November, 1988] © *1988 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***61**, 4051—4055 (1988)*

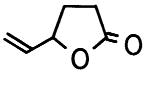
Highly Regio- and Stereoselective Ring-Opening Reaction of γ-Alkenyl-γ-butyrolactones with Allylsilanes in the Presence of Trimethyloxonium Salt Leading to Methyl 4,8-Alkadienoates

Masatoshi KAWASHIMA and Tamotsu FUJISAWA*
Chemistry Department of Resources, Mie University, Tsu, Mie 514
(Received June 29, 1988)

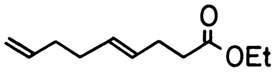
The reaction of γ-alkenyl-γ-butyrolactones with allylic trimethylsilanes in the presence of trimethyloxonium tetrafluoroborate proceeded regio- and stereoselectively with an allylic rearrangement of the substrate to afford methyl (*E*)-4,8-alkadienoates in high yields. On the other hand, the ring opening of 4-hexen-6-olide afforded exclusively methyl (*Z*)-4,8-alkadienoates in high yields. The synthetic utility of the reaction was demonstrated by the short step synthesis of β-sinensal and β-farnesene.

Alkadienoic acids possessing 1,5-diene structure such as 2,6-, 3,7-, and 4,8-alkadienoic acids are incorporated in terpenoid carboxylic acids and many synthetic methods have been developed. For example, the Claisen rearrangement of 2-alkenoic acid allylic esters via trimethylsilylketene acetals produces 3-carboxy-1,5-diene derivatives, which are subsequently converted into 2,6-alkadienoic acids by the Cope rearrangement.[1] Palladium-catalyzed carbonylation accompanying allylic rearrangement of 3-hydroxy-1,6-diene derivatives gives 3,7-alkadienoic acids.[2] The Claisen rearrangement of 3-acetoxy-1,6-heptadiene via *t*-butyldimethylsilylketene acetal gives 4,8-nonadienoic acid.[3] In these synthetic methods, there is no example which satisfies both convenience of the operative procedure and the stereoselectivity of the carbon–carbon double bond. In our laboratory, the ring opening of ω-alkenyllactones such as β-alkenyl-β-propiolactone, γ-vinyl-γ-butyrolactone, and δ-vinyl-δ-valero lactone with organocopper reagents were developed and utilized for the synthesis of the various kinds of alkenoic acids.[4] Alkadienoic acids such as 3,7- ,4,8-, and 5,9-alkadienoic acids were prepared by this method using diallylcuprate, however, the product yields are not so high and the predomination of *E*-configuration of the carbon–carbon double bond is not perfect. The reason may be due to the lack of thermal stability of the cuprate and formation of copper π-allyl complex.[5] The yield and the stereoselectivity of the carbon–carbon double bond of 4,8-nonadienoic acid obtained by the ring opening of γ-vinyl-γ-butyrolactone are the lowest among these alkadienoic acids and not adequate for the further utilization of the acid. Therefore to develop more stereoselective synthetic method of 4,8-alkadienoic acids or their esters, allylsilane, which is thermally stable compound, was noticed for the nucleophile as the source of allyl group toward the ring opening of γ-vinyl-γ-butyrolactone. The present paper describes details on the regio- and stereoselective reaction of γ-alkenyl-γ-butyrolactones and the analogous lactone, 4-hexen-6-olide, with allylsilanes in the presence of trimethyloxonium tetrafluoroborate to afford methyl (4*E*)- and (4*Z*)-4,8-alkadienoates in high yields, respectively.[6]

The reactions of allylsilane with acetal,[7] aldehyde,[8] enone,[9] and so on,[10] are achieved in the presence of the activator of the electrophile such as Lewis acids because of the low nucleophilicity of allylsilane. Therefore, the reactions of γ-vinyl-γ-butyrolactone (**1**) with allyltrimethylsilane were carried out in the presence of catalytic or equimolar amount of Lewis acid such as $TiCl_4$, $SnCl_4$, $AlCl_3$, $Me_3SiOSO_2CF_3$, and Me_3SiI, however, the desired allylation of the lactone did not proceed to result in a recovery of the starting material **1**. When the Meerwein reagent, triethyloxonium tetrafluoroborate, which was known as the ethylating agent of the oxygen atom of γ-butyrolactone,[11] was used as the activator of the lactone **1**, the reaction of **1** with allylsilane proceeded in CH_2Cl_2 at room temperature to afford ethyl 4,8-nonadienoate (**2**) in 49% yield accompanying with many complex products formed by the over alkylation of the initial product **2**. Since the side reaction seemed to be attributed to the high reactivity of triethyloxonium salt, trimethyloxonium tetrafluoroborate was used instead of triethyloxonium salt resulting in remarkable increase of the yield of the corresponding methyl ester, methyl 4,8-nonadienoate (**3a**) (100%) in spite of heterogeneous reaction. The product showed the regioselective attack of allylsilane to the terminal vinyl carbon of the lactone **1** without accompanying the attack to the γ-carbon. The present result of the allylic rearrangement of the electrophile in the reaction of allylic silanes has been rarely reported.[12] Moreover the exclusive *E*-configuration of the newly formed carbon–carbon double bond of the ester **3a** was confirmed by NMR, IR spectra, and GLPC analysis in



1



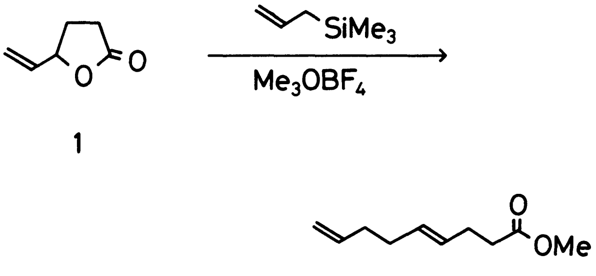
2

Table 1. Ring Opening of γ-Vinyl-γ-butyrolactone[a]

Oxonium salt	Solvent	Temp	Time/h	Yield of Ester/%
Et_3OBF_4	CH_2Cl_2	rt	13	49
Me_3OBF_4	CH_2Cl_2	rt	94	100
Me_3OBF_4	CH_2Cl_2	reflux	8	83
Me_3OBF_4	$CHCl_3$	reflux	10	72
Me_3OBF_4	Benzene	rt	94	—[b]
Me_3OBF_4	CH_2Cl_2-CH_3NO_2	rt	13	26

a) The molar ratio of lactone, oxonium salt, and allylsilane is 1:2:3. b) No reaction proceeded.

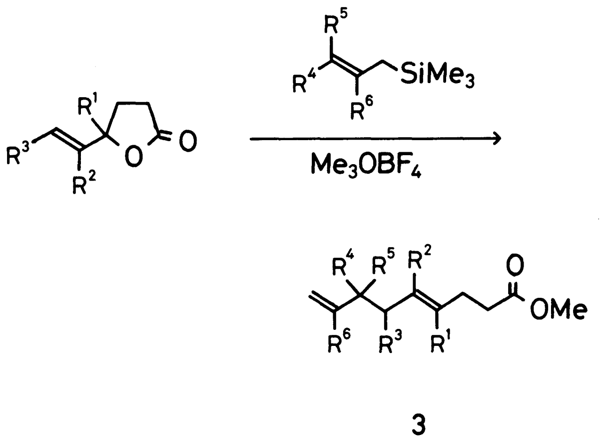
comparison with those of methyl ester of 4,8-nonadienoic acid obtained by the reaction of **1** with diallylcuprate.[4] The reaction did not proceed at all in nonpolar solvent such as benzene. When nitromethane was used as the co-solvent of dichloromethane to dissolve the oxonium salt, the yield of the methyl ester **3a** was remarkably decreased. The reactions in refluxing CH_2Cl_2 and $CHCl_3$ decreased the yields to 83% and 72%, respectively, although the reaction time was markedly shortened to about a tenth. These representative results are summarized in Table 1.



1

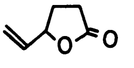
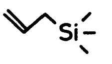
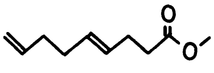
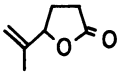
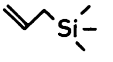
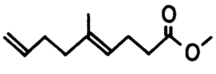
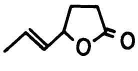
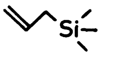
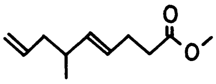
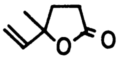
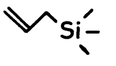
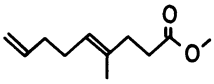
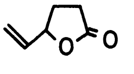
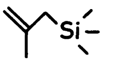
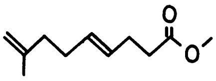
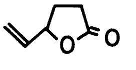
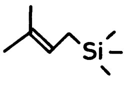
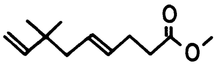
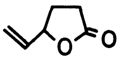
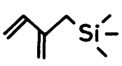
3a

Wide applicability of this ring opening of γ-vinyl-γ-butyrolactones was elucidated by the reaction of various γ-alkenyl-γ-butyrolactones with allylic silanes. In the reactions of allyltrimethylsilane with methyl substituted γ-vinyl-γ-butyrolactones such as γ-isopropenyl- and γ-(1-propenyl)-γ-butyrolactones, the ring opening of both lactones afforded the corresponding methyl 4,8-alkadienoates **3b,c** with methyl group at 5- and 6-positions in high yields (81% and 85%, respectively). The reaction of γ-methyl-γ-vinyl-γ-butyrolactone gave the corresponding ester **3d** with methyl group at 4-position in 74% yield. The ring opening of γ-vinyl-γ-butyrolactone with substituted allylsilanes such as (2-methyl-2-propenyl)trimethylsilane, (3-methyl-2-butenyl)trimethylsilane, and 2-(trimethylsilylmethyl)-1,3-butadiene also proceeded regio- and stereoselectively to afford the corresponding methyl 4,8-alkadienoates **3e—g** with substituent at 7- and 8-positions. In a recent report on the ring opening of 2-vinyltetrahydrofuran with allylsilanes, the regioselectivity is affected by the substituent on the allylsilane.[12a)] In the present ring opening of γ-alkenyl-γ-butyrolactones, no formation of regioisomer produced by the attack of allylsilane to the γ-carbon of γ-alkenyl-γ-butyrolactones could be confirmed. Moreover, IR spectra and GLPC analyses of



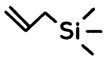
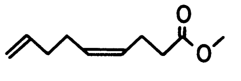
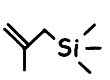
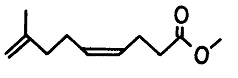
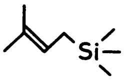
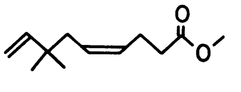
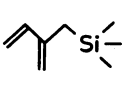
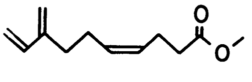
3

Table 2. Ring Opening of γ-Alkenyl-γ-butyrolactones[a]

Lactone	Allylsilane		Product	Yield/%
		**3a**		100
		**3b**		85
		**3c**		81
		**3d**		90
		**3e**		93
		**3f**		74
		**3g**		74

a) All reactions were performed at room temperature for 94 h in CH_2Cl_2. The molar ratio of lactone, oxonium salt, and allylsilane is 1:2:3.

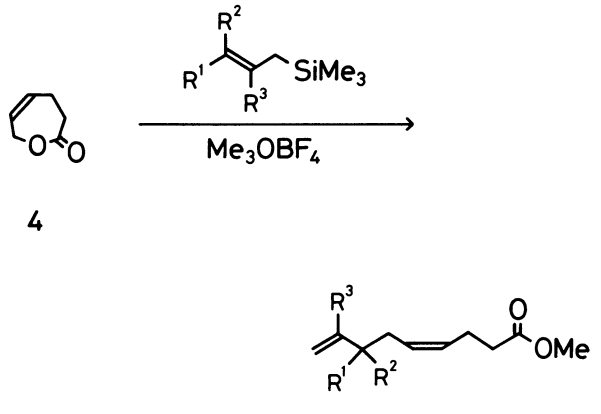
Table 3. Ring Opening of 4-Hexen-6-olide[a)]

Allylsilane		Product	Yield/%
	**5a**		87
	**5b**		84
	**5c**		86
	**5d**		60

a) All reactions were performed at room temperature for 94 h in CH_2Cl_2. The molar ratio of lactone, oxonium salt, and allylsilane is 1:2:3.

the products showed exclusive *E*-configuration of the newly formed carbon–carbon double bond on 4-position of the esters. These results are summarized in Table 2.

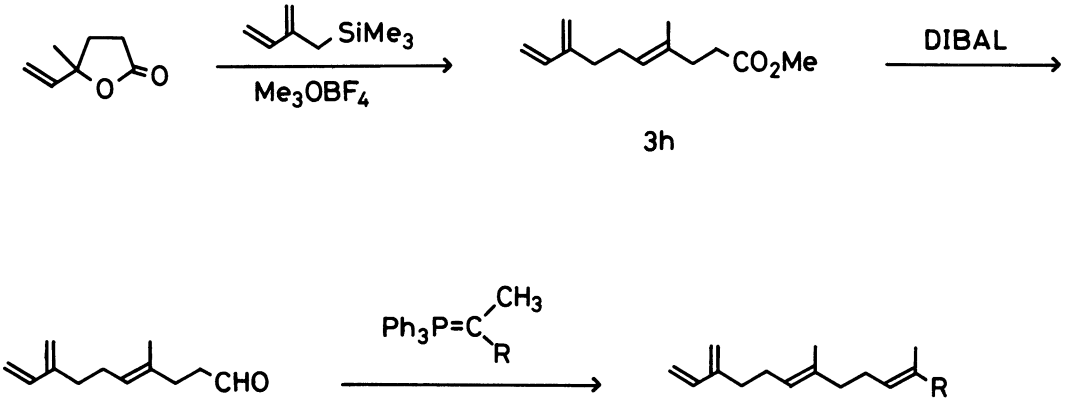
4-Hexen-6-olide (**4**) is also a kind of allylic esters similar to γ-alkenyl-γ-butyrolactones. It is significant to investigate whether allylic rearrangement of the lactone **4** in reaction of **4** with allylic silane in the presence of trimethyloxonium tetrafluoroborate arises or not. Reaction with allyltrimethylsilane was carried out under the same conditions for the ring opening of **1**, in CH_2Cl_2 at room temperature to give a single product. Surprisingly, the product was methyl 4,8-nonadienoate, without accompanying a trace amount of methyl 4-vinyl-6-heptenoate. Moreover the carbon–carbon double bond at 4-position of the obtained ester retained completely the *Z*-configuration of 4-hexen-6-olide. This is noticeable result compared with the ring opening of 4-hexen-6-olide with organocuprate to give a mixture of (*E*)- and (*Z*)-4-alkenoic acids (SN2 product) and 4-vinylalkanoic acid (SN2′ product).[13)] Oxonium salt-promoted reaction of **4** with other methyl-substituted allylsilanes proceeded with high regio- and stereoselectivity to afford methyl (4*Z*)-4,8-alkadienoate **5**. The results are summarized in Table 3. Thus perfect SN2′ reaction in the ring opening of γ-alkenyl-γ-butyrolactones and perfect SN2 reaction in that of 4-hexen-6-olide provide both geometrically pure (4*E*)- and (4*Z*)-4,8-alkadienoates.



4

5

The applicability of the present stereoselective synthetic method of methyl 4,8-alkadienoate is demonstrated in a short step synthesis of β-sinensal **6**, an important constituent of the odor and taste of Chinese orange oil (*Citrus sinensus* L.)[14)] and β-farnesene **7**, natural aphid alarm pheromone. Methyl 4-methyl-8-methylene-4,9-decadienoate (**3h**), obtained in a yield of 65% by the reaction of γ-methyl-γ-vinyl-γ-butyrolactone with 2-(trimethylsilylmethyl)-



3h

8

R = CHO 6

R = CH_3 7

1,3-butadiene, was reduced by diisobutylaluminum hydride in THF–toluene to give 4-methyl-8-methylene-4,9-decadienal (**8**) in 83% yield. The Wittig reaction of the aldehyde **8** with (α-formylethylidene)triphenylphosphorane and with isopropylidenetriphenylphosphorane afforded the desired *trans,trans-β*-sinensal **6** and *trans-β*-farnesene **7** in 82% and 54% yields, respectively.

The present ring opening reaction of γ-alkenyl-γ-butyrolactone and 4-hexen-6-olide with allylsilanes in the presence of trimethyloxonium tetrafluoroborate involves several characteristic features as follows: (1) Both isomers of (*E*)- and (*Z*)-4,8-alkadienoic acid methyl esters are obtained in high yields, respectively, by selecting the starting lactone, either γ-alkenyl-γ-butyrolactone or 4-hexen-6-olide. (2) High regio- and stereoselectivity is easily achieved at room temperature. (3) The operative procedure is extremely simple.

Experimental

General. Boiling points were measured at the pressure indicated and are uncorrected. Infrared spectra were recorded on a Hitachi EPI-G2 spectrometer. ^{1}H NMR spectra were recorded on a Varian A-60 spectrometer and on a Jeol JNM-PMX60SI spectrometer and are reported in parts per million (δ) from TMS. Samples were dissolved in CCl_4 containing TMS as an internal standard. Preparative thin-layer chromatography (TLC) was performed on 20×20 cm glass plates coated with 1.5 mm of silica gel (Wakogel B-5F). All reactions were run under a positive pressure of dry argon. Reactions requiring anhydrous conditions were performed in a flame-dried glassware that was cooled under argon. Anhydrous solvents were transferred by an oven-dried syringe. Solvents were distilled before use: Dichloromethane was distilled from phosphorus pentaoxide.

Materials. γ-Vinyl-, γ-isopropenyl-, and γ-(1-propenyl)-γ-butyrolactones were prepared according to the published method.[16] γ-Methyl-γ-vinyl-γ-butyrolactone[17] and 4-hexen-6-olide[13] were prepared by the reported method. Trimethyl-[18] and triethyloxonium tetrafluoroborates[19] were prepared by the published method. Allyltrimethylsilane, (3-methyl-2-butenyl)trimethylsilane, and 2-(trimethylsilylmethyl)-1,3-butadiene were purchased from Petrarch Systems Inc. (2-Methyl-2-propenyl)trimethylsilane was prepared by the reported procedure.[20]

Procedure for the Reaction of γ-Alkenyl-γ-butyrolactones with Allylsilanes in the Presence of Trimethyloxonium Tetrafluoroborate. In a typical experiment, a flask equipped with a magnetic stirring bar and septum was charged 592 mg (4.00 mmol) of Me_3OBF_4. After flushing with dry argon, a solution of 686 mg (6.00 mmol) of allyltrimethylsilane in CH_2Cl_2 (6 ml) was added to the flask at room temperature. Then a solution of 224 mg (2.00mmol) of γ-vinyl-γ-butyrolactone in CH_2Cl_2 (6 ml) was added and the reaction mixture was stirred at the same temperature for 94 h. The reaction was quenched with 10 ml of saturated $NaHCO_3$. The organic layer was separated and aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried with anhydrous $MgSO_4$, and concentrated. The residue was purified by TLC (hexane:CH_2Cl_2=2:1) to afford 336 mg (2.00 mmol) (100%) of methyl 4,8-nonadienoate (**3a**). R_f=0.5; ^{1}H NMR δ=2.07 (br d, J=3 Hz, 4H), 2.27 (br s, 4H), 3.55 (s, 3H), 4.70—5.95 (m, 5H); IR (neat) 1740, 1000, 970, 910 cm^{-1}; Anal. ($C_{10}H_{16}O_2$) C, H.

In the same manner as above, all other ring opening reactions of γ-alkenyl-γ-butyrolactones and 4-hexen-6-olide were performed.

Methyl (*E*)-5-Methyl-4,8-nonadienoate (3b): R_f=0.5; ^{1}H NMR δ=1.60 (s, 3H), 2.08 (br s, 4H), 2.27 (br d, J=4 Hz, 4H), 3.57 (s, 3H), 4.73—5.97 (m, 4H); IR (neat) 1740, 990, 910, 840 cm^{-1}; Anal. ($C_{11}H_{18}O_2$) C, H.

Methyl (*E*)-6-Methyl-4,8-nonadienoate (3c): R_f=0.5; ^{1}H NMR δ=0.94 (d, J=7 Hz, 3H), 1.80—2.13 (m, 3H), 2.25 (br s, 4H), 3.57 (s, 3H), 4.67—5.97 (m, 5H); IR (neat) 1740, 990, 970, 910 cm^{-1}; Anal. ($C_{11}H_{18}O_2$) C, H.

Methyl (*E*)-4-Methyl-4,8-nonadienoate (3d): R_f=0.5; ^{1}H NMR δ=1.60 (s, 3H), 1.93—2.18 (m, 4H), 2.27 (br s, 4H), 3.57 (s, 3H), 4.73—5.98 (m, 4H); IR (neat) 1740, 990, 910, 840 cm^{-1}; Anal. ($C_{11}H_{18}O_2$) C, H.

Methyl (*E*)-8-Methyl-4,8-nonadienoate (3e): R_f=0.5; ^{1}H NMR δ=1.72 (s, 3H), 2.07 (br s, 4H), 2.29 (br s, 4H), 3.57 (s, 3H), 4.65 (br s, 2H), 5.27—5.59 (m, 2H); IR (neat) 1740, 970, 890 cm^{-1}; Anal. ($C_{11}H_{18}O_2$) C, H.

Methyl (*E*)-7,7-Dimethyl-4,8-nonadienoate (3f): R_f=0.5; ^{1}H NMR δ=0.92 (s, 6H), 1.82—2.08 (m, 2H), 2.25 (br s, 4H), 3.55 (s, 3H), 4.58—5.98 (m, 5H); IR (neat) 1740, 1000, 970, 910 cm^{-1}; Anal. ($C_{12}H_{20}O_2$) C, H.

Methyl (*E*)-8-Methylene-4,9-decadienoate (3g): R_f=0.5; ^{1}H NMR δ=2.17 (br s, 4H), 2.23 (br s, 4H), 3.55 (s, 3H), 4.80—5.50 (m, 6H), 6.28 (dd, J=18 Hz, 11 Hz, 1H); IR (neat) 1740, 990, 970, 890 cm^{-1}; Anal. ($C_{12}H_{18}O_2$) C, H.

Methyl (*Z*)-4,8-Nonadienoate (5a): R_f=0.5; ^{1}H NMR δ=2.05 (br d, J=3 Hz, 4H), 2.24 (br s, 4H), 3.55 (s, 3H), 4.60—5.97 (m, 5H); IR (neat) 1740, 990, 910 cm^{-1}; Anal. ($C_{10}H_{16}O_2$) C, H.

Methyl (*Z*)-8-Methyl-4,8-nonadienoate (5b): R_f=0.5; ^{1}H NMR δ=1.72 (s, 3H), 2.07 (br s, 4H), 2.27 (br s, 4H), 3.57 (s, 3H), 4.60 (br s, 2H), 5.20—5.50 (m, 2H); IR (neat) 1740, 890 cm^{-1}; Anal. ($C_{11}H_{18}O_2$) C, H.

Methyl (*Z*)-7,7-Dimethyl-4,8-nonadienoate (5c): R_f=0.5; ^{1}H NMR δ=0.95 (s, 6H), 1.83—2.17 (m, 2H), 2.28 (br s, 4H), 3.57 (s, 3H), 4.57—6.03 (m, 5H); IR (neat) 1740, 990, 910 cm^{-1}; Anal. ($C_{12}H_{20}O_2$) C, H.

Methyl (*Z*)-8-Methylene-4,9-decadienoate (5d): R_f=0.5; ^{1}H NMR δ=2.20 (br s, 4H), 2.27 (br s, 4H), 3.57 (s, 3H), 4.83—5.57 (m, 6H), 6.30 (dd, J=18 Hz, 11 Hz, 1H); IR (neat) 1740, 990, 890 cm^{-1}; Anal. ($C_{12}H_{18}O_2$) C, H.

Methyl (*E*)-4-Methyl-8-methylene-4,9-decadienoate (3h).[21] In the same manner as above, **3h** was prepared in a yield of 65% by the reaction of γ-methyl-γ-vinyl-γ-butyrolactone 131 mg (1.04 mmol) with (trimethylsilylmethyl)-1,3-butadiene 438 mg (3.12 mmol) in the presence of trimethyloxonium tetrafluoroborate 154 mg (1.04 mmol) in CH_2Cl_2 10 ml at room temperature for 71 h. R_f=0.5; IR (neat) 1740, 990, 890, 850 cm^{-1}.

(*E*)-4-Methyl-8-methylene-4,9-decadienal (8).[22] Under an argon atmosphere, to a solution of **3h** 140 mg (0.676 mmol) in THF 2 ml, was added dropwise a toluene solution of 1 M (1 M=1 mol dm^{-3}) diisobutylaluminum hydride 0.7 ml (0.7 mmol) at −78 °C. After the mixture was stirred at the same temperature for 2.7 h, the reaction was quenched by the addition of 10 ml of saturated aqueous NH_4Cl solution. Organic layer was separated and aqueous layer was extracted with twice of 10 ml of ether. The combined organic layer was washed with brine, dried with anhydrous $MgSO_4$, and concentrated. The residual crude product was purified by preparative TLC (hexane:Et_2O=2:1, R_f=0.7) to afford 100 mg (0.561 mmol) of **8**.

β-Sinensal (6).[22] According to the published procedure,[22] **6** was prepared by the Wittig reaction of **8** with (α-formylethylidene)triphenylphosphoran in refluxing benzene.

β-Farnesene (7).[23] Under an argon atmosphere, to a solution of isopropylidenetriphenylphosphorane, prepared from isopropyltriphenylphosphonium bromide 1.40 g (3.64 mmol) and 1.59 M butyllithium 2.40 ml (3.82 mmol) in ether (10 ml) at room temperature for 3 h, a solution of **8** (324 mg, 1.82 mmol) in ether (2 ml) was added at the same temperature. After the mixture was stirred at room temperature for 3 h, precipitated phosphine oxide was removed by filtration. The filtrate was concentrated to give an oil. The crude product was purified by preparative TLC (Hexane, R_f=0.8) to afford 200 mg (0.979 mmol) of **7**.

We thank Mr. Shogo Ando for his invaluable assistance in the experimental work.

References

1) G. Fráter, *Helv. Chim. Acta*, **58**, 442 (1975).

2) W. Himmele, W. Hoffmann, and L. Janitschke, Ger. Offen. DE 3345375 Al, (1985); *Chem. Abstr.*, **104**, 33773y (1986).

3) R. Rossi, A. Carpita, and M. G. Quirici, *Gazz. Chim. Ital.*, **111**, 173 (1981).

4) T. Sato, M. Takeuchi, T. Itoh, M. Kawashima, and T. Fujisawa, *Tetrahedron Lett.*, **22**, 1817 (1981); T. Fujisawa, T. Sato, M. Kawashima, and M. Nakagawa, *Chem. Lett.*, **1981**, 1307; T. Fujisawa, T. Sato, M. Kawashima, K. Naruse, and K. Tamai, *Tetrahedron Lett.*, **23**, 3583 (1982); M. Kawashima and T. Fujisawa, *Chem. Lett.*, **1984**, 1851; T. Fujisawa, T. Sato, and M. Takeuchi, *ibid.*, **1982**, 71; M. Kawashima, T. Sato, and T. Fujisawa, *Bull. Chem. Soc. Jpn.*, **61**, 3255 (1988).

5) H. L. Goering and S. S. Kantner, *J. Org. Chem.*, **48**, 721 (1983).

6) For preliminary reports on aspects of the present study, see: T. Fujisawa, M. Kawashima, and S. Ando, *Tetrahedron Lett.*, **25**, 3213 (1984).

7) T. Mukaiyama, H. Nagaoka, M. Murakami, and M. Ohshima, *Chem. Lett.*, **1985**, 977; M. Kawai, M. Onaka, and Y. Izumi, *ibid.*, **1986**, 381; A. Hosomi, M. Ando, and H. Sakurai, *ibid.*, **1986**, 365, and references cited therein.

8) S. Danishefsky and M. DeNinno, *Tetrahedron Lett.*, **26**, 823 (1985), and references cited therein.

9) R. L. Danheiser and D. M. Fink, *Tetrahedron Lett.*, **26**, 2509 (1985); G. Majetich, J. Defauw, K. Hull, and T. Shawe, *ibid.*, **26**, 4711 (1985), and references cited therein.

10) M. Ohno, S. Matsuoka, and S. Eguchi, *J. Org. Chem.*, **51**, 4553 (1986); H. Hamana and T. Sugasawa, *Chem. Lett.*, **1985**, 921; S. L. Schreiber, T. Sammakia, and W. E. Crowe, *J. Am. Chem. Soc.*, **108**, 3128 (1986); S. A. Carr and W. P. Weber, *J. Org. Chem.*, **50**, 2782 (1985); T. S. Tan, A. N. Mather, G. Procter, and A. H. Davidson, *J. Chem. Soc., Chem. Commun.*, **1984**, 585, and references cited therein.

11) M. K. Kaloustian and F. Khouri, *Tetrahedron Lett.*, **22**, 413 (1981); H. Meerwein, *Angew. Chem.*, **67**, 374 (1955); H. Meerwein, P. Borner, O. Fuchs, H. J. Sasse, H. Schrodt, and J. Spille, *Chem. Ber.*, **89**, 2060 (1956); P. Deslongchamps, R. Chenevert, R. J. Taillefer, C. Moreau, and J. K. Saunders, *Can. J. Chem.*, **53**, 1601 (1975).

12) a) A. Oku, Y. Homoto, and T. Harada, *Chem. Lett.*, **1986**, 1495; b) S. Danishefsky and J. F. Kerwin, Jr., *J. Org. Chem.*, **47**, 3803 (1982).

13) T. Fujisawa, K. Umezu, and M. Kawashima, *Chem. Lett.*, **1984**, 1795.

14) T. Hiyama, A. Kanakura, H. Yamamoto, and H. Nozaki, *Tetrahedron Lett.*, **1978**, 3051.

15) W. S. Bowers, L. R. Nault, R. E. Webb, and S. R. Dutky, *Science* (Washington, D. C.), **1778**, 1121 (1972).

16) S. Danishefsky, R. L. Funk, and J. F. Kerwin, Jr., *J. Am. Chem Soc.*, **101**, 6756 (1979); M. Kawashima and T. Fujisawa, *Bull. Chem. Soc. Jpn.*, **61**, 3377 (1988).

17) B. M. Trost, D. E. Keeley, H. C. Arndt, and M. J. Bogdanowicz, *J. Am. Chem. Soc.*, **99**, 3088 (1977).

18) T. J. Curphey, *Org. Synth.*, **51**, 142 (1971).

19) H. Meerwein, *Org. Synth.*, Coll. Vol. V, 1080 (1973).

20) A. Hosomi and H. Sakurai, *Tetrahedron Lett.*, **1977**, 4041.

21) Y. Masaki, K. Sakuma, and K. Kaji, *Chem. Pharm. Bull.*, **33**, 1930 (1985).

22) E. Bertele and P. Schudel, *Helv. Chim. Acta*, **50**, 2445 (1967).

23) A. Yasuda, S. Tanaka, H. Yamamoto, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, **52**, 1752 (1979).