Pergamon

Tetrahedron Vol. 50, No. 4, pp. 1073-1082, 1994
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0040-4020/94 $6.00+0.00

0040-4020(93)E0077-S

Conjugate Addition of Allylsilanes to α,β-Unsaturated N-Acyloxazolidinones[1]

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Abstract: The conjugate addition of allyltrimethylsilane to α,β-unsaturated N-acyloxazolidinone at -78 °C in the presence of $TiCl_4$ gave the allylation product **3**. However, when the reaction was carried out at room temperature, a small amount of cyclopentane adduct **4** was observed. The cyclopentane product formation can be prevented by employing $BF_3{\cdot}OEt_2$ as a Lewis acid. The enantioselective synthesis of optically pure 3-substituted-5-hexenoic acids was achieved by employing chiral oxazolidinone as a chiral auxiliary.

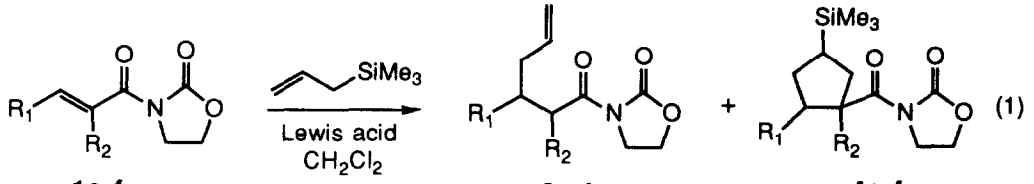
INTRODUCTION

The conjugate addition of allyltrimethylsilanes to α,β-unsaturated carboxylic acid derivatives has been a considerable challenge in synthetic organic chemistry. Since Hosomi and Sakurai reported that allyltrimethylsilanes failed to react with α,β-unsaturated carboxylic acids and esters even in the presence of Lewis acid,[2] efforts associated with this problem have been made by many research groups. Among them, Majetich and co-workers[3] have reported fluoride ion induced conjugate addition of allyltrimethylsilane to α,β-unsaturated esters to produce the conjugate addition adducts. In addition, Jella and Santelli[4] have demonstrated the reactivity of α,β-unsaturated acyl cyanides in conjugate allylation with allyltrimethylsilanes and hydrolysis of the addition adducts with water lead to δ, ε-ethylenic acids. Danheiser and Fink[5] have also shown that α,β-unsaturated acylsilanes serve as highly reactive carboxylic acid equivalents in the same conjugate allylation with allylsilane derivatives.

In searching for a new synthetic useful α,β-unsaturated carboxylic acid equivalent in conjugate allylation with allylsilane derivatives, α,β-unsaturated N-acyloxazolidinones appear to be the most attractive Michael acceptors. The unsaturated N-acyloxazolidinones have been ultilized as excellent electrophiles in many reactions. For instances, asymmetric conjugate addition with organocuprates[6], dialkyl aluminum chlorides[7] and enamines[8] to α,β-unsaturated N-acyloxazolidinones, chiral titanium reagent catalyzed asymmetric [2 + 2] cycloaddition reactions,[9] Lewis acids catalyzed Diels-Alder reaction,[10] and ene reaction.[11] We report herein the Lewis acid catalyzed conjugate addition of allyltrimethylsilane to α,β-unsaturated N-acyloxazolidinone and the enantioselectivity of the conjugate allylation induced by the chiral N-acyloxazolidinones.

RESULTS AND DISCUSSION

Conjugate Allylation of 1. All the α,β-unsaturated N-acyloxazolidinones were readily synthesized by successive treatment of the corresponding acylchloride with the oxazolidinones (after deprotonation with BuLi).[10a] The conjugate addition of allyltrimethylsilane to α,β-unsaturated N-acyloxazolidinones indeed proceeds very rapidly even at -78 °C in the presence of $TiCl_4$. The general reaction was done by using three molar equivalents of both $TiCl_4$ and allyltrimethylsilane (**2**) to the substrate. (eq. 1) The results are summarized in Table I. Based on the described reaction condition as above, substrate **1a** gave the allylation product **3a** in 76 % yield. However, when the reaction was carried out at room temperature, a small amount of cyclopentane product **4a** was observed.[12] Interestingly, when $BF_3{\cdot}OEt_2$ was employed as a Lewis acid in this reaction, the conjugate addition adduct **3a** was obtained in 45 % yield (based on recovered 28 % of starting **1a**) as the only product. In a similar manner, the reaction of **1b** with allyltrimethylsilane catalyzed by $BF_3{\cdot}OEt_2$, **3b** was obtained in 74 % yield. Again no cyclopentane adduct was observed. A control experiment demonstrated that the allylation adduct **3a** could not be converted to cyclopentane **4a** by warming the cold (-78 °C) reaction mixture to room temperature prior to aqueous workup. With this experiment, compound **3a** was obtained in 76 % yield and no cyclopentane product **4a** was observed.



1a-f **3a-f** **4a-f**

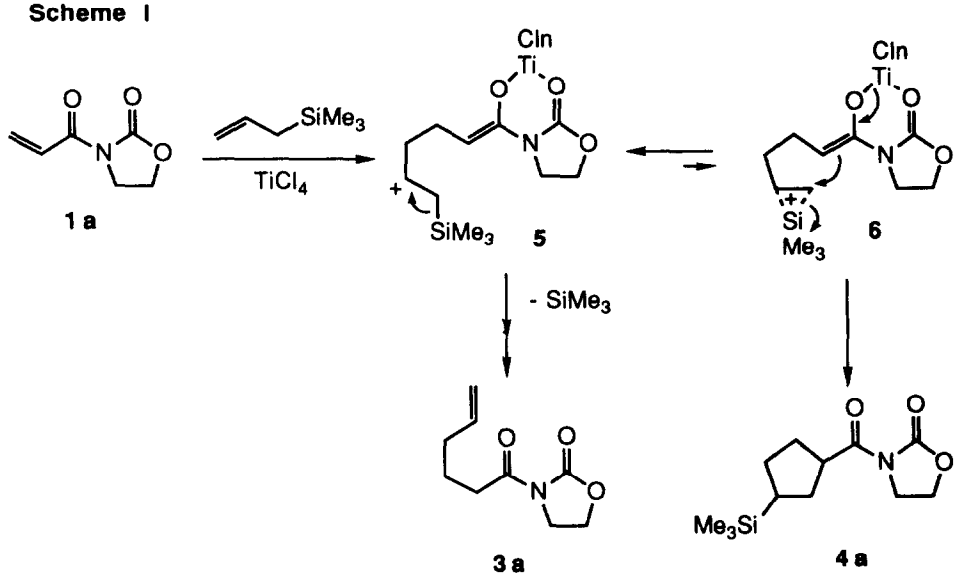
Table I. Conjugate Addition of **1a-f** with Allyltrimethylsilane[a]

entry	substrate	R_1	R_2	Lewis acid[b]	T(°C)/t(h)[c]	yield of **3**,%	yield of **4**, %
1	**1a**	H,	H	$TiCl_4$	25/5	41	38
2	**1a**	H,	H	$TiCl_4$	-78/5	76	0
3	**1a**	H,	H	$BF_3{\cdot}OEt_2$	25/168	45	0
4	**1b**	CH_3,	H	$TiCl_4$	25/2	65	7
5	**1b**	CH_3,	H	$BF_3{\cdot}OEt_2$	25/96	74	0
6	**1c**	H,	CH_3	$TiCl_4$	-78/5	65	0
7	**1d**	CH_3,	CH_3	$TiCl_4$	25/2	81[d]	0
8	**1e**	Ph,	H	$TiCl_4$	25/2	45	0
9	**1f**	CO_2Et,	H	$TiCl_4$	-78/5	87	0
10	**1g**	(E)-CH_3CH=CH	H	$BF_3{\cdot}OEt_2$	25/216	32	0

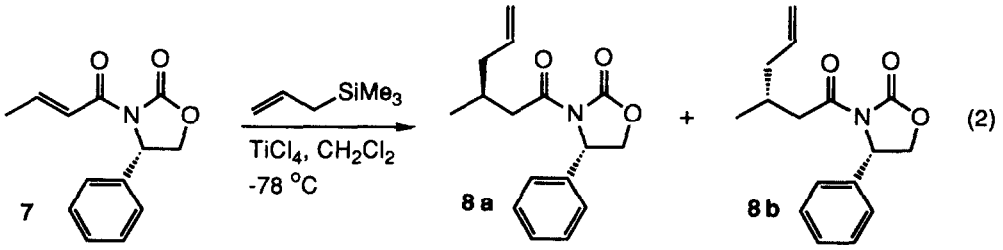
[a]CH_2Cl_2 as a solvent unless otherwise mentioned. [b]$AlCl_3$, $ZnCl_2$, and $SnCl_4$ were found not to be sufficient to promote this reaction. [c]T = temperature, t = time. [d]as a 3 to 1 mixture of erytho and threo isomers, the stereochemistry of the major diastereomer has not been decided.

The reaction pathways for the formation of cyclopentanes and conjugate allylation adducts have previously been described by Snider and Zhang.[11b] Addition of allyltrimethylsilane to **1a** affords the cation intermediate **5** which can loss the trimethylsilyl group to give **3a** or undergo 1,2-trimethylsilyl shift followed by ring closure to give **4a** as shown in scheme I. The rate of these two competing pathways will be the facter to determine the ratio of these two products. According to our observation, when the reaction was promoted by $TiCl_4$, the activation energy of the ring closure process seems to be higher than that of the loss of trimethylsilyl group. Therefore, the conjugate allylation adduct was formed predominently at -78 °C and as increasing of the reaction temperature (25 °C), the cyclopentane adduct was observed. On the other hand, the absense of cyclopentane adduct when $BF_3{\cdot}OEt_2$ was used as a Lewis acid could be due to the fast loss of trimethylsilyl group induced by the more electronegative fluoride ion generated in the reaction mixture. A typical example was shown by the reaction of dienic N-acyl oxazolidinone **1g** with allyltrimethylsilane. When the reaction was promoted by $TiCl_4$ at room temperature, a very complex products mixture was obtained. But when $BF_3{\cdot}OEt_2$ was employed in this reaction, 1,4-addition adduct **3g** was isolated very cleanly in 32 % yield and recovered 10 % of starting **1g**.

Scheme I

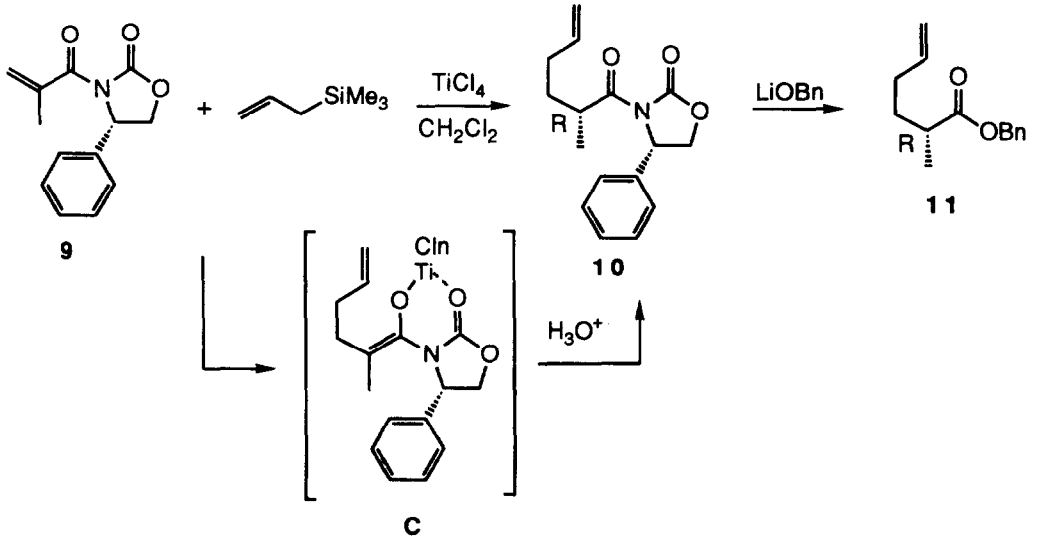


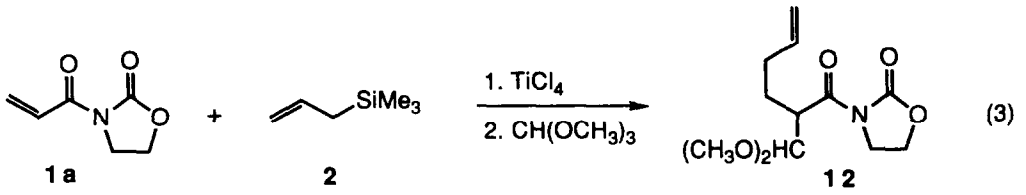
Asymmetric Conjugate Allylation of 7 and 9. Recently, we have reported[13] the asymmetric conjugate addition of allyltrimethylsilane to α,β-unsaturated N-acylamides by employing chiral oxazolidinones and camphor sultam[14] as chiral auxiliaries. In the case of reaction of compound **7** with allyltrimethylsilane in the presence of $TiCl_4$ at -78 °C, products **8a**[15] and **8b**[15] were obtained as a 89:11 mixture of diastereoisomers.(eq. 2) Purification by flash column chromatography gave **8a** in 88% yield with 84% de.



We next turn our attention to the diastereoselectivity of conjugate addition of allyltrimethylsilane to α-substituted α,β-unsaturated N-acyloxazolidinones. Thus compound **9** was prepared from methacryloyl chloride and (4S)-4-phenyloxazolidinone according to Evan's method. The reaction of **9** with allyltrimethylsilane in the presence of 3 molar equiv of $TiCl_4$ at -78 °C gave the conjugate allylation adduct **10** as a 94:6 diastereomeric mixture in 93% yield. The optically pure **10** was obtained by purification with column chromatography on silica gel (ethyl acetate-hexane, 1:9). The absolute configuration of **10** was determined as **R** by the convertion of **10** to the corresponding benzyl ester **11** ($PhCH_2OLi$-THF) and comparison of the optical rotation of this benzyl ester with that of the literature.[16] The stereoselectivity can be rational as that addition of allyltrimethylsilane to compound **9** in the presence of $TiCl_4$ would generate titanium enolate **C**. Upon aqueous workup, protonation occurrs from top face to produce the **R** configuration at C(α). (scheme II) In order to approve that titanium enolate[17] has involved in this reaction, a trapping experiment was carried out. Reaction of allyltrimethylsilane and **1a** in the presence of $TiCl_4$ at -78 °C, followed by addition of trimethyl orthoformate gave **12** in 74 % yield. (eq. 3)

Scheme II





1a 2 12

Solvent Effect. When the reaction of **9** with allyltrimethylsilane in the presence of $TiCl_4$ was carried out at room temperature, **10** was obtained in only 44 % diastereomeric excess. In order to make this reaction more practical useful, the stereoselectivity should be optimized by carring out the reaction at room temperature. Since Narasaka and coworkers[10b] have reported that the donor and acceptor ability of the solvent is an important factor to display the enantioselectivity of chiral titanium reagent catalyzed Diels-Alder reaction, we therefore examined the possibility of using less polar solvent to achieve high diastereoselectivity in the presented conjugate addition reaction. The results are summerized in Table II. The same tendency was observed as that of the report by Narasaka. The diastereoselectivity is dependent on the number of methyl group on the benzene ring. The highest selectivity was attained by employment of mesitylene as the solvent and the allylation adduct **10** was obtained in 86% yield with 68% de. We have also found that fluorobenzene provided higher stereoselectivity than chlorobenzene. This is due to the stronger inductive ability of fluorine to reduce the molecular interaction. Therefore, the stability of the titanium complex with the electrophile is very important to the stereoselectivity. However, when ethyl ether or single hydrocarbon (hexane, pet ether, or $CF_2ClCFCl_2$) was employed in this reaction, no reaction occured due to the poor solubility of **9** in these solvents.

Table II. Diastereoselectivity in the Reaction of **9** with Allyltrimethylsilane in Various Solvents

sovent	de of **10**, %[a]	yield, %
methylene chloride	44	80
benzene	36	35
toluene	60	56
mesitylene	68	86
chlorobenzene	52	76
fluorobenzene	58	87
benzene-ligroin (1:1)	62	36
toluene-$CF_2ClCFCl_2$ (1:1)	68	42
toluene-PE (2:1)	62	44

[a]Determined by using 200-MHz ^{1}H-NMR spectroscopy of the crude product.

Additive Effect. On the other hand, by addition of powdered 4A molecular sieve (MS 4A) to enhance the enantioselectivity has been found in many asymmetric synthesis.[10b,18] We thus test the stereoselectivity by addition

of powdered 4A molecular sieve (0.1 g for 1 mmol of substrate)[19] into the reaction mixture of **9** with allyltrimethylsilane, the allylation adduct was obtained in 76% de. 3A molecular sieve was also employed in this study and only 55 % de was obtained. Some other additives having dehydrating ability, such as $CaCl_2$, Na_2CO_3, and $MgSO_4$, were found to have less effect on the stereoselectivity. Although the exact role of molecular sieve in this reaction is still unknown, it is possible due to the so-called "transition-state shape selectivity".[20]

CONCLUSION

We have demonstrated that conjugate addition of allyltrimethylsilane to α,β-unsaturated carboxylic acid can be achieved by derivation of the acid to its corresponding N-acyloxazolidinone. The highly enantioselective conjugate allylation has been achieved by employing the chiral oxazolidinones. To enhance the diastereoselectivity at ambient temperature, mesitylene can be chosen as a solvent or by addition of powdered 4A molecular sieve into the reaction mixture. The application of this methodology to the synthesis of optically pure medicinally interest compounds are currently under investigation.

EXPERIMENTAL SECTION

Melting points were determined on a Yanaco MP apparatus and uncorrected. Infrared spectra were recorded on a Hitachi 260-30 spectrometer. ^1H NMR and ^{13}C NMR were recorded on a Varian XL-200E spectrometer. All chemical shifts are reported in ppm using tetramethylsilane as internal standard. Elemental analysis were performed on a Hereus CHNO rapid analyser. Low resolution mass spectra were recorded on a JEOL SX-102A and high resolution spectra were recorded on a JEOL JMX-HX 110 spectrometer. Methylene chloride was distilled from CaH_2. Allyltrimethylsilane was purchased from Janssen and titanium tetrachloride was purchased from Merck. All substrate unsaturated N-acyloxazolidinones were readily synthesized by the treatment of the corresponding acid chloride with the oxazolidinone (after deprotonation with BuLi).[10a] All reactions were carried out in predried glassware and under nitrogen atmosphere.

General Procedure for the Reaction of Allyltrimethylsilane and α,β-Unsaturated N-Acyloxazolidinones. To a CH_2Cl_2 solution of α,β-unsaturated N-acyloxazolidinone (1 mmol in 10 mL of CH_2Cl_2) was added $TiCl_4$ (0.569 g, 3 mmol) at the described temperature under nitrogen atmosphere. After stirring for 10 min, allyltrimethylsilane (0.342 g, 3 mmol) was added into the reaction mixture. The resulting solution was stirred and quenched with a saturated sodium bicarbonate solution. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic extracts were washed with brine and dried over anhydrous magnesium sulfate. After removal of solvent, the residue was purified by flash chromatography on silica gel to afford the desired product.

3-(5-Hexenoyl)-2-oxazolidinone (3a). Reaction of allyltrimethylsilane, **1a**, and $TiCl_4$ at -78 °C for 5 h. Flash column chromatography (25 % ethyl acetate in hexane as eluent) gave **3a** (76 %) as a pale-yellow oil: IR (neat) 1780, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.79 (ddt, 1 H, J = 17.0, 10.2, 6.6 Hz), 4.93-5.08 (m, 2 H), 4.40 (t, 2 H, J = 8.0 Hz), 4.00 (t, 2 H, J = 8.0 Hz), 2.92 (t, 2 H, J = 7.2 Hz), 2.04-2.17 (m, 2 H), 1.76 (quintet, 2 H);

^{13}C NMR ($CDCl_3$) δ 173.3, 153.5, 137.7, 115.2, 62.0, 42.5, 34.4, 32.9, 23.3; MS(EI) 183 (M^+, 14.2), 129 (100); HRMS calcd for $C_9H_{13}NO_3$ 183.0896, found 183.0902.

3-(((3-Trimethylsilyl)cyclopentyl)carbonyl)-2-oxazolidinone (4a). Reaction of allyltrimethylsilane, **1a**, and $TiCl_4$ at 25 °C for 2 h. Flash column chromatography (10 % ethyl acetate in hexane as eluent) gave **3a** (41 %) and **4a** (38 %) as a pale-yellow oil: IR (neat) 1790, 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.36-4.44 (m, 2 H), 3.96-4.05 (m, 2 H), 3.82-3.93 (m, 1 H), 1.02-2.02 (m, 7 H), -0.03 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 176.9, 153.3, 61.8, 43.5, 42.9, 32.3, 31.1, 28.9, 26.2, -3.1; MS(EI) 255 (M^+, 3.9), 214 (100); HRMS calcd for $C_{12}H_{21}NO_3Si$ 255.1291, found 255.1293.

3-(3-Methyl-5-hexenoyl)-2-oxazolidinone (3b) and 3-(((2-methyl-4-trimethylsilyl)cyclopentyl)carbonyl)-2-oxazolidinone (4b). Reaction of allyltrimethylsilane, **2b**, and $TiCl_4$ at 25 °C for 2 h. Flash column chromatography (10 % isopropyl alcohol in hexane as eluent) gave **3b** (65 %) and **4b** (7 %). Both were pale-yellow oil.

The data for **3b**: IR (neat) 1780, 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.76 (ddt, 1 H, J = 16.8, 10.2, 6.6 Hz), 4.96-5.06 (m, 2 H), 4.39 (t, 2 H, J = 8.1 Hz), 3.94 (t, 2 H, J = 8.1 Hz), 2.83 (m, 2 H), 1.96-2.20 (m, 3 H), 0.95 (d, 3 H, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 172.6, 153.4, 136.4, 116.3, 61.8, 42.4, 41.1, 40.8, 29.2, 19.5; MS(EI) 197 (M^+, 6.6), 41 (100); HRMS calcd for $C_{10}H_{15}NO_3$ 197.1052, found 197.1057.

The data for **4b**: IR (neat) 1795, 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.33-4.99 (m, 2 H), 3.96-4.06 (m, 2 H), 3.40-3.73 (m, 1 H), 0.89-2.44 (m, 9 H), -0.04 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 176.6, 153.3, 61.8, 50.9, 42.9, 39.9, 37.7, 32.8, 25.7, 18.8, -3.2; MS(EI) 269 (M^+, 2.3), 228 (100); HRMS calcd for $C_{13}H_{23}NO_3Si$ 269.1448, found 269.1450.

3-(2-Methyl-5-hexenoyl)-2-oxazolidinone (3c). Reaction of allyltrimethylsilane, **1c**, and $TiCl_4$ at -78 °C for 5 h. Flash column chromatography (25 % ethyl acetate in hexane as eluent) gave **3c** (65 %) as a colorless oil: IR (neat) 1790, 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.76 (ddt, 1 H, J = 16.8, 10.2, 6.6 Hz), 4.90-5.02 (m, 2 H), 4.38 (t, 2 H, J = 7.7 Hz), 3.99 (t, 2 H, J = 7.7 Hz), 3.72 (sextet, 1 H, J =6.9 Hz), 2.03-2.08 (m, 2 H), 1.49-2.00 (m, 2 H), 1.13 (d, 3 H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 177.7, 153.6, 138.5, 115.3, 62.3, 43.3, 37.3, 33.1, 31.8, 17.5; MS(EI) 197 (M^+, 2.5), 84 (100); HRMS calcd for $C_{10}H_{15}NO_3$ 197.1052, found 197.1054.

3-(2,3-Dimethyl-5-hexenoyl)-2-oxazolidinone (3d). Reaction of allyltrimethylsilane, **1d**, and $TiCl_4$ at 25 °C for 2 h. Flash column chromatography (20 % ethyl acetate in hexane as eluent) gave a pale-yellow oil **3d** (81 %) as a 2:1 mixture of stereoisomers: IR (neat) 1780, 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.63-5.81 (m, 1 H), 4.92-5.00 (m, 2 H), 4.37 (t, 2 H, J = 7.9 Hz), 3.92-4.09 (m, 2 H), 3.63-3.70 (m, 1 H), 1.76-2.21 (m, 3 H), 1.10 (d, 2 H, J = 6.9 Hz), 1.05 (d, 1 H, J = 6.9 Hz) (minor), 0.89 (d, 2 H, J = 6.4 Hz), 0.83 (d, 1 H, J = 6.6 Hz) (minor); ^{13}C NMR ($CDCl_3$) δ 176.9, 153.2, 136.9 (minor), 136.5, 116.2, 115.9 (minor), 61.7, 42.7, 41.7, 41.3 (minor), 39.8 (minor), 36.7, 35.4, 34.7 (minor), 17.4, 15.1 (minor), 13.6, 12.4 (minor); MS(EI) 211 (M^+, 5.4), 143 (100); HRMS calcd for $C_{11}H_{17}NO_3$ 211.1209, found 211.1205.

3-(3-Phenyl-5-hexenoyl)-2-oxazolidinone (2e). Reaction of allyltrimethylsilane, **1e**, and $TiCl_4$ at 25 °C for 2 h. Flash column chromatography (25 % ethyl acetate in hexane as eluent) gave **3e** (45 %) as a colorless solid: mp 160-161 °C; IR (KBr) 1785, 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.15-7.33 (m, 5 H), 5.67 (ddt, 1 H, J = 17.0, 10.0, 7.0 Hz), 4.93-5.07 (m, 2 H), 3.80-4.38 (m, 4 H), 3.16-3.46 (m, 3 H), 2.42 (t, 2 H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 172.4, 153.9, 144.2, 136.6, 128.8, 128.1, 126.9, 117.2, 62.4, 42.9, 41.7, 41.2, 41.1; MS(EI) 259 (M^+, 3.0), 131 (100); HRMS calcd for $C_{15}H_{17}NO_3$ 259.1209, found 259.1205.

3-(3-Ethoxycarbonyl-5-hexenoyl)-2-oxazolidinone (3f). Reaction of allyltrimethylsilane, **1f**, and $TiCl_4$ at -78 °C for 5 h. Flash column chromatography (50 % ethyl acetate in hexane as eluent) gave **3f** (87 %) as a colorless oil: IR (neat) 1780, 1730, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.85 (ddt, 1 H, J = 16.8, 10.2, 6.6 Hz), 5.01-5.12 (m, 2 H), 4.39 (t, 2 H, J = 8.1 Hz), 4.11 (q, 2 H, J = 7.1 Hz), 3.97 (t, 2 H, J = 8.1 Hz), 3.33 (dd, 1 H, J = 19.0, 10.8 Hz), 2.90-3.30 (m, 2 H), 2.24-2.43 (m, 2 H), 1.22 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 174.3, 171.7, 153.5, 134.4, 117.7, 62.1, 60.6, 42.3, 40.2, 36.3, 35.9, 14.1; MS(EI) 255 (M^+, 24), 28 (100); HRMS calcd for $C_{12}H_{17}NO_5$ 255.2207, found 255.1108.

3-(3-(1-Propenyl)-5-hexenoyl)-2-oxazolidinone (3g). Reaction of allyltrimethylsilane (3 eq), **1g**, and $BF_3{\cdot}OEt_2$ (3 eq) at 25 °C for 9 days. Flash column chromatography (25 % ethyl acetate in hexane as eluent) recovered starting **1g** (10 %) and gave **3g** (32 %) as a colorless oil: IR (neat) 1785, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.64-5.84 (m, 1 H), 5.24-5.55 (m, 2 H), 4.97-5.06 (m, 2 H), 3.94-4.42 (m, 4 H), 2.84-3.05 (m, 2 H), 2.68 (sextet, 1 H, J = 7.0 Hz), 2.14 (t, 2 H, J = 7.0 Hz), 1.62 (d, 3 H, j = 6.0 Hz); ^{13}C NMR ($CDCl_3$) δ 172.3, 153.4, 136.3, 133.3, 125.6, 116.4, 61.9, 42.5, 39.6, 39.4, 38.3, 17.9; MS(EI) 223 (M^+, 6.0), 95 (100); HRMS calcd for $C_{12}H_{17}NO_3$ 223.1209, found, 223.1205.

(4S)-3-(3-Methyl-5-hexenoyl)-4-phenyl-2-oxazolidinone (8a and 8b). Reaction of allyltrimethylsilane, **7**, and $TiCl_4$ at -78 °C for 3 h. Flash chromatography (9:1 hexane-EtOAc) gave 88 % of a 11.5 to 1 mixture of **8a** and **8b** as an oil.

The data for **8a** and **8b**: IR (neat) 1780, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.22-7.37 (m, 5 H), 5.60-5.80 (m, 1 H), 5.37 (dd, 1 H, J = 8.8, 3.8 Hz), 4.95 (d, 2 H, J =12.1 Hz), 4.60 (t, 1 H, J = 8.8 Hz), 4.17 (dd, 1 H, J = 8.8, 3.8 Hz), 2.60-3.02 (m, 2 H), 1.80-2.15 (m, 3 H), 0.85 (**8a**), 0.84 (**8b**) (two sets of doublet, 3 H overall, J = 6.4 Hz each); ^{13}C NMR ($CDCl_3$) δ 173.71, 155.20, 140.69, 137.84, 130.36, 129.85, 127.09, 117.60, 70.60, 58.21, 42.21, 41.23, 29.88, 19.86; MS (EI) 273 (M^+, 52), 205 (100); HRMS cacld for $C_{16}H_{19}NO_3$ 273.1365, found 273.1378.

(4S)-3-((2R)-Methyl-5-hexenoyl)-4-phenyl-2-oxazolidinone (10). Reaction of allyltrimethylsilane, **9**, and $TiCl_4$ at -78 °C for 2 h gave crude **10** as a 16:1 mixture of diastereoisomers. Flash column chromatography (10 % ethyl acetae in hexane as eluent) gave the optically pure **10** (88 %) as a colorless solid: $[\alpha]_D^{25}$ +37.4 (c 1.00, $CHCl_3$); mp 53-54 °C; IR (KBr) 1780, 1695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.27-7.43 (m, 5 H), 5.60-5.77 (m, 1 H), 5.43 (dd, 1 H), J = 8.8, 4.0 Hz), 4.85-4.95 (m, 2 H), 4.67 (t, 1 H, J = 8.8 Hz), 4.24 (dd, 1 H, J = 8.8 Hz), 3.77 (sextet, 1 H, J = 6.8 Hz), 1.42-1.98 (m, 4 H), 1.14 (d, 3 H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 176.5, 153.3,

139.2, 137.9, 129.1, 128.7, 126.0, 114.9, 69.7, 57.8, 37.1, 32.8, 30.9, 16.4; MS(EI) 273 (M^+, 25.6), 219 (100); HRMS calcd for $C_{16}H_{19}NO_3$ 273.1366, found 273.1360; Anal. Calcd for $C_{16}H_{19}NO_3$: C, 70.31; H, 7.00; N, 5.12. Found: C, 70,00; H, 6.98; N, 5.15.

(2R)-(-)-Benzyl 2-Methyl-5-hexenoate (11). To a stirred solution of benzyl alcohol (0.108 g, 1 mmol) in dry THF (10 mL) was added nBuLi (1.6 M in hexane, 0.63 mL, 1 mmol) at 0 °C. After stirring at 0 °C for 10 min, a solution of **10** (0.273 g, 1 mmol) in dry THF (10 mL) was added into the reaction mixture. The resulting solution was stirred for additional 2 h at 0 °C, quenched with saturated ammonium chloride solution, and extracted with ethyl acetate (10 mL x 3). The combined organic extracts were washed with brine and dried over anhydrous $MgSO_4$. Removal of solvent gave **11** (0.20 g, 89 %) as a colorless oil: $[\alpha]_D^{25}$ -14.1 (c 1.01, $CHCl_3$) [lit.[16] $[\alpha]_D^{25}$ -11.3 (c 2.9, $CHCl_3$)]; IR (neat) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.36 (s, 5 H), 5.78 (ddt, 1 H, J = 16.9, 10.4, 6.6 Hz), 5.13 (s, 2 H), 4.93-5.06 (m, 2 H), 2.54 (sextet, 1 H, J = 7.0 Hz), 1.98-2.12 (m, 2 H), 1.47-1.91 (m, 2 H), 1.19 (d, 3 H); ^{13}C NMR ($CDCl_3$) δ 176.3, 137.8, 136.2, 128.5, 128.0, 127.9, 115.0, 66.0, 38.8, 32.8, 31.3, 16.9; MS(EI) 218 (M^+, 24.6), 91 (100).

3-(2-Dimethoxymethyl-5-hexenoyl)-2-oxazolidinone (12). To a stirring solution of **1a** (0.14 g, 1 mmol) in dry CH_2Cl_2 (10 mL) containing $TiCl_4$ (0.36 mL, 3 mmol) was added allyltrimethylsilane (0.48 mL, 3 mmol) at -78 °C. After stirring at -78 °C for 5 h, trimethyl orthoformate (0.53 g, 5 mmol) was added into the reaction mixture. The resulting solution was allowed to warm to room temperature and stirred for additional 25 h, quenched with saturated ammonium chloride, and extracted with ethyl acetate (15 mL x 3). The combined organic extracts were washed with brine and dried over anhydrous $MgSO_4$. After removal of solvent, the residue was purified with flash column chromatography (20 % ethyl acetate in hexane as eluent) to give **12** (0.19 g, 74 %) as a pale-yellow oil: IR (neat) 1780, 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.75 (ddt, 1 H, J = 16.8, 10.2, 6.6 Hz), 4.90-5.04 (m, 2 H), 4.34-4.57 (m, 4 H), 3.97-4.06 (m, 2 H), 3.31 (s, 6 H), 1.70-2.08 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 173.7, 153.2, 137.9, 115.0, 105.1, 61.6, 55.2, 51.8, 44.6, 42.7, 31.1, 27.8; MS(EI) 257 (M^+, 0.07), 75 (100); HRMS calcd for $C_{12}H_{19}NO_5$ 257.1264, found 257.1263.

ACKNOWLEDGEMENT

We are grateful to the National Science Council of Republic of China for the financial support. We thank Dr. Lendon Pridgen, SmithKline & Beecham Pharmaceuticals for the gift of chiral oxazolidinones.

REFERENCES AND NOTES

1. This work was presented in part at the 204th National ACS Meeting in Washington D. C., Aug. 1992.
2. Hosomi, A.; Sakurai, H. *J. Am. Chem. Soc.* **1977**, *99*, 1673.
3. Majetich, G.; Casares, A. M.; Chapman, D.; Behnke, M. *Tetrahedron Lett.* **1983**, *24*, 1909.
4. Jellal, A.; Santelli, M. *Tetrahedron Lett.* **1980**, *21*, 4487.
5. Danheiser, R. L.; Fink, D. M. *Tetrahedron Lett.* **1985**, *26*, 2509.
6. Nicolas, E.; Russell, K. C.; Hruby, V. J. *J. Org. Chem.* **1993**, *58*, 766.
7. Ruck, K.; Kunz, H. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 694.

8. Hayashi, Y.; Otaka, K.; Saito, N.; Narasaka, K. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2122.
9. Narasaka, K.; Hayashi, Y.;Shimadzu, H.; Niihata, S. *J. Am. Chem. Soc.* **1992**, *114*, 8869.
10. (a) Evans, D. A.; Chapman, K. T.; Bisaha, J. *J. Am. Chem. Soc.* **1988**, *110*, 1238. (b) Narasaka, K.; Iwasawa, N.; Inoue, M.; Yamada, T.; Nakashima, M.; Sugimori, J. *J. Am. Chem. Soc.* **1989**, *111*, 5340.
11. (a) Narasaka, K.; Hayashi, Y.; Shimada, S. *Chem. Lett.* **1988**, 1609. (b) Snider, B. B.; Zhang, Q. *J. Org. Chem.* **1991**, *56*, 4908.
12. The annulation adducts have occasionally been observed in Sakurai reaction involving allylsilanes: (a) Hartman, G. D.; Traylor, T. G. *Tetrahedron Lett.* **1975**, 939. (b) Pardo, R.; Zahra, J. P.; Santelli, M. *Tetrahedron Lett.* **1979**, 4557. (c) Hosomi, A.; Kobayashi, H.; Sakurai, H. *Tetrahedron Lett.* **1980**, *21*, 955. (d) Danishefsky, S.; Kahn, M. *Tetrahedron Lett.* **1981**, *22*, 485. (e) House, H. O.; Gaa, P. C.; Van-Derveer, D. *J. Org. Chem* **1983**, *48*, 1661. (f) Nickisch, K.; Laurent, H. *Tetrahedron Lett.* **1988**, *29*, 1533. (g) Majetich, G.; Defauw, J.; Ringold, C. *J. Org. Chem.* **1988**, *53*, 50. (h) Knolker, H. J.; Jones, P. G.; Pannek, J. B. *Synlett* **1990**, 429. (i) Imazu, S.; Shimizu, N.; Tsuno, Y. *Chem. Lett.* **1990**, 1845. (j) Danheiser, R. L.; Dixon, B. R.; Gleason, R. W. *J. Org. Chem.* **1992**, *57*, 6094. (k) Knolker, H. J.; Foitzik, N.; Goesmann, H.; Graf, R. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1081. (l) Panek, J. S.; Jain, N. F. *J. Org. Chem.* **1993**, *58*, 2345.
13. Wu, M. J.; Wu, C. C.; Lee, P. C. *Tetrahedron Lett.* **1992**, *33*, 2547.
14. (a) Oppolzer, W.; Poli, G.; Kingma, A. J.; Starkemann, C.; Bernardinelli, G. *Helv. Chim. Acta* **1987**, *70*, 2201. (b) Oppolzer, W. *Tetrahedron* **1987**, *43*, 1969. (c) Curran, D. P.; Heffner, T. A. *J. Org. Chem.* **1990**, *55*, 4585.
15. The stereochemistry of **8a** and **8b** were not exactly determined. However, based on the proposed reaction mechanism in ref. 13, we presumed that the absolute configuration at C(β) of **8a** is **S** and that of **8b** is **R**.
16. Boeckman, Jr. R. K.; Charette, A. B.; Asberom, T.; Johnston, B. H. *J. Am. Chem. Soc.* **1991**, *113*, 5337.
17. Evans, D. A.; Urpi, F.; Somers, T. C., Clark, J. S.; Bilodeau, M. T. *J. Am. Chem. Soc.* **1990**, *112*, 8215.
18. (a) Mikami, K.; Terada, M.; Nakai, T. *J. Am. Chem. Soc.* **1990**, *112*, 3949. (b) Maruoka, K.; Hoshino, Y.; Shirasaka, T.; Yamamoto, H. *Tetrahedron Lett.* **1988**, *29*, 3967. (c) Hanson, R. M.; Sharpless, K. B. *J. Org. Chem.* **1986**, *51*, 1922.
19. These reactions were carried out with 1 mmol of **9** in CH_2Cl_2 (10 mL) at room temperature. The amount of molecular sieve required to obtained the highest stereoselectivity has been examined and found that 0.1 g of 4A emolecular sieve to 1 mmol of substrate is the minimun quantity.
20. (a) Haber, M.; Pindur, U.*Tetrahedron* **1991**, *47*, 1925. (b) Pindur, U.; Lutz, G.; Otto, C. *Chem. Rev.* **1993**, *93*, 741.

(*Received in Japan* 27 *September* 1993; *accepted* 25 *October* 1993)