  Bull. Chem. Soc. Jpn., 54, 505—508 (1981) 

# Jasmonoid Synthesis from *cis*-4-Heptenoic Acid

Toshio SATO, Tatsuo KAWARA, Kazumi SAKATA, and Tamotsu FUJISAWA*

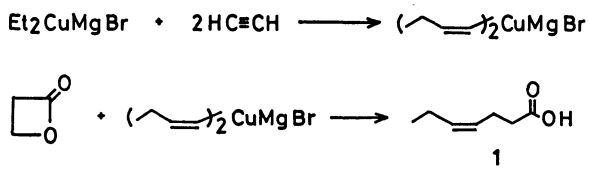
*Chemistry Department of Resources, Mie University, Tsu, Mie 514*

(Received August 25, 1980)

Jasmonoids with *cis*-2-pentenyl side chain such as *cis*-jasmone, methyl jasmonate, and jasmolone were easily synthesized from *cis*-4-heptenoic acid obtained by the ring opening reaction of β-propiolactone with di-*cis*-butenylcuprate.

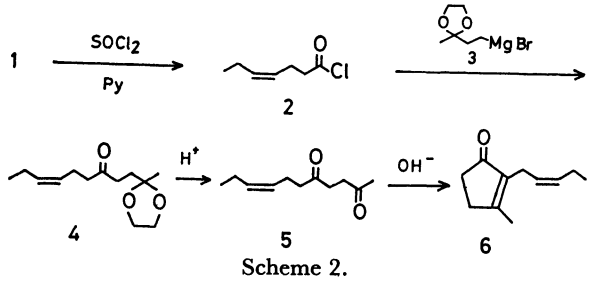
Recently there have been a large amount of researches developing synthetic routes to 2-(*cis*-2-alkenyl)-2-cyclopentenones.[1a] This has been due in large part to interest in several biologically active natural products which have this moiety as a major structural feature. In the synthesis of these compounds, stereoselective introduction of *cis*-2-alkenyl side chain has been one of the major subjects. For example, as for the synthesis of jasmonoids,[1b] the *cis*-2-pentenyl group has been formed by elaborate routes, *e.g.*, the partial hydrogenation of carbon-carbon triple bond with the Lindlar catalyst,[2,3] the Wittig reaction of a formylmethyl group with propylidenetriphenylphosphorane under salt free conditions,[4] and the reductive desulfurization of 5,6-dihydro-2*H*-thiopyran derivative.[5] Recently *cis*-4-alkenoic acids were found to be synthesized in one-pot operation from dialkylcuprates, acetylene, and β-propiolactone.[6] Among them, *cis*-4-heptenoic acid would be a useful precursor of these jasmonoids, because it has a structure corresponding to a skeleton from the side chain to the carbonyl carbon of the cyclopentenone in the jasmonoids with *cis*-2-pentenyl moiety such as *cis*-jasmone, methyl jasmonate and jasmolone. Thus, the synthetic route to the jasmonoids from *cis*-4-heptenoic acid as a key intermediate was investigated *via* well documented cyclization of 1,4-diketones.

*cis*-4-Heptenoic acid (**1**) was easily synthesized in a high yield by utilizing two reactions, *i.e.*, the *syn* addition of dialkylcuprates to acetylene for the formation of di-*cis*-1-alkenylcuprates[7] and the regioselective ring opening reaction of β-propiolactone with diorganocuprates.[8] Thus, acetylene was introduced at −78 °C into bromomagnesium diethylcuprate, which was prepared from copper(I) iodide and ethylmagnesium bromide in THF–$Me_2S$ (9 : 1) at −30 °C. After the reaction mixture was allowed rapidly to warm to −30 °C and stirred for 30 min, the reaction of β-propiolactone with the cuprate was performed at −30 °C for 2 h. By quenching the reaction with 3 M (1 M=1 mol $dm^{-3}$) HCl solution, the desired acid **1** was isolated by distillation in a yield of 81%.



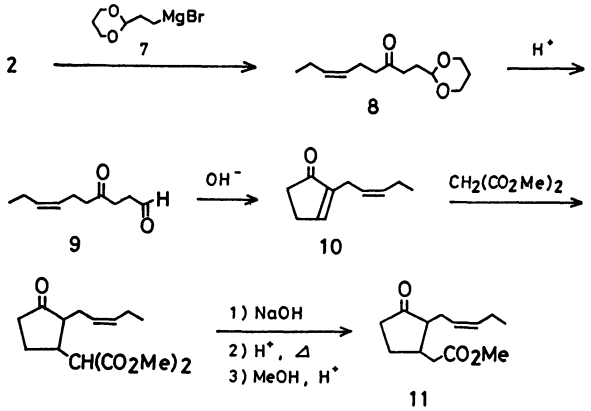

Scheme 1.

The precursor of *cis*-jasmone, *cis*-8-undecene-2,5-dione (**5**) was easily derived from *cis*-4-heptenoic acid and 3-oxo-butyl equivalent. As a latter compound, 3,3-ethylenedioxybutyl group was chosen. Treatment of **1** with thionyl chloride and pyridine in ether gave *cis*-4-heptenoyl chloride (**2**) in a yield of 74%. Condensation of **2** with the Grignard reagent **3**[9] prepared from magnesium metal and 3,3-ethylenedioxybutyl bromide, which was derived from methyl vinyl ketone, ethylene glycol, and hydrogen bromide, in THF at −78 °C and then warming to room temperature, afforded *cis*-2,2-ethylenedioxy-8-undecen-5-one (**4**) quantitatively. Deacetalization of the keto acetal **4** with dilute hydrochloric acid solution afforded the dione **5**, which was then cyclized with dilute aqueous base in the usual manner[10] to give *cis*-jasmone (**6**) in 68% yield from **3**.




Scheme 2.

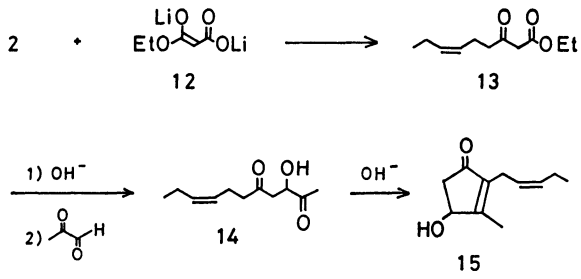
Methyl jasmonate (**11**) can also be synthesized from *cis*-4-heptenoic acid *via* 2-(*cis*-2-pentenyl)-2-cyclopentenone (**10**). In this case, 3,3-trimethylenedioxypropyl group was chosen for the stability of the Grignard reagent as functional group for the three carbon elongation. Condensation of **2** with the Grignard reagent **7**[11] of 3,3-trimethylenedioxypropyl bromide, prepared from acrylaldehyde, hydrogen bromide, and 1,3-propanediol, furnished *cis*-1,1-trimethylenedioxy-7-decen-4-one (**8**). Deacetalization of **8** with aqueous oxalic acid gave *cis*-4-oxo-7-undecenal (**9**) in 68% yield from **2**. Cyclization of aldehyde **9** with 1% sodium




Scheme 3.

hydroxide in water–dioxane (1 : 1) afforded the cyclopentenone **10** in 69% yield. According to the standard procedure[2,12] **10** was converted into methyl jasmonate (**11**), *i.e.*, the Michael addition of dimethyl malonate to **10**, followed by hydrolysis, decarboxylation, and esterification furnished **11** in a yield of 66%.

Jasmolone, an ester component of jasmoline, was also prepared from *cis*-4-heptenoic acid *via* cyclization of 1,4-diketone. The dianion **12**[13] of ethyl hydrogen malonate reacted with **2** in THF at −65 °C for 1 h to afford ethyl *cis*-3-oxo-6-nonenoate (**13**) in a yield of 76%. Then, according to the procedure by LaForge *et al.*,[14] **13** was hydrolyzed with dilute potassium hydroxide solution, followed by condensation with methylglyoxal and successive decarboxylation to give *cis*-3-hydroxy-8-undecene-2,5-dione (**14**), which was cyclized by the treatment with 2% sodium hydroxide aqueous solution to give jasmolone (**15**) in 23% yield from **13**.




Scheme 4.

As mentioned above, *cis*-4-heptenoic acid, easily prepared from β-propiolactone and di-*cis*-1-butenylcuprate, was proved to be a very useful precursor for the synthesis of the jasmonoids with *cis*-pentenyl moiety. Further, by the use of various *cis*-alkenylcuprates, the regioselective ring opening of β-propiolactone should provide a promising method for the synthesis of a wide variety of natural products possessing *cis* carbon-carbon double bond.

## Experimental

The IR spectra were recorded on a Hitachi EPI-G2 spectrometer. The NMR spectra were taken with a Varian A-60 spectrometer using TMS as an internal standard. Grignard reagents and butyllithium were titrated by Eastham's method.[15] All boiling points are uncorrected.

cis-*4-Heptenoic Acid (1).* To a solution of copper(I) iodide (5.713 g, 30 mmol) in THF (90 ml) and dimethyl sulfide (10 ml) was added an ethereal solution of ethylmagnesium bromide (1.85 M, 32.5 ml, 60 mmol) at −30 °C. Then, acetylene (2160 ml, 90 mmol) was introduced using a gas buret through a drying tube ($CaCl_2$) into a suspension of the cuprate at −78 °C at an approximate rate of 20 ml/min. After introduction of acetylene, the temperature was allowed to warm rapidly to −30 °C and the mixture was stirred for 30 min. β-Propiolactone (1.081 g, 15 mmol) in THF (2 ml) was added dropwise and stirring was continued at −30 °C for additional 2 h. The reaction was quenched with 3 M hydrochloric acid solution (20 ml) and extracted with ether. The separated organic layer was extracted with 3 M sodium hydroxide solution. The alkaline solution was washed with ether, acidified with 6 M hydrochloric acid solution, and then extracted with ether. The ether extracts were washed with brine (10 ml) and dried over anhydrous $MgSO_4$. Distillation gave **1** (1.56 g, 81%): bp 97—99 °C/5 mmHg (lit,[16] bp 97—99 °C/4 mmHg); IR (neat) 1710 (C=O) and 720 $cm^{-1}$ (*cis*-CH=CH); NMR ($CCl_4$) δ 0.95 (3H, t, $J$=7 Hz), 1.90—2.40 (6H, m), 5.10—5.60 (2H, m), and 11.90 (1H, s).

cis-*4-Heptenoyl Chloride (2).* A mixture of **1** (4.35 g, 34.0 mmol) and pyridine (3.06 g, 40.8 mmol) in ether (20 ml) was added to a solution of thionyl chloride (4.45 g, 37.4 mmol) in ether (50 ml) at −15 °C. The reaction mixture was stirred at room temperature for 2 h. The precipitate formed was filtered off. Distillation of the filtrate gave **2** (3.66 g, 74%): bp 63—64 °C/13 mmHg (lit,[17] bp 72—76 °C/35 mmHg); IR (neat) 1800 (C=O) and 720 $cm^{-1}$ (*cis*-CH=CH); NMR ($CCl_4$) δ 0.98 (3H, t, $J$=7 Hz), 1.72—2.63 (4H, m), 2.63—3.07 (2H, m), 4.83—5.61 (2H, m).

*3,3-Ethylenedioxybutyl Bromide.* To a solution of hydrogen bromide (12.0 g, 133 mmol) in ethylene glycol (20.0 g, 327 mmol) was added dropwise methyl vinyl ketone (7.00 g, 100 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 1 h and extracted with hexane. The extracts were washed with 5% sodium hydrogencarbonate solution and dried over anhydrous $MgSO_4$. Distillation gave 3,3-ethylenedioxybutyl bromide (9.26 g, 48%): bp 88—94 °C/27 mmHg; (lit,[18] bp 58—60 °C/12 mmHg); IR (neat) 1120 (C=O) and 540 $cm^{-1}$ (CBr); NMR ($CCl_4$) δ 1.31 (3H, s), 2.20 (2H, t, $J$=9 Hz), 3.45 (2H, t, $J$=9 Hz), and 3.95 (4H, s).

cis-*2,2-Ethylenedioxy-8-undecen-5-one (4).* To a solution of **2** (0.784 g, 5.28 mmol) in THF (5 ml) was added the Grignard reagent **3** (0.61 M, 7.87 ml, 4.80 mmol), prepared from 3,3-ethylenedioxybutyl bromide and magnesium in THF at room temperature,[9] at −78 °C. The mixture was allowed to warm to room temperature for 1.5 h. It was poured into a saturated sodium hydrogencarbonate solution (10 ml), extracted with ether, and dried over anhydrous $MgSO_4$. The crude product was purified by TLC on silica gel ($R_f$ 0.6, benzene) to afford **4** quantitatively (1.087 g): IR (neat) 1710 (C=O), 1150, 1050 (C–O), and 720 $cm^{-1}$ (*cis*-CH=CH); NMR ($CCl_4$) δ 0.95 (3H, t, $J$=7 Hz), 1.30 (3H, s), 1.66—2.67 (10H, m), 4.01 (4H, s), and 5.23—5.67 (2H, m).

cis-*8-Undecene-2,5-dione (5).* A solution of **4** (0.279 g, 1.23 mmol) and two drops of 3 M hydrochloric acid solution in acetone (5 ml) and water (5 ml) was refluxed for 4 h. After evaporation of the acetone, the residue was extracted with ether. The ether extracts were washed with brine and dried over anhydrous $MgSO_4$. Removal of the solvent gave **5** (0.187 g, 84%): IR (neat) 1720 (C=O), and 720 $cm^{-1}$ (*cis*-CH=CH); NMR ($CCl_4$) δ 0.97 (3H, t, $J$=7 Hz), 2.00—2.57 (9H, m), 2.67 (4H, s), and 5.20—5.59 (2H, m). The spectral data of **5** were in agreement with the literature.[10]

cis-*Jasmone (6).* According to the procedure of Büchi *et al.*,[10] a solution of the diketone **5** in 0.5 M sodium hydroxide solution and ethanol was refluxed for 6 h to give **6** (82%): IR (neat) 1720 (C=O) and 720 $cm^{-1}$ (*cis*-CH=CH); NMR ($CCl_4$) δ 1.00 (3H, t, $J$=7 Hz), 2.00—3.00 (11H, m), and 5.20—5.70 (2H, m). The spectral data of **6** were in agreement with the literature.[10]

*3,3-Trimethylenedioxypropyl Bromide.* To a solution of hydrogen bromide (21.6 g, 0.27 mol) in 1,3-propanediol (43.6 g, 0.57 mol) was slowly added acrylaldehyde (11.0 g, 0.18 mol, 90% purity) at room temperature. The reaction mixture was stirred at room temperature for 1 h and extracted with hexane. The extracts were washed with 5% sodium hydrogencarbonate solution and dried over anhydrous $MgSO_4$. Distillation gave 3,3-trimethylenedioxypropyl bromide (25.3 g,

† 1 mmHg=133.322 Pa.

74%): bp 89—91 °C/10 mmHg† (lit,[11] bp 67—70 °C/2.8 mmHg); NMR ($CCl_4$) $\delta$ 1.00—1.50 (1H, m), 1.50—2.47 (3H, m), 3.36 (2H, t, $J$=8 Hz), 3.75—4.25 (4H, m), and 4.57 (1H, t, $J$=5 Hz).

cis-*1,1-Trimethylenedioxy-7-decen-4-one (8).* To a solution of *cis*-4-heptenoyl chloride (**2**) (3.64 g, 24.8 mmol) in THF (20 ml) was added dropwise the Grignard reagent **7** (0.72 M, 31.3 ml, 22.5 mmol), prepared from 3,3-trimethylenedioxypropyl bromide and magnesium in THF,[11] at −78 °C. The mixture was allowed to warm to room temperature for 2 h and the THF was removed. The residue was extracted with ether and the organic layer was washed with water, and then dilute sodium carbonate solution, dried over anhydrous $K_2CO_3$. Removal of the solvent afforded **8** (5.77 g), which was used in the next reaction without purification. IR (neat) 1720 (C=O), 1150, 1050 (C–O), and 720 $cm^{-1}$ (*cis*-CH=CH); NMR ($CCl_4$) $\delta$ 0.97 (3H, t, $J$=7 Hz), 1.25—2.67 (13H, m), 3.32—4.25 (4H, m), 4.40 (1H, t, $J$=5 Hz), and 5.10—5.43 (2H, m).

cis-*4-Oxo-7-undecenal (9).* A mixture of crude **8** (2.53 g), oxalic acid (1 g), and water (20 ml) was refluxed for 3 h, during which time the product was continuously steam-distilled into a Dean Stark trap. The distillate was extracted with ether. The ether extracts were dried over anhydrous $Na_2SO_4$. Distillation under reduced pressure gave **9** (1.26 g, 68% from **7**): bp 104—105 °C/1.7 mmHg; IR (neat) 1725 (C=O), 1715 (CHO), and 730 $cm^{-1}$ (*cis*-CH=CH); NMR ($CCl_4$) $\delta$ 0.95 (3H, t, $J$=7 Hz), 1.77—2.50 (6H, m), 2.62 (4H, s), 5.20—5.63 (2H, m), and 9.60 (1H, s). The spectral data of **9** were in agreement with the literature.[12]

*2-(*cis*-2-Pentenyl)-2-cyclopentenone (10).* To a refluxing solution of water (45 ml), dioxane (45 ml) and 10% sodium hydroxide solution (10 ml) was added dropwise a dioxane solution of **9** (0.922 g, 5.49 mmol) for 1.5 h. The mixture was refluxed for 10 min. After neutralization with 1 M hydrochloric acid solution, it was extracted with chloroform. The extracts were dried over anhydrous $Na_2SO_4$. Distillation afforded **10** (0.565 g, 69%): bp 90 °C (bath)/0.6 mmHg (lit,[2] bp 70 °C/0.05 mmHg); IR (neat) 1700 (C=O), 1625 (CH=CH, ring), and 730 $cm^{-1}$ (*cis*-CH=CH); NMR ($CCl_4$) $\delta$ 0.97 (3H, t, $J$=7 Hz), 1.60—3.08 (8H, m), 5.16—5.70 (2H, m), and 7.25 (1H, m). The spectral data of **10** were in agreement with the literature.[2]

*Methyl Jasmonate (11).* Sodium hydride (0.02 g, 0.46 mmol, 55% in mineral oil) was washed with dry hexane, and dry methanol (0.7 ml) was added. To the mixture was added dropwise dimethyl malonate (0.258 g, 1.95 mmol) and then cyclopentenone (**10**) (0.187 g, 1.25 mmol) in dry methanol (1 ml) at −5 °C for 40 min. The resulting mixture was stirred at −10—−5 °C for 3 h. After the reaction was quenched with acetic acid (2 ml), the methanol was evaporated. The residue was dissolved in ether, washed with water and dried over anhydrous $Na_2SO_4$. Distillation gave 3-[bis(methoxycarbonyl)methyl]-2-(*cis*-2-pentenyl) cyclopentenone (0.325 g, 92%): bp 200 °C (bath)/2 mmHg; IR (neat) 1740 ($COOCH_3$), 1700 (C=O), and 735 $cm^{-1}$ (*cis*-CH=CH); NMR ($CCl_4$) $\delta$ 0.95 (3H, t, $J$=7 Hz), 1.75—2.50 (10H, m), 3.47 (1H, s), 3.70 (6H, s), and 5.00—5.50 (2H, m).

To 0.269 g (1.05 mmol) of the cyclopentenone was added dropwise 10% sodium hydroxide aqueous solution (0.9 ml) for 4 h and the mixture was allowed to stand overnight. Then 3% sulfuric acid solution (0.35 ml) was added and the resulting mixture was refluxed for 5 h. The cooled reaction mixture was extracted with ether and washed with water. The ether extract were then extracted with 3 M sodium hydroxide solution. The alkaline solution was washed with ether, acidified with 6 M hydrochloric acid solution, and then extracted with ether. The extracts were dried over anhydrous $Na_2SO_4$ and evaporated to afford jasmonic acid (0.172 g, 78%): IR (neat) 3150 (OH), 1740 (C=O), 1750 (COOH) and 720 $cm^{-1}$ (*cis*-CH=CH); NMR ($CCl_4$) $\delta$ 0.97 (3H, t, $J$=7 Hz), 1.65—3.08 (12H, m), 5.15—5.67 (2H, m), and 11.0 (1H, s).

A solution of jasmonic acid (0.142 g, 0.68 mmol) in methanol (5 ml) was stirred at 40 °C for 3 h with a catalytic amount of concd $H_2SO_4$. The reaction mixture was cooled, and a small amount of $NaHCO_3$ and water (5 ml) was added. The mixture was extracted with ether and the extracts were dried over anhydrous $Na_2SO_4$. Removal of the solvent gave **11** (0.138 g, 92%): IR (neat) 1740 (C=O), 720 $cm^{-1}$ (*cis*-CH=CH); NMR ($CCl_4$) $\delta$ 0.95 (3H, t, $J$=7 Hz), 1.55—3.05 (12H, m), 3.65 (3H, s), and 4.82—5.55 (2H, m). The spectral data of **11** were identical with the literature.[2]

*Ethyl* cis-*3-Oxo-6-nonenoate (13).* To a solution of ethyl hydrogen malonate (0.231 g, 1.75 mmol) and 2,2′-bipyridyl (3 mg) in THF (4 ml) was added a hexane solution of butyllithium (1.52 M, 2.30 ml, 3.5 mmol) at −70 °C, during which time the temperature was raised from −70 to −5 °C.[13] To a solution of the dianion **12** was added **2** (0.147 g, 1.00 mmol) in THF (1 ml) at −65 °C. After 1 h ether (7 ml) and 1 M hydrochloric acid solution (3 ml) were added. The organic layer was washed with saturated sodium hydrogencarbonate solution and then water, and dried over anhydrous $Na_2SO_4$. Removal of the ether gave the crude product, which was purified by TLC on silica gel ($R_f$ 0.5, hexane : ether=2 : 1) to give **13** (0.151 g, 76%): IR (neat) 1750 (COO), 1730 (C=O), and 730 $cm^{-1}$ (*cis*-CH=CH); NMR ($CCl_4$) $\delta$ 0.95 (3H, t, $J$=7 Hz), 1.20 (3H, t, $J$=7 Hz), 1.70—2.60 (6H, m), 3.22 (3H, s), 4.12 (2H, q, $J$=7 Hz), and 4.85—5.55 (2H, m).

cis-*3-Hydroxy-8-undecene-2,5-dione (14).* To **13** (0.135 g, 0.70 mmol) was added dropwise 10% potassium hydroxide solution (0.46 ml) and the mixture was allowed to stand at −3—−2 °C for 3 d. After washed with ether, the reaction mixture was acidified with 0.5 M hydrochloric acid solution to pH 3—4, extracted with ether, and dried over anhydrous $Na_2SO_4$. Evaporation of the solvent gave *cis*-3-oxo-6-nonenoic acid (0.086 g, 73%): IR (KBr) 3150 (OH), 1710 (C=O), and 720 $cm^{-1}$ (*cis*-CH=CH); NMR ($CCl_4$) $\delta$ 1.00 (3H, t), 1.78—2.80 (6H, m), 4.80—5.50 (2H, m), and 10.88 (1H, s).

*cis*-3-Oxo-6-nonenoic acid (0.816 g, 1.86 mmol) in water (1 ml) was neutralized with 10% sodium hydroxide solution using phenolphthalein as an indicator at 0 °C. To the solution was added methylglyoxal (0.156 g, 2.20 mmol, 40% aqueous soln) and then 10% sodium hydroxide solution to make the mixture basic (pH 8). The resulting mixture was allowed to stand at room temperature for 2.5 d and extracted with ether. The extracts were dried over anhydrous $Na_2SO_4$, and evaporated. Purification by TLC on silica gel ($R_f$ 0.4, ether : hexane=2 : 1) gave **14** (0.220 g, 60%): IR (neat) 3450 (OH), 1720 (C=O), and 720 $cm^{-1}$ (*cis*-CH=CH); NMR ($CCl_4$) $\delta$ 0.95 (3H, t, $J$=7 Hz), 1.80—2.90 (11H, m), 4.00—4.40 (2H, m), and 4.80—5.50 (2H, m). The spectral data of **14** were in agreement with the literature.[19]

*Jasmolone (15).* To **14** (0.148 g, 0.75 mmol) was added dropwise 2% potassium hydroxide solution (0.6 ml) and the mixture was allowed to stand at room temperature for overnight. The reaction mixture was extracted with ether, washed with brine, and dried over anhydrous $Na_2SO_4$. Purification by TLC on silica gel ($R_f$ 0.4, ether : hexane=3 : 1, developed twice) gave **15** (0.069 g, 52%): IR (neat) 3400 (OH), 1710 (C=O), 710 $cm^{-1}$ (*cis*-CH=CH); NMR ($CCl_4$) $\delta$ 0.95 (3H, t, $J$=7 Hz), 1.60—3.00 (9H, m), 4.10 (1H, broad), 4.45 (1H, m), and 4.80—5.50 (2H, m). The spectral

data were in agreement with the literature.[19]

The present work was partially supported by a Grant-in-Aid for Scientic Research No. 554144 from the Ministry of Education, Science and Culture.

**References**

1) a) R. A. Ellison, *Synthesis*, **1973**, 397; b) T.-L. Ho, *Synth. Commun.*, **4**, 265 (1974); S. Torii and H. Tanaka, *Koryo*, **1976**, 41.

2) G. Büchi and B. Egger, *J. Org. Chem.*, **36**, 2021 (1971).

3) J. E. McMurry and J. Melton, *J. Am. Chem. Soc.*, **93**, 5309 (1971); J. L. Herrmann, J. E. Richman, and R. H. Schlessinger, *Tetrahedron Lett.*, **1973**, 3275; A. E. Greene and P. Crabbe, *ibid.*, **1976**, 4867; H. J. Monteiro, *J. Org. Chem.*, **42**, 2324 (1977); S. Torii, H. Tanaka, and Y. Kobayasi, *ibid.*, **42**, 3474 (1977); K. Kondo, Y. Takahatake, K. Sugimoto, and D. Tunemoto, *Tetrahedron Lett.*, **1978**, 907.

4) H. Tanaka and S. Torii, *J. Org. Chem.*, **40**, 462 (1975); P. Bakuzis and M. L. F. Bakuzis, *ibid.*, **42**, 2362 (1977).

5) S. Torii, H. Tanaka, and Y. Tomotaki, *Bull. Chem. Soc. Jpn.*, **50**, 537 (1977).

6) T. Fujisawa, T. Sato, T. Kawara, and K. Naruse, *Chem. Lett.*, **1980**, 1123.

7) H. Westmijze, J. Meijer, H. J. T. Bos, and P. Vermeer, *Recl. Trav. Chim. Pays-Bas*, **95**, 304 (1976); A. Alexakis, G. Cahiez, and J. F. Normant, *Synthesis*, **1979**, 826.

8) T. Fujisawa, T. Sato, T. Kawara, M. Kawashima, H. Shimizu, and Y. Ito, *Tetrahedron Lett.*, **21**, 2181 (1980).

9) A. A. Ponaras, *Tetrahedron Lett.*, **1976**, 3105.

10) G. Büchi and H. Wüest, *J. Org. Chem.*, **31**, 977 (1966).

11) J. C. Stowell, *J. Org. Chem.*, **41**, 560 (1976).

12) P. Dubs and R. Stüssi, *Helv. Chim. Acta*, **61**, 990 (1978).

13) W. Wierenga and H. I. Skulnick, *J. Org. Chem.*, **44**, 310 (1979).

14) M. S. Schechter, N. Green, and F. B. LaForge, *J. Am. Chem. Soc.*, **71**, 3165 (1949).

15) S. C. Watson and J. F. Eastham. *J. Organomet. Chem.*, **9**, 165 (1967).

16) K. Furukawa and M. Iwakiri, *Yuki Gosei Kagaku Kyokai Shi*, **33**, 496 (1975).

17) L. Crombie, S. H. Harper, R. E. Stedman, and D. Thompson, *J. Chem. Soc.*, **1951**, 2445.

18) C. Feugeas, *Bull. Soc. Chim. Fr.*, **1963**, 2568.

19) L. Crombie, P. Hemesley, and G. Pattenden, *J. Chem. Soc., C*, **1969**, 1016.