Sn), 414, 413 (M^+ for ^{118}Sn), 412, 358, 356, 316, 314, 312 (base peak), 259, 257, 202, 200, 177, 175.

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4-(3-Tri-*n*-butylstannyl-2-butenyl)-2-azetidinone (12a)——IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3425, 2920, 2870, 2840, 1750, 1615, 1460, 1410, 1365, 1290, 1180, 1070, 1000, 960, 880, 865, 840. ^{1}H-NMR δ (ppm): 0.50—1.08 (15H, m), 1.08—1.84 (12H, m), 1.92 (3H, br s), 2.30 (2H, br t, J=7 Hz), 2.64 (1H, br d, J=15 Hz), 3.06 (1H, ddd, J=15, 5, 2 Hz), 3.64 (1H, m), 5.99 (1H, t, J=7 Hz), 6.30 (1H, br s). MS *m/e*: 414, 413 (M^+ for ^{118}Sn), 400, 398, 372, 370, 358, 356, 354, 316, 314, 312 (base peak).

1-*tert*-Butyldimethylsilyl-4-(2-tri-*n*-butylstannyl-2-butenyl)-2-azetidinone (11b)——IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2960, 2925, 2855, 1740, 1465, 1328, 1267, 1258, 1188, 999, 840, 822, 810. ^{1}H-NMR δ (ppm): 0.23 (6H, s), 0.66—1.10 (24H, m), 1.12—1.16 (12H, m), 1.72 (3H, d, J=6 Hz), 2.12 (1H, dd, J=13, 12 Hz), 2.59 (1H, dd, J=15, 3 Hz), 2.84 (1H, br d, J=13 Hz), 2.96 (1H, dd, J=15, 5 Hz). MS *m/e*: 514 (M^+ −methyl, for ^{120}Sn), 512 (M^+ −methyl, for ^{118}Sn), 472, 470, 430, 428, 315, 313, 259, 257, 177, 175.

1-*tert*-Butyldimethylsilyl-4-(3-tri-*n*-butylstannyl-2-butenyl)-2-azetidinone (12b)——IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2940, 2930, 2855, 1725, 1468, 1333, 1315, 1258, 1190, 1090, 1004, 911, 840, 822, 809. ^{1}H-NMR δ (ppm): 0.24 (6H, s), 0.50—1.10 (24H, m), 1.12—1.80 (12H, m), 1.92 (3H, br s), 2.14 (1H, m), 2.51 (1H, m), 2.67 (1H, dd, J=15, 3 Hz), 3.11 (1H, dd, J=15, 5 Hz), 3.56 (1H, m), 5.93 (1H, qt, J=5, 1 Hz). MS *m/e*: 528, 527 (M^+ for ^{118}Sn), 514, 512, 472, 470, 315, 313.

1-*tert*-Butyldimethylsilyl-4-(4-hydroxy-2-tri-*n*-butylstannyl-2-pentenyl)-2-azetidinone (11c)——IR ν_{max}^{film} cm^{-1}: 3425, 2955, 2855, 1750 (shoulder), 1720, 1460, 1325, 1260, 1188, 1075, 998, 838, 824, 810, 768, 680. ^{1}H-NMR δ (ppm): 0.26 (6H, s), 0.15—1.10 (24H, m), 1.10—1.70 (15H, m), 1.78 (1H, s), 2.13 (1H, dd, J=13, 11.5 Hz), 2.60 (1H, dd, J=15, 3 Hz), 2.87 (1H, br d, J=13 Hz), 3.02 (1H, dd, J=15, 5 Hz), 3.57 (1H, m), 4.11 (1H, m), 6.07 (1H, br d, J=8 Hz). MS *m/e*: 526 (M^+ −methyl and H_2O, for ^{120}Sn), 524 (M^+ −methyl and H_2O, for ^{118}Sn), 502, 500, 388, 386, 251, 249.

1-*tert*-Butyldimethylsilyl-4-(4-hydroxy-3-tri-*n*-butylstannyl-2-pentenyl)-2-azetidinone (12c)——IR ν_{max}^{film} cm^{-1}: 3430, 2940, 2925, 2840, 1720, 1460, 1320, 1253, 1190, 1080, 1002, 838, 820, 808, 780, 687. ^{1}H-NMR δ (ppm): 0.26 (6H, s), 0.40—1.03 (24H, m), 1.07—1.82 (15H, m), 1.89 (1H, br s), 2.24 (1H, m), 2.53 (1H, m), 2.65 (1H, dd, J=15, 3 Hz), 3.10 (1H, dd, J=15, 5 Hz), 3.58 (1H, m), 4.36 (1H, q, J=6 Hz), 6.07 (1H, br t, J=7 Hz). MS *m/e*: 502 (M^+ −butyl, for ^{120}Sn), 500 (M^+ −butyl, for ^{118}Sn), 251, 249.

1-*tert*-Butyldimethylsilyl-4-[2-tri-*n*-butylstannyl-4-[(2-methoxyethoxy)methoxy]-2-pentenyl]-2-azetidinone (11d)——IR ν_{max}^{film} cm^{-1}: 2960—2850, 1750, 1460, 1313, 1258, 1180, 1103, 1035, 995, 938, 822, 810, 770. ^{1}H-NMR δ (ppm): 0.26 (6H, s), 0.53—1.12 (24H, m), 1.12—1.70 (15H, m), 2.15 (1H, dd, J=14, 11 Hz), 2.60 (1H, dd, J=15, 3 Hz), 2.87 (1H, br d, J=14 Hz), 3.00 (1H, dd, J=15, 5.5 Hz), 3.39 (3H, s), 3.20—3.73 (5H, m), 4.04 (1H, m), 4.66, 4.69 (2H, two s), 5.94, 5.98 (1H, two d, J=8 Hz). MS *m/e*: 645 (M^+ for ^{118}Sn), 631, 619, 602, 585, 559, 541, 485, 483, 481, 432, 430, 400, 308, 306, 304.

1-*tert*-Butyldimethylsilyl-4-[3-tri-*n*-butylstannyl-4-[(2-methoxyethoxy)methoxy]-2-pentenyl]-2-azetidinone (12d)——IR ν_{max}^{film} cm^{-1}: 2950—2840, 1742, 1613, 1460, 1363, 1312, 1250, 1180, 1085, 1100, 838, 821, 808, 780, 678. ^{1}H-NMR δ (ppm): 0.26 (9H, s), 0.54—1.12 (24H, m), 1.12—1.94 (15H, m), 2.18 (1H, m), 2.63 (1H, m), 2.66 (1H, dd, J=15, 3 Hz), 3.10 (1H, dd, J=15, 5.5 Hz), 3.46 (3H, s), 3.44—3.86 (5H, m), 4.27 (1H, br q, J=7 Hz), 4.63 (2H, br s), 6.04 (1H, br t, J=7 Hz). MS *m/e*: 645 (M^+ for ^{118}Sn), 631, 619, 587, 559, 541, 487, 485, 483, 445, 443, 441, 432, 430, 310, 309.

3-Tri-*n*-butylstannyl-7-phenyl-3-hepten-2-ol (12e)——IR ν_{max}^{film} cm^{-1}: 3400, 3080, 3040, 2970, 2940, 2860, 1615, 1458, 1380, 1125, 1065, 740, 700. ^{1}H-NMR δ (ppm): 0.73—1.03 (15H, m), 1.07—1.82 (17H, m), 1.89—2.23 (2H, m), 2.65 (2H, t, J=8 Hz), 5.37 (1H, br q, J=7.5 Hz), 6.23 (1H, t, J=7 Hz), 7.22 (5H, m). MS *m/e*: 479 (M^+ for ^{120}Sn), 477 (M^+ for ^{118}Sn), 461, 459, 423, 421, 419, 405, 403, 401, 291, 289, 287, 255.

2-Acetoxy-4-tri-*n*-butylstannyl-7-phenyl-3-heptene (11f)——IR ν_{max}^{film} cm^{-1}: 3075, 3030, 2960, 2930, 2850, 1735, 1600, 1455, 1370, 1243, 1040, 750, 700. ^{1}H-NMR δ (ppm): 0.75—1.08 (17H, m), 1.12—1.86 (15H, m), 2.00 (2H, t, J=7 Hz), 2.62 (2H, t, J=8 Hz), 5.12, 5.22 (1H, two q, J=6 Hz), 6.08 (1H, d, J=10 Hz), 7.06—7.43 (5H, m). MS *m/e*: 522 (M^+ for ^{120}Sn), 520 (M^+ for ^{118}Sn), 465, 463, 405, 403, 302, 300 (base peak), 298, 293, 291, 289.

2-Acetoxy-3-tri-*n*-butylstannyl-7-phenyl-3-heptene (12f)——IR ν_{max}^{film} cm^{-1}: 2960, 2930, 2875, 1735, 1450, 1368, 1240, 1039, 700. ^{1}H-NMR δ (ppm): 0.76—1.04 (15H, m), 1.08—1.92 (17H, m), 1.88—2.19 (5H, m), 2.63 (2H, t, J=7.5 Hz), 5.39 (1H, q, J=7 Hz), 6.24 (1H, t, J=6 Hz), 7.06—7.38 (5H, m). MS *m/e*: 522 (M^+ for ^{120}Sn), 520 (M^+ for ^{118}Sn), 519, 465, 463, 405, 403, 349, 347.

2-Benzyloxy-4-tri-*n*-butylstannyl-7-phenyl-3-heptene (11g)——IR ν_{max}^{film} cm^{-1}: 3075, 3035, 2970, 2940, 2855, 1500, 1455, 1370, 1098, 1075, 735, 700. ^{1}H-NMR δ (ppm): 0.71—1.06 (15H, m), 1.10—1.86 (17H, m), 2.29 (2H, t, J=7.5 Hz), 2.64 (2H, t, J=7.5 Hz), 3.89 (1H, m), 4.50 (2H, ABq, J=12 Hz), 6.06 (1H, d, J=8 Hz), 7.08—7.46 (10H, m). MS *m/e*: 569 (M^+ −1, for ^{120}Sn), 568, 567 (M^+ −1, for ^{118}Sn), 513, 511, 421, 419, 405, 403, 365, 363, 341, 339, 235, 233, 231.

2-Benzyloxy-3-tri-*n*-butylstannyl-7-phenyl-3-heptene (12g)——IR ν_{max}^{film} cm^{-1}: 3090, 3070, 3030, 2960, 2925, 2850, 1610, 1498, 1455, 1378, 1368, 1090, 1070, 1030, 880, 735, 700. ^{1}H-NMR δ (ppm): 0.70—1.08 (15H, m), 1.08—2.92 (17H, m), 1.94—2.38 (2H, m), 2.67 (2H, t, J=7 Hz), 3.98 (1H, q, J=7 Hz), 4.40 (2H, ABq, J=12 Hz), 6.20 (1H, t, J=7 Hz), 7.00—7.52 (10H, m). MS *m/e*: 513 (M^+ −butyl, for ^{120}Sn), 512, 511 (M^+ −butyl, for ^{118}Sn), 423, 421, 419, 405, 403 (base peak), 291, 289, 255, 253, 249, 247.

Conversion of Alkenylstannanes to Ketones. General Procedure——Alkenylstannanes (**11** or **12**) were allowed to react with *m*CPBA in CH_2Cl_2 at room temperature to give epoxystannanes (**13**). The reaction mixture was diluted with

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ether and then washed with sat. Na_2SO_3 aq., sat. $NaHCO_3$ aq., and brine successively. After drying, the solvent was evaporated off *in vacuo*. The crude epoxystannanes were used for the next step without further purification. The epoxystannanes were treated with *ca.* 90% formic acid (*ca.* 20 eq) in CH_2Cl_2 at room temperature under an argon atmosphere. The following work-up procedures were employed for isolating the products;

Procedure A: The reaction mixture was neutralized with sat. $NaHCO_3$ aq. and the products were extracted with AcOEt. The extracts were worked up as usual to give a crude product, which was purified by silica gel column chromatography.

Procedure B: From the reaction mixture, volatile material was removed *in vacuo* to give an oil, which was dissolved in THF. The solution was treated with 0.5 M (w/v) aqueous solution of lithium hydroxide (excess) at room temperature for 1 h. The products were extracted with ether.

Conversion of 11b——In CH_2Cl_2 (2 ml), **11b** (458 mg, 0.8 mmol) was allowed to react with *m*CPBA (225 mg) at room temperature for 1.7 h to give epoxystannanes, 420 mg; 1 : 2 mixture of diastereo isomers, $Rf = 0.25$ and 0.29 (ether–petr. ether (1 : 2)). In this case, the epoxystannanes were purified on a short column of silica gel (35 g, ether–petr. ether (1 : 4, then 1 : 3)). Since slight decomposition of the products was observed after chromatography, purification was omitted in the other cases.

1-*tert*-Butyldimethylsilyl-4-(2-tri-*n*-butylstannyl-2,3-epoxybutyl)-2-azetidinone: IR and MS spectra for the mixture of diastereomers. IR ν_{max}^{film} cm^{-1}: 2950, 2925, 2850, 1748, 1462, 1317, 1263, 1252, 1186, 1000, 839, 822, 810, 773, 678. MS *m/e*: 545 (M^+ for ^{120}Sn), 488, 486, 448, 376, 374, 332, 330, 235, 233. ^{1}H-NMR for less polar diastereomer, δ (ppm): 0.22 (6H, s), 0.58—1.10 (24H, m), 1.12—2.00 (16H, m), 1.30 (3H, d, $J = 15$ Hz), 2.40 (1H, dd, $J = 14$, 3 Hz), 2.77 (1H, q, $J = 5$ Hz), 2.79 (1H, dd, $J = 15$, 3 Hz), 3.14 (1H, dd, $J = 15$, 5 Hz), 3.57 (1H, m); more polar diastereomer, δ (ppm): 0.24 (6H, s), 0.40—1.10 (24H, m), 1.10—1.90 (16H, m), 2.64 (1H, dd, $J = 13.5$, 3 Hz), 2.69 (1H, dd, $J = 14$, 2.5 Hz), 2.84 (1H, q, $J = 5$ Hz), 3.08 (1H, dd, $J = 14.5$, 5 Hz), 3.51 (1H, m).

The epoxystannane (diastereomeric mixture, 372 mg, 0.68 mmol) was dissolved in CH_2Cl_2 (5 ml) and treated with 0.5 ml of *ca.* 90% formic acid. The mixture was stirred at room temperature for 67.7 h. Work-up according to procedure A gave the crude product, which could be separated by silica gel column chromatography (35 g, ether–petr. ether (1 : 5, then 1 : 2, and finally 2 : 1)). The less polar product ($Rf = 0.21$, ether–petr. ether (1 : 1)) was 1-*tert*-butyldimethylsilyl-4-(2-formyloxy-2-butenyl)-2-azetidinone, **15** (73 mg, 39%) and the more polar product ($Rf = 0.16$) was found to be 1-*tert*-butyldimethylsilyl-4-(2-oxobutyl)-2-azetidinone, **14** (51 mg, 31%).

14: IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2950, 2930, 2855, 1737 (shoulder), 1723, 1718 (shoulder), 1367, 1323, 1257, 1188, 839, 820, 808. ^{1}H-NMR δ (ppm): 0.22 (3H, s), 0.26 (3H, s), 0.99 (9H, s), 1.08 (3H, t, $J = 8$ Hz), 2.47 (2H, q, $J = 8$ Hz), 2.56 (1H, dd, $J = 16.5$, 3 Hz), 2.64 (1H, dd, $J = 16$, 4 Hz), 2.98 (1H, dd, $J = 16.5$, 4 Hz), 3.33 (1H, dd, $J = 16$, 5 Hz), 3.91 (1H, m). MS *m/e*: 256 ($M^+ + 1$), 240, 198, 129, 100; *m/e*: 256.1732 (Calcd for $C_{13}H_{26}NO_2Si$, 256.1726, $M^+ + 1$).

15: IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2950, 2930, 2855, 1737 (shoulder), 1728, 1680 (shoulder), 1318, 1188, 1150, 838, 820. ^{1}H-NMR δ (ppm): 0.24 (3H, s), 0.26 (3H, s), 0.99 (9H, s), 1.72 (3H, d, $J = 7$ Hz), 2.40 (1H, dd, $J = 15$, 10.5 Hz), 2.69 (1H, dd, $J = 15$, 2.5 Hz), 2.84 (1H, br d, $J = 15$ Hz), 3.18 (1H, dd, $J = 15$, 5 Hz), 3.68 (1H, m), 5.60 (1H, q, $J = 7$ Hz), 8.09 (1H, s). MS *m/e*: 226 ($M^+ -$ butyl), 198, 184, 167, 149 (base peak), 129; *m/e*: 226.0907 (Calcd for $C_{10}H_{16}NO_3Si$, 226.0899, $M^+ -$ butyl).

The enol formate **15** (73 mg) was treated with lithium hydroxide (13 mg, 1.1 eq) in aq. THF (THF–water (1 : 1), 0.5 ml) at 0 °C for 40 min. After being stirred at room temperature for 20 min, the reaction mixture was diluted with AcOEt (60 ml). Usual work-up and purification by silica gel column chromatography (25 g, ether–petr. ether (1 : 1)) gave **14**, 58 mg (89%).

4-(4-Acetoxy-3-tri-*n*-butylstannyl-2-pentenyl)-1-*tert*-butyldimethylsilyl-2-azetidinone (12h)——Acetic anhydride (0.11 ml, 1.16 mmol) was added to a solution of **12c** (204 mg, 0.37 mmol) in 1 ml of pyridine containing a catalytic amount of 4-dimethylaminopyridine, and the whole was stirred at room temperature for 2 h under an argon atmosphere. After dilution with ether (80 ml), the mixture was washed with sat. $CuSO_4$ aq. (30 ml, 2 times), water, and brine successively. After drying, evaporation of the solvent gave nearly pure **12h**, 164 mg (75%). IR ν_{max}^{film} cm^{-1}: 2950, 2925, 2850, 1743, 1460, 1368, 1312, 1239, 1182, 1036, 1004, 838, 822, 810, 780. ^{1}H-NMR δ (ppm): 0.25 (6H, s), 0.54—1.14 (24H, m), 1.14—1.86 (15H, m), 2.00 (3H, s), 2.28 (1H, m), 2.42—2.84 (2H, m), 3.12 (1H, dd, $J = 15$, 5 Hz), 3.59 (1H, m), 5.37 (1H, q, $J = 7$ Hz), 6.11 (1H, t, $J = 7$ Hz). MS *m/e*: 599 (M^+ for ^{118}Sn), 586, 548, 544, 430, 428.

Conversion of 12h——In 4 ml of CH_2Cl_2, **12h** (164 mg, 0.27 mmol) was allowed to react with *m*CPBA (119 mg) to give two epoxystannanes. The crude epoxystannanes were treated with 90% formic acid (0.23 ml) in 2.3 ml of CH_2Cl_2 for 2.7 h at room temperature. Work-up according to procedure A gave products which were separated by silica gel column chromatography (35 g, AcOEt–petr. ether (1 : 4—1 : 7)). 4-(2-Acetoxy-3-oxopentyl)-1-*tert*-butyldimethylsilyl-2-azetidinone (**17**) was obtained as the less polar product (45 mg, 50%), and 4-(4-acetoxy-3-oxopentyl)-1-*tert*-butyldimethylsilyl-2-azetidinone (**16**) was isolated as the more polar product (33 mg, 37%).

16: IR ν_{max}^{film} cm^{-1}: 2960, 2930, 1760—1690, 1468, 1374, 1320, 1240, 1190, 1008, 840, 825, 810, 780, 680. ^{1}H-NMR δ (ppm): 0.24, 0.26 (6H, two s), 0.97 (9H, s), 1.40 (3H, d, $J = 7$ Hz), 2.14 (3H, s), 2.22—2.67 (5H, m), 3.11 (1H, dd, $J = 15$, 5 Hz), 3.54 (1H, m), 5.07 (1H, q, $J = 7$ Hz). MS *m/e*: 328, 327 (M^+), 270, 269, 210, 141, 100; *m/e*: 327.1899 (Calcd for $C_{16}H_{29}NO_4Si$, 327.1864, M^+).

17: IR ν_{max}^{film} cm^{-1}: 2950, 2930, 2855, 1730, 1464, 1370, 1308, 1230, 838, 822, 808, 779, 678. ^{1}H-NMR δ (ppm): 0.24

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(6H, s), 0.97 (9H, s), 1.08 (3H, t, $J=7$ Hz), 2.15 (3H, s), 2.22—2.61 (4H, m), 2.73 (1H, dd, $J=15.5$, 3 Hz), 3.19 (1H, dd, $J=15.5$, 5 Hz), 3.61 (1H, m), 5.06 (1H, m). MS *m/e*: 328 ($M^+ + 1$), 312, 270, 228, 210, 186, 168, 141, 117, 100; *m/e*: 328.1940 (Calcd for $C_{16}H_{30}NO_4Si$, 328.1942, $M^+ + 1$).

Conversion of 12e——In 5 ml of CH_2Cl_2, **12e** (229 mg, 0.48 mmol) was epoxidized with *m*CPBA (146 mg). The crude epoxystannanes were treated with 90% formic acid (0.36 ml) in 8 ml of CH_2Cl_2 for 24 h at room temperature. The reaction was worked up by procedure B and the crude products were separated by silica gel column chromatography (50 g, benzene–*n*-hexane (10 : 1), then benzene, finally benzene–AcOEt (20 : 1)). The following four products were identified.

2-Hydroxy-7-phenyl-3-heptanone (**18**, 18 mg, 18%, $Rf=0.22$; benzene–*n*-hexane (20 : 1)). IR ν_{max}^{film} cm^{-1}: 3450, 3030, 2940, 2860, 1710, 1603, 1500, 1455, 1260, 1090, 1030, 750, 703. ^{1}H-NMR δ (ppm): 1.37 (3H, d, $J=7$ Hz), 1.67 (2H, m), 2.36—2.82 (4H, m), 3.54 (1H, br), 4.26 (1H, q, $J=7$ Hz), 7.24 (5H, m). MS *m/e*: 208, 207, 206 (M^+), 161, 145 (base peak), 117, 92, 91; *m/e*: 206.1299 (Calcd for $C_{13}H_{18}O_2$, 206.1307, M^+).

4-Hydroxy-7-phenyl-3-heptanone (**19**, 21 mg, 21%, $Rf=0.32$). IR ν_{max}^{film} cm^{-1}: 3475, 3030, 2935, 2860, 1710, 1604, 1500, 1455, 1100, 1030, 750, 703. ^{1}H-NMR δ (ppm): 1.10 (3H, t, $J=8$ Hz), 1.58—1.98 (4H, m), 2.44 (2H, q, $J=8$ Hz), 2.68 (2H, t, $J=6$ Hz), 3.51 (1H, br d, $J=4.5$ Hz), 4.24 (1H, br t, $J=4.5$ Hz), 7.24 (5H, m). MS *m/e*: 207, 206 (M^+), 149, 131, 104, 91; *m/e*: 206.1300 (Calcd for $C_{13}H_{18}O_2$, 206.1307, M^+).

(*E*)-7-Phenyl-3-hepten-2-one (**20**, 19 mg, 21%, $Rf=0.45$). IR ν_{max}^{film} cm^{-1}: 3020, 2920, 2845, 1718, 1668, 1622, 1603, 1498, 1458, 1360, 1253, 980, 750, 700. ^{1}H-NMR δ (ppm): 1.64—2.00 (2H, m), 2.14—2.46 (5H, s, m), 2.68 (2H, t, $J=7.5$ Hz), 6.12 (1H, d, $J=16$ Hz), 6.83 (1H, td, $J=16$, 6.5 Hz), 7.10—7.46 (5H, m). MS *m/e*: 189, 188 (M^+), 130, 104, 97, 91, 84; *m/e*: 188.1218 (Calcd for $C_{13}H_{16}O$, 188.1201, M^+).

(*E*)-7-Phenyl-2-hepten-4-one (**21**, 0.7 mg, 0.8%, $Rf=0.52$). IR ν_{max}^{film} cm^{-1}: 3060, 3025, 2940, 2850, 1665, 1628, 1600, 1497, 1440, 1375, 1282, 1070, 768, 698. ^{1}H-NMR δ (ppm): 1.85 (3H, dd, $J=7$, 2 Hz), 1.76—2.14 (2H, m), 2.53 (2H, t, $J=8$ Hz), 2.65 (2H, t, $J=8$ Hz), 6.10 (1H, qd, $J=16$, 2 Hz), 6.80 (1H, qd, $J=16$, 7 Hz), 7.04—7.41 (5H, m). MS *m/e*: 190, 189, 188 (M^+), 173, 170, 105, 104, 91, 84, 83, 77; *m/e*: 188.1197 (Calcd for $C_{13}H_{16}O$, 188.1201, M^+).

Conversion of 12f——In CH_2Cl_2 (3 ml), **12f** (360 mg, 0.69 mmol) was epoxidized with *m*CPBA (219 mg) to give two epoxystannanes. The crude epoxystannanes were treated with 90% formic acid (1.52 ml) in 11.5 ml of CH_2Cl_2 for 47 h at room temperature. Work-up using procedure A gave the crude product, which was chromatographed over silica gel (80 g, *n*-hexane–AcOEt (10 : 1, then 5 : 1)) to give a mixture of acetoxyketones (**22** and **23**, 106 mg, 62%). The ratio of **22** and **23** in the mixture was estimated to be 1 : 1 based on integration of the two methyl signals, from which the yields of the acetoxyketones shown in Table I were calculated. A part of the mixture was separated by preparative TLC (20 × 20 cm, 0.25 mm, *n*-hexane–AcOEt, (8 : 1), two developments) to afford the pure **22** and **23**.

2-Acetoxy-7-phenyl-3-heptanone (**22**): IR ν_{max}^{film} cm^{-1}: 3030, 2980, 2940, 2860, 1740, 1728, 1603, 1453, 1372, 1238, 1088, 1028, 750, 700. ^{1}H-NMR δ (ppm): 1.38 (3H, d, $J=7$ Hz), 1.53—1.82 (4H, m), 2.11 (3H, s), 2.20—2.80 (4H, m), 5.11 (1H, q, $J=7$ Hz), 7.22 (5H, m). MS *m/e*: 250, 249, 248 (M^+), 206, 188, 170, 161, 117, 104, 91; *m/e*: 248.1406 (Calcd for $C_{15}H_{20}O_3$, 248.1412, M^+).

4-Acetoxy-7-phenyl-3-heptanone (**23**): IR ν_{max}^{film} cm^{-1}: 3030, 2930, 2850, 1740, 1728, 1600, 1450, 1370, 1238, 1087, 1030, 748, 700. ^{1}H-NMR δ (ppm): 1.06 (3H, t, $J=8$ Hz), 1.76 (2H, m), 2.14 (3H, s), 2.46 (2H, dq, $J=8$, 3 Hz), 2.66 (2H, br t, $J=6$ Hz), 5.08 (1H, t-like, $J=5.5$ Hz), 7.23 (5H, m). MS *m/e*: 250, 249, 248 (M^+), 206, 188 (base peak), 170, 161, 132, 131, 117, 105, 104, 91; *m/e*: 248.1414 (Calcd for $C_{15}H_{20}O_3$, 248.1412, M^+).

Conversion of 12g——In 2 ml of CH_2Cl_2, **12g** (130 mg, 0.23 mmol) was epoxidized with *m*CPBA (65 mg) to give two epoxystannanes. The crude epoxystannanes were treated with 90% formic acid (0.18 ml) in 3.8 ml of CH_2Cl_2 for 68.3 h at room temperature. Work-up by procedure B gave the product, which was separated by silica gel column chromatography (30 g, benzene–*n*-hexane (1 : 1—2 : 1)) to give 2-benzyloxy-7-phenyl-3-heptanone (**24**, 6.3 mg, 9.3%) and 15 mg (36%) of **20**.

24: IR ν_{max}^{film} cm^{-1}: 3600, 3252, 2929, 2850, 1720, 1600, 1495, 1450, 1368, 1270, 1110, 1028, 740, 695. ^{1}H-NMR δ (ppm): 1.33 (3H, d, $J=7$ Hz), 1.61 (4H, m), 2.60 (4H, m), 3.93 (1H, q, $J=7$ Hz), 4.55 (2H, s), 7.24 (5H, m), 7.36 (5H, m). MS *m/e*: 296 (M^+), 205, 190, 161, 149, 135, 118, 105, 91; *m/e*: 296.1776 (Calcd for $C_{20}H_{24}O_2$, 296.1776, M^+).

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References and Notes

1) This paper is dedicated to Professor Shun-ichi Yamada on the occasion of his 70th birthday, in recognition of his outstanding contribution to asymmetric synthesis and related areas of chemistry.
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