[Chem. Pharm. Bull. 27(3) 726—730 (1979)]

UDC 547.594.4.04 : 547.315.2.04

# The Stereochemistry of Diels-Alder Adduct of 2-(3-Acetoxypropyl)-5-methylcyclohex-2-en-1-one with Butadiene

TAKASHI HARAYAMA, MUNEO TAKATANI, and YASUO INUBUSHI

*Faculty of Pharmaceutical Sciences, Kyoto University*[1]

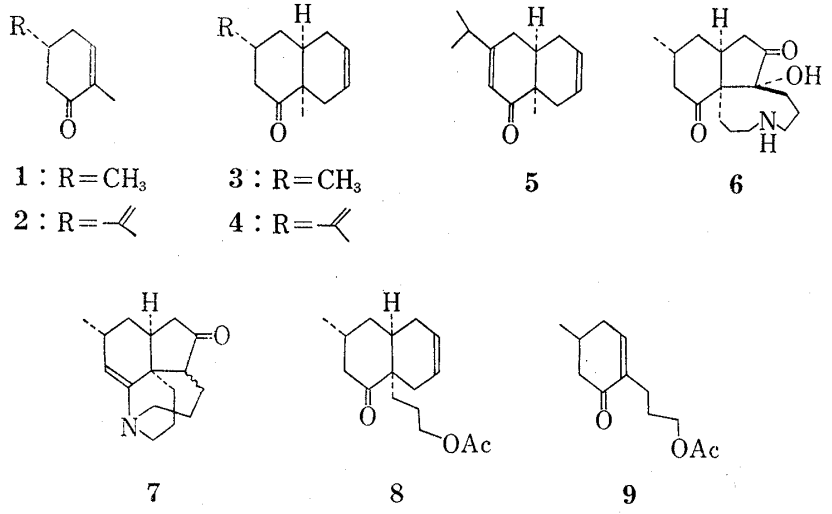
(Received October 18, 1978)

The Diels-Alder reaction of 2-(3-acetoxypropyl)-5-methylcyclohex-2-en-1-one (**9**) with butadiene in the presence of aluminum chloride was examined. Inspection of the stereostructure of the adduct (**8**) indicated that addition of butadiene to the dienophile (**9**) took place stereoselectively from the side opposite to a secondary methyl group at $C_5$ of the dienophile and that this type of Diels-Alder reaction is useful for synthesis of 8-deoxyserratinine type alkaloids. The dienophile (**9**) was regioselectively prepared from the ketone (**10**) by two routes. The first route involved the Claisen rearrangement of **12** obtained from **10** *via* **11**. Subsequent conversions of the rearrangement product (**13**; yield, 60% from **11**) gave the dienophile (**9**; yield, 26.5% from **14**) *via* **14**, **15**, **16**, **17**, **18**, and **19**. The second route consisted in conversion of the acetal (**20**) obtained from the ketone (**10**) and acrolein diethyl acetal into the dienophile (**9**; yield, 70% from **20**) *via* **21** and **22**.

**Keywords**——8-deoxyserratinine type alkaloid; Diels-Alder reaction; stereoselective cycloaddition; regioselective alkylation; Claisen rearrangement; dialkyl *cis*-decalones

In a previous paper, we reported that the Diels-Alder addition of butadiene to 2,5-dialkylcyclohex-2-en-1-ones such as 2,5-dimethylcyclohex-2-en-1-one (**1**) and *l*-carvone (**2**), in the presence of aluminum chloride took place stereoselectively from the side opposite to the $C_5$-substituent of the dienophile, that is, **1** gave **3**[2] and **2** provided **4** and **5**,[2] respectively.

In connection with synthetic studies of 8-deoxyserratinine type of alkaloids, such as alopecuridine (**6**)[3] and fawcettidine (**7**),[4] it was suggested that this type of Diels-Alder reac-




**1** : R=$CH_3$ **3** : R=$CH_3$ **5** **6**

**2** : R= **4** : R=

**7** **8** **9**

Chart 1

1) Location: *Yoshida-Shimoadachi-cho, Sakyo-ku, Kyoto.*
2) T. Harayama, H. Cho, and Y. Inubushi, *Chem. Pharm. Bull.* (Tokyo), **25**, 2273 (1977).
3) W.A. Ayer, B. Altenkirk, and Y. Fukazawa, *Tetrahedron*, **30**, 4213 (1974).
4) H. Ishii, B. Yasui, R. Nishino, T. Harayama, and Y. Inubushi, *Chem. Pharm. Bull.* (Tokyo), **18**, 1880 (1970).

tion may be useful for synthesis of the key intermediate (**8**), which bears three chiral centers as a common stereostructural feature to 8-deoxyserratinine type alkaloids. Thus, we presumed that the key intermediate (**8**) is stereoselectively synthesized by taking advantage of Diels-Alder reaction of the dienophile (**9**) with butadiene in the presence of aluminum chloride. We now wish to describe here the synthetic method of the dienophile (**9**) and stereochemistry of the adduct (**8**).

The vinylogous ester (**11**)[5] obtained from the ketone (**10**)[6] was reduced with lithium aluminum hydride to give the allyl alcohol (**12**). Reflux of **12** in toluene and subsequent treatment with *p*-toluenesulfonic acid provided the enone (**14**) regioselectively in 62.3% yield from **11** *via* the Claisen rearrangement product (**13**). The infrared (IR) spectrum of **14** revealed the bands due to $\alpha,\beta$-unsaturated ketone at 1670 $cm^{-1}$ and vinyl group at 1000 and 921 $cm^{-1}$. Since acetalization of the enone (**14**) with ethyleneglycol was not fruitful, the enone (**14**) was reduced with $LiAlH_4$ to lead to the alcohol (**15**), which was converted into the tetrahydropyranyl ether (**16**) in 95.7% yield from **14**. Hydroboration of **16** with diisoamylborane,[7] followed by treatment with alkaline hydrogen peroxide gave the alcohol (**17**), which was converted to the acetate (**18**) in 90.2% yield from **16**. Removal of pyranyl group of **18** with 6% hydrochloric acid in tetrahydrofuran gave the alcohol (**19**) in 86.4% yield, which was oxidized with Jones' reagent to furnish the dienophile (**9**) in 35.1% yield.

Another synthetic route to **9** was examined. Thus, the reaction of **10** with acrolein diethyl acetal in the presence of pyridinium *p*-toluenesulfonate (PPTS)[8] provided the acetal (**20**) in 50.7% yield, which showed a carbonyl absorption band at 1623 $cm^{-1}$ in the IR spectrum and no signal due to olefinic protons in the nuclear magnetic resonance (NMR) spectrum. Successive treatments of **20** with $LiAlH_4$ and 10% sulfuric acid afforded quantitatively the enone-aldehyde (**21**). Reduction of **21** with $LiAl(t\text{-}BuO)_3H$ and acetylation of the resulting alcohol (**22**) gave the dienophile (**9**) in 70% yield from **20**.

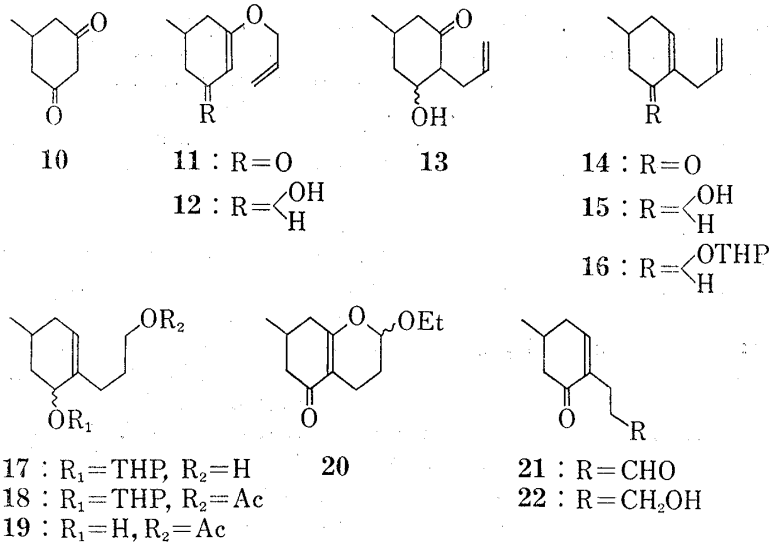
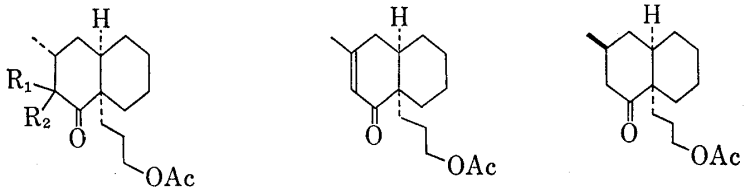



Chart 2

The Diels-Alder reaction of the dienophile (**9**) with butadiene was carried out in the presence of 0.5 eq. aluminum chloride in $CH_2Cl_2$ at room temperature for 5 days to provide the adduct (**8**) in 40.3% yield. The IR spectrum of **8** showed the band due to six-membered ketone at 1700 $cm^{-1}$ and the NMR spectrum revealed the signals attributable to olefinic

5) Y. Tamura, Y. Kita, M. Shimagaki, and M. Terashima, *Chem. Pharm. Bull.* (Tokyo), **19**, 571 (1971).
6) A.W. Crossley and N. Renouf, *J. Chem. Soc.*, **107**, 605 (1915).
7) H.C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 1241 (1961).
8) M. Miyashita, A. Yoshikoshi, and P.A. Grieco, *J. Org. Chem.*, **42**, 3772 (1977).

protons at $\delta$ 5.62 (2H, m.). The stereochemistry of **8** was determined as follows. Thus, catalytic hydrogenation of **8** over 10% Pd-C gave the ketone (**23**) in almost quantitative yield, which was brominated to afford dibromide (**24**) and monobromide (**25**) in 9.5% and 62.5% yields, respectively. Dehydrobromination of **25** with LiBr–$Li_2CO_3$ provided the $\alpha,\beta$-unsaturated ketone (**26**) in 68.9% yield. Catalytic hydrogenation of **26** over 10% Pd–C gave the ketone (**27**), spectral data of which were distinct from those of the ketone (**23**). Since hydrogen attacks a double bond of the *cis* decalin derivatives from the less hindered convex face, the stereostructure of the ketone (**27**) is represented by the formula (**27**). Consequently, the stereostructure of the ketone (**23**) can be represented by the formula (**23**), indicating in turn the stereostructure (**8**) of the adduct (**8**). This result suggests that addition of butadiene to the dienophile (**9**) took place stereoselectively from the side opposite to $C_5$-methyl group of **9**. The synthetic study of 8-deoxyserratinine type alkaloids starting from the Diels-Alder adduct (**8**) is under investigation.



**23** : $R_1=R_2=H$
**24** : $R_1=R_2=Br$
**25** : $R_1=H$, $R_2=Br$

**26**

**27**

Chart 3

## Experimental

Melting point was measured on a microscopic hot stage (Yanagimoto Melting Point Apparatus) and uncorrected. All NMR spectra were taken on a Varian A-60 spectrometer in $CDCl_3$ solution with tetramethylsilane as an internal standard and IR spectra were recorded on a Shimadzu IR 400 spectrometer in $CHCl_3$. Low-resolution mass spectra were taken with a Hitachi RMU-6C spectrometer with a heated direct inlet system and high-resolution mass spectrum with a JEOL JMS-01SG-2 spectrometer. Column chromatography was performed on silica gel (Mallinckrodt Silicic Acid, 100 mesh) (A) or (Merck Kieselgel 60, 70—230 mesh) (B).

**The Enone** (**14**)——To a solution of 19 g (0.5 mol) of $LiAlH_4$ in 500 ml of dry ether was added dropwise a solution of 160 g (0.96 mol) of the vinylogous ester (**11**) in 100 ml of dry ether at 0° under stirring. The reaction mixture was stirred for 2 hr at room temperature. The excess reagent was decomposed with AcOEt and wet ether. The organic layer was decanted, dried over $MgSO_4$ and evaporated to leave 161 g of the allyl alcohol (**12**). IR $cm^{-1}$: $\nu_{O-H}$ 3445, $\nu_{C=O}$ 1661, $\delta_{C-H}$ 1010, 927. A solution of 161 g (0.96 mol) of the compound (**12**) in 300 ml of dry toluene was refluxed for 3.5 hr and then, 0.8 g of *p*-TsOH was added to the reaction mixture. The mixture was refluxed for 2.5 hr, while water was separated with Dean-Stark apparatus. After cooling, $Na_2CO_3$ powder was added to the reaction mixture and filtered off. The filtrate was evaporated to leave the residue. Distillation of the residue gave 90 g (62.3%) of the enone (**14**), bp 116—122°/35 mmHg. IR $cm^{-1}$: $\nu_{C=O}$ 1670, $\delta_{C-H}$ 1000, 921. NMR $\delta$: 1.05 (3H, m, $\langle CH-CH_3$), 2.93 (2H, m, C=C–$CH_2$–C=C), 4.82—6.18 (3H, m, olefinic protons), 6.70 (1H, m, olefinic proton). MS *m/e*: 150 ($M^+$). *Anal.* Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.65; H, 9.62.

**The Allyl Alcohol** (**15**)——To a solution of 41 g (1.08 mol) of $LiAlH_4$ in 650 ml of dry ether was added dropwise a solution of 280 g (1.87 mol) of the compound (**14**) in 150 ml of dry ether at 0° under stirring. The mixture was stirred for 2 hr at room temperature. Excess reagent was decomposed with AcOEt and wet ether. The organic layer was decanted, dried over $MgSO_4$ and evaporated to give 280 g (99%) of the allyl alcohol (**15**), bp 87—88°/3 mmHg. IR $cm^{-1}$: $\nu_{O-H}$ 3590, 3425, $\nu_{C=C}$ 1640, $\delta_{C-H}$ 996, 916. *Anal.* Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 79.10; H, 10.84.

**The Tetrahydropyranyl Ether** (**16**)——To a solution of 56 g (0.368 mol) of the allyl alcohol (**15**) in 140 ml of dry $CH_2Cl_2$ were added 0.15 g of *p*-TsOH and 47.7 g (0.567 mol) of dihydropyran at 0° under stirring. The mixture was stirred at 0° for 1 hr and then at room temperature for 2.5 hr. The reaction mixture was diluted with 10% $NaHCO_3$ solution and extracted with $CH_2Cl_2$. The extract was dried over $K_2CO_3$ and evaporated. Distillation of the residue gave 83.1 g (95.7%) of the compound (**16**), bp 134—135°/3 mmHg. IR $cm^{-1}$: $\nu_{C=C}$ 1640, $\delta_{CH}$ 1000, 913. NMR $\delta$: 0.96 (3H, m, $\rangle CH-CH_3$), 2.87 (2H, m, C=C–$CH_2$–C=C), 4.71

(1H, m, $-CH\langle^{O}_{O}$), 4.75—6.21 (3H, m, olefinic protons), 5.51 (1H, m, olefinic proton). *Anal.* Calcd. for $C_{15}H_{24}O_2$: C, 76.22; H, 10.24. Found: C, 76.16; H, 10.29.

**The Pyranyl Ether-Acetate (18)**——To a solution of diisoamylborane prepared from 4.1 g (0.11 mol) of $NaBH_4$, 19.6 g (0.28 mol) of 2-methyl-2-butene and 19.9 g (0.14 mol) of boron trifluoride etherate in 120 ml of dry diglyme was added a solution of 19 g (0.08 mol) of the compound (**16**) in 20 ml of dry diglyme. The reaction mixture was stirred at 0° for 2 hr and then at room temperature for 1 hr. Excess reagent was destroyed by addition of 10 ml of water and then 45 ml of cold 3 N NaOH solution was added. The reaction mixture was cooled to −30°. To this cooled mixture was added dropwise 45 ml of 30% $H_2O_2$ at such a rate that the temperature did not exceed 25°. The mixture was extracted with ether and the ether extract was washed with several portions of water. The extract was dried over $MgSO_4$ and evaporated to leave 20 g of the crude alcohol (**17**), bp 173—174°/1.5 mmHg. *Anal.* Calcd. for $C_{15}H_{26}O_3$: C, 70.83; H, 10.30. Found: C, 70.74; H, 10.05. To a solution of 20 g of the crude alcohol (**17**) in 25 ml of pyridine was added 12.3 g (0.12 mol) of $Ac_2O$ under ice-cooling. The mixture was allowed to stand at room temperature for 14 hr and evaporated to dryness under reduced pressure. The residue was made acidic with 5% HCl and extracted with ether. The extract was washed with water, 2% $NaHCO_3$ solution, dried over $MgSO_4$, and evaporated. Distillation of the residue gave 21.5 g (90.2%) of pyranyl ether-acetate (**18**), bp 162—163.5°/2 mmHg. IR $cm^{-1}$: $\nu_{C=O}$ 1725, $\nu_{C-O}$ 1200—1270. NMR $\delta$: 0.96 (3H, m, >CH–$CH_3$), 2.01 (3H, s, $OCOCH_3$), 4.07 (2H, m, $-CH_2$–OAc), 4.76 (1H, m, $-CH\langle^{O}_{O}$), 5.51 (1H, m, olefinic proton). *Anal.* Calcd. for $C_{17}H_{28}O_4$: C, 68.89; H, 9.52. Found: C, 69.08; H, 9.80.

**The Alcohol (19)**——To a solution of 15.2 g (51.4 mmol) of the compound (**18**) in 240 ml of freshly distilled tetrahydrofuran (THF) was added 61 ml of 6% HCl solution. The mixture was stirred for 24 hr at room temperature and concentrated under reduced pressure. The concentrated solution was diluted with water and extracted with $CHCl_3$. The extract was dried over $MgSO_4$ and evaporated. The residue was chromatographed on silica gel (B) and elution with $CHCl_3$ provided 9.4 g (86.4%) of the compound (**19**), bp 145—145.5°/1.7 mmHg. IR $cm^{-1}$: $\nu_{O-H}$ 3600, 3425, $\nu_{C=O}$ 1726, $\nu_{C-O}$ 1200—1270. NMR $\delta$: 0.95 (3H, d, $J$=5 Hz, >CH–$CH_3$), 2.03 (3H, s, $OCOCH_3$), 3.06 (1H, br. s, OH), 4.07 (2H, t, $J$=7 Hz, $-CH_2$–OAc), 4.00—4.40 (1H, m,—>CH–OH), 5.46 (1H, m, olefinic proton). *Anal.* Calcd. for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 68.08; H, 9.77.

**The Dienophile (9)**——To a solution of 89 g (0.42 mol) of the compound (**19**) in 300 ml of acetone was added dropwise 125 ml (0.34 mol) of Jones' reagent at 0° under stirring. The mixture was stirred at room temperature for 30 min. The excess reagent was decomposed with methanol. The reaction mixture was diluted with water and extracted with ether. The extract was dried over $MgSO_4$ and evaporated. Distillation of the residue gave 31 g (35.1%) of the dienophile (**9**), bp 117—122°/0.7 mmHg. IR $cm^{-1}$: $\nu_{C=O}$ 1728, 1670, $\nu_{C-O}$ 1200—1270. NMR $\delta$: 1.05 (3H, m, >CH–$CH_3$), 2.03 (3H, s, $OCOCH_3$), 4.05 (2H, t, $J$=6.5 Hz, $-CH_2$–OAc), 6.70 (1H, m, olefinic proton). MS $m/e$: 210 ($M^+$). *Anal.* Calcd. for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.50; H, 8.81.

**The Acetal (20)**——To a solution of 6.30 g (50 mmol) of the compound (**10**) were added 9.10 g (70 mmol) of acrolein diethyl acetal and 1.25 g of pyridinium *p*-toluenesulfonate. The mixture was refluxed for 2 hr, while generated EtOH was separated with $CaCl_2$ and molecular sieves 4A. After cooling, the mixture was made basic with 5% $NaHCO_3$ solution and extracted with ether. The extract was dried over $MgSO_4$ and evaporated. Distillation of the residue gave 5.32 g (50.7%) of the acetal (**20**), bp 125—132°/4 mmHg. IR $cm^{-1}$: $\nu_{C=O}$ 1623. NMR $\delta$: 1.05 (3H, m, >CH–$CH_3$), 1.21 and 1.23 (total 3H, t, $J$=7 Hz, $-CH_2CH_3$), 3.43—4.08 (2H, m, $OCH_2$–$CH_3$), 5.01—5.23 (1H, m, >CH–OEt). MS $m/e$: 210 ($M^+$). *Anal.* Calcd. for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.43; H, 8.63.

**The Dienophile (9) from the Acetal (20)**——To a solution of 1.14 g (30 mmol) of $LiAlH_4$ in 270 ml of dry ether was added dropwise a solution of 6.3 g (30 mmol) of the acetal (**20**) in 30 ml of dry ether at 0°. The reaction mixture was stirred for 1 hr at room temperature. After cooling, excess reagent was decomposed with AcOEt and wet ether. The mixture was acidified with 10% $H_2SO_4$ solution and extracted with ether. The extract was dried over $MgSO_4$ and evaporated to afford 4.98 g of the aldehyde (**21**). IR $cm^{-1}$: $\nu_{CH}$ 2825, 2725, $\nu_{C=O}$ 1725, 1670. NMR $\delta$: 1.06 (3H, m, >CH–$CH_3$), 6.75 (1H, m, olefinic proton), 9.77 (1H, t, $J$=1.5 Hz, CHO). MS $m/e$: 166 ($M^+$). To a solution of 4.98 g (30 mmol) of the aldehyde (**21**) in 90 ml of dry ether was added 13.14 g (51.7 mmol) of $LiAl(t\text{-}BuO)_3H$ at −65°. The mixture was stirred for 35 min. Excess reagent was decomposed with water at −65°. The organic layer was decanted, dried over $MgSO_4$, and evaporated to leave 5.0 g of the alcohol (**22**). IR $cm^{-1}$: $\nu_{O-H}$ 3570, 3450, $\nu_{C=O}$ 1665. NMR $\delta$: 1.06 (3H, m, >CH–$CH_3$), 2.92 (1H, br. s, OH), 3.58 (2H, t, $J$=6 Hz, $-CH_2$–OH), 6.76 (1H, m, olefinic proton). MS $m/e$: 168 ($M^+$). To a solution of 5.0 g of (30 mmol) of the alcohol (**22**) in 60 ml of pyridine was added 4.59 g (45 mmol) of $Ac_2O$ and the mixture was allowed to stand at room temperature for 14 hr. The reaction mixture was evaporated under reduced pressure. The residue was diluted with 5% HCl and extracted with ether. The extract was washed with water, 2% $NaHCO_3$, dried over $MgSO_4$, and evaporated. The residue in $CHCl_3$ was chromatographed on silica gel (A) and eluted with the same solvent to give 4.43 g (70%) of the dienophile (**9**). A sample was identified with an authentic sample.

**The Adduct (8)**——To a solution of 2.9 g (13.8 mmol) of the dienophile (**9**) in 5 ml of dry $CH_2Cl_2$ were added 0.92 g (6.9 mmol) of $AlCl_3$ powder and 2.3 g (42.6 mmol) of butadiene at −30°. The mixture was allowed to stand at room temperature in a sealed tube for 5 days. The reaction mixture was diluted with water and extracted with ether. The extract was dried over $MgSO_4$ and evaporated to leave the residue. The residue in *n*-hexane was chromatographed on silica gel (A) and elution with $CHCl_3$ gave 1.47 g (40.3%) of the adduct (**8**), bp 128—130°/0.11 mmHg. IR $cm^{-1}$: $\nu_{C=O}$ 1728, 1700, $\nu_{C-O}$ 1200—1280. NMR $\delta$: 1.04 (3H, d, $J$=6 Hz, >CH–$CH_3$), 2.05 (3H, s, $OCOCH_3$), 4.03 (2H, t, $J$=6 Hz, –$CH_2$–OAc), 5.62 (2H, m, olefinic protons). MS *m/e*: 264 ($M^+$). *Anal.* Calcd. for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.41; H, 9.45.

**Catalytic Hydrogenation of the Adduct (8)**——To a solution of 2.547 g (9.65 mmol) of the adduct (**8**) in 150 ml of 99% EtOH was added 1 g of 10% Pd-C and the mixture was stirred under the hydrogen atmosphere at room temperature. After the absorption o hydrogen had ceased, the catalyst was filtered off and the filtrate was evaporated. The residue in $CHCl_3$ was chromatographed on silica gel (B) and elution with $CHCl_3$ afforded 2.539 g (98.9%) of the ketone (**23**), bp 127—128°/0.11 mmHg. IR $cm^{-1}$: $\nu_{C=O}$ 1730, 1698, $\nu_{C-O}$ 1200—1280. NMR $\delta$: 1.00 (3H, d, $J$=5 Hz, >CH–$CH_3$), 2.03 (3H, s, $OCOCH_3$), 4.01 (2H, t, $J$=6 Hz, –$CH_2$OAc). MS *m/e*: 266 ($M^+$). *Anal.* Calcd. for $C_{16}H_{26}O_3$: C, 72.14; H, 9.84. Found: C, 72.02; H, 10.14.

**Bromination of the Ketone (23)**——To a solution of 450 mg (1.7 mmol) of the ketone (**23**) in 10 ml of $CHCl_3$ was added 1.9 ml of 1 M $Br_2$–$CHCl_3$ solution at room temperature under stirring. After 30 min, the reaction mixture was diluted with water and extracted with $CHCl_3$. The extract was dried over $MgSO_4$ and evaporated. The residue in *n*-hexane was chromatographed on silica gel (A) and the column was eluted with 10% ether–*n*-hexane. The earlier eluate gave 68 mg (9.5%) of the dibromide (**24**), bp 124—125°/$10^{-4}$ mmHg. IR $cm^{-1}$: $\nu_{C=O}$ 1728, 1718, $\nu_{C-O}$ 1200—1280. NMR $\delta$: 1.41 (3H, d, $J$=6 Hz, >CH–$CH_3$), 2.01 (3H, s, $OCOCH_3$), 4.02 (2H, t, $J$=7 Hz, –$CH_2$OAc). MS *m/e*: 384, 382, 380 ($M^+$−42), 366, 364, 362 ($M^+$−60). Further elution of the column with the same solvent afforded a solid mass. Recrystallization from *n*-hexane gave 365 mg (62.5%) of the monobromide (**25**), as colorless pillars, mp 92.5—95°. IR $cm^{-1}$: $\nu_{C=O}$ 1720. NMR $\delta$: 1.27 (3H, d, $J$=6 Hz, <CH–$CH_3$), 2.06 (3H, s, $OCOCH_3$), 4.03 (2H, t, $J$=6 Hz, –$CH_2$OAc), 4.58 (1H, d, $J$=11.5 Hz, >CH–Br). *Anal.* Calcd. for $C_{16}H_{25}O_3Br$: C, 55.65; H, 7.29. Found: C, 55.38; H, 7.36.

**The α,β-Unsaturated Ketone (26)**——To a solution of 345 mg (1 mmol) of monobromide (**25**) in 5 ml of dimethylformamide (DMF) were added 222 mg (3 mmol) of $Li_2CO_3$ and 261 mg (3 mmol) of LiBr under stirring. The mixture was heated at 114° under the argon atmosphere for 3 hr with stirring. After cooling, the mixture was made acidic with dil. $H_2SO_4$ and extracted with ether. The extract was dried over $MgSO_4$ and evaporated under reduced pressure. The residue in *n*-hexane was chromatographed on silica gel (B) and elution of the column with $CHCl_3$ gave 182 mg (68.9%) of the α,β-unsaturated ketone (**26**), bp 127—128°/0.10 mmHg. IR $cm^{-1}$: $\nu_{C=O}$ 1728, 1655, $\nu_{C-O}$ 1200—1270. NMR $\delta$: 1.91 (3H, br. s, vinyl methyl), 2.02 (3H, s, $OCOCH_3$), 3.99 (2H, m, –$CH_2$OAc), 5.74 (1H, m, olefinic proton). MS *m/e*: 264 ($M^+$). *Anal.* Calcd. for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.72; H, 9.13.

**Catalytic Hydrogenation of the Compound (26)**——To a solution of 212 mg (0.8 mmol) of the compound (**26**) in 25 ml of 99% EtOH was added 150 mg of 10% Pd-C and the mixture was stirred under the hydrogen atmosphere. Catalyst was filtered off and the filtrate was evaporated. The residue in $CHCl_3$ was chromatographed on silica gel (B) and elution of the column with the same solvent afforded 197 mg (92.2%) of the ketone (**27**), bp 129—130°/0.12 mmHg. IR $cm^{-1}$: $\nu_{C=O}$ 1728, 1692, $\nu_{C-O}$ 1200—1280. NMR $\delta$: 1.02 (3H, m, >CH–$CH_3$), 2.06 (3H, s, $OCOCH_3$), 4.08 (2H, t, $J$=6 Hz, >CH–OAc). High resolution mass spectrum: Calcd. for $C_{16}H_{26}O_3$: 266.188. Found: 266.189.