[Chem. Pharm. Bull. 30(11)4000—4005(1982)]

Intramolecular Diels-Alder Reaction of Undeca-2,8,10-trienoate

Kei Takeda, Mikako Shinagawa, Toru Koizumi, and Eiichi Yoshii*

Faculty of Pharmaceutical Sciences, Toyama Medical and Pharmaceutical University, Sugitani 2630, Toyama 930-01, Japan

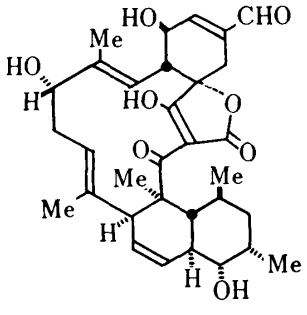
(Received May 6, 1982)

Thermal intramolecular Diels–Alder reaction of methyl (or ethyl) (2*E*,8*E*,10*E*)-12-methoxymethoxy-2-methyl-2,8,10-dodecatrienoate (**4**) was found to give a *ca.* 1: 1 mixture of *trans* and *cis* octalins (**10**, **11**) in a good combined yield. The stereochemistries of **10** and **11** were determined by comparisons of their ^{1}H nuclear magnetic resonance spectra and by the observation that only **10** formed a γ-lactone (**12**) on acid treatment. Preparation of **4** from 6-(tetrahydropyran-2-yl)oxyhexan-1-ol (**5**) by seven step sequence of reactions is also described.

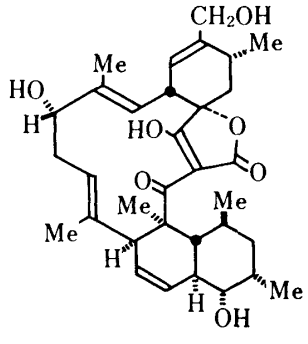
Keywords——cycloaddition; intramolecular Diels–Alder reaction; Wittig reaction; octahydronaphthalene; undeca-2,8,10-trienoate

In connection with studies on the total synthesis of tetronolide (**1**)[1] and kijanolide (**2**),[2] we required an effective method for constructing the bottom half **3** of these compounds. It occurred to us that intramolecular Diels–Alder reaction[3] of (*E*,*E*,*E*)-undeca-2,8,10-trienoate possessing the requisite functionalities would be an effective strategy. Through the *endo* addition mode, the four contiguous asymmetric centers in the cyclohexene ring of **3** are expected to be introduced with the correct relative configurations. At the outset of the present investigation, there was no report of intramolecular Diels–Alder reaction of 2,8,10-trienoate,[4] and therefore we commenced the study by dealing with methyl (or ethyl) (*E*, *E*, *E*)-2-methyl-12-methoxymethoxy-2,8,10-dodecatrienoate (**4**), which was expected to give a parent compound of **3**.

The substrates **4a** and **4b** were prepared as outlined in Chart 3. 6-(Tetrahydropyran-2-yl)-oxyhexan-1-ol (**5**)[5] was oxidized with Collins reagent or better by Swern's procedure using dimethyl sulfoxide and oxalyl chloride[6] to give the aldehyde **6** in 53% yield. Condensation of **6** with methyl diethylphosphonocrotonate anion[7] afforded the (*E*, *E*)-dienoate (**7**). The compound **7** was then subjected to reduction with diisobutylaluminum hydride and the resulting dienol was treated with chloromethyl methyl ether in the presence of diisopropylethyl-amine to afford the di-protected deca-2,4-dien-1,10-diol (**8**). The tetrahydropyranyl (THP) group of **8** was removed with pyridinium tosylate[8] in methanol and the product monoalcohol



1



2

Chart 1

NII-Electronic Library Service

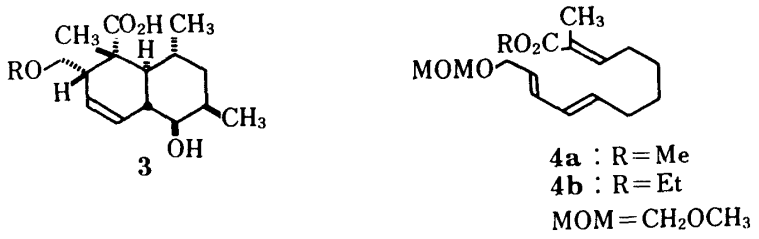
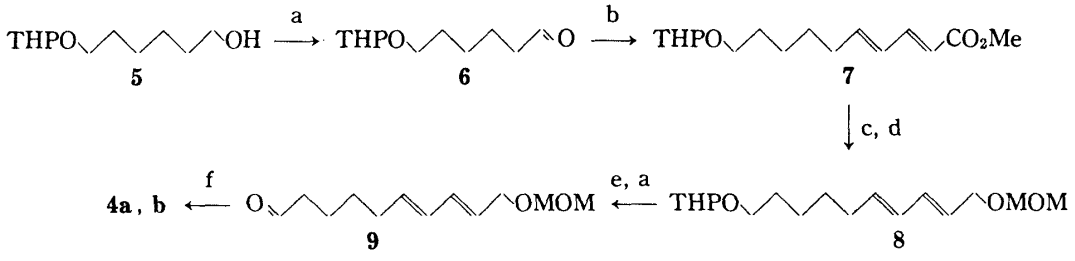


Chart 2

was oxidized by Swern's technique[6] to give the dienal **9**. Finally, the reaction of **9** with 1-(methoxycarbonyl)ethylidenetriphenylphosphorane[9] in benzene at reflux provided the required (*E*,*E*,*E*)-trienoate (**4a**) as a stereochemically homogeneous oil. The corresponding ethyl ester **4b** was similarly prepared from **9**.



a:DMSO-$(COCl)_2$; b:$(EtO)_2P(O)CH_2CH=CH-COOCH_3$, LDA-HMPA; c:iso-$Bu_2AlH$;
d:$ClCH_2OCH_3$, iso-Pr_2NEt; e:pyridine-TsOH; f:$Ph_3P = C(CH_3)COOR$

Chart 3

Intramolecular Diels–Alder reaction of the trienoate **4a** proceeded smoothly in refluxing xylene, the reaction being completed within about 50 h. Two major products, formed in a ratio of 55: 45 (80% yield), were separable by gas–liquid chromatography or high-performance liquid chromatography and were characterized by mass and ^1H nuclear magnetic resonance (NMR) spectroscopic analysis as stereoisomeric octalines, **10a** (shorter retention time) and **11a** (longer retention time). Although there was a remarkable difference in the chemical shifts of allylic angular hydrogens (**10a**, δ 2.28; **11a**, δ 3.07), which was later shown to be diagnostic of the stereoisomers, we intially attempted to differentiate them chemically. When each isomer was exposed to methanolic hydrochloric acid for deprotection of the methoxymethyl group, compound **10a** readily formed a crystalline γ-lactone (**12**) mp 93.5—95°C, but compound **11a** resisted lactone formation and remained at the stage of the γ-hydroxy ester (**13**), bp 146—152°C (3—5 Torr). This result could be rationalized by assigning the *trans* junction to compound **10a** (*endo* addition product) and the *cis* junction to compound **11a** (*exo* addition product). While the *cis*-γ-lactone ring formation observed for **10a** would not cause any severe distortion of the adjacent octalin ring, in the case of **11a** *trans*-γ-lactone formation would require the conformation **13A**, in which severe 1,3-diaxial interaction between the C-1 methyl group and the remaining ring exists, and thus lactonization of **13** would be strongly inhibited. The anomalously low field (δ 3.07) absorption of the C-4a proton of **11a** referred to above (Δ: 0.79 ppm) is also in accord with this conclusion. This chemical shift could be rationalized by invoking a 1,3-diaxial deshielding relationship of the proton at C-4a and the axial methoxycarbonyl in the preferred conformation **13B**.

Having been able to obtain an NMR spectral and chemical basis for differentiating *trans* and *cis* products, we next attempted cycloaddition of the ethyl ester **4b** instead of the methyl ester **4a**. The ethyl ester was subjected to thermal cycloaddition under the same conditions

NII-Electronic Library Service

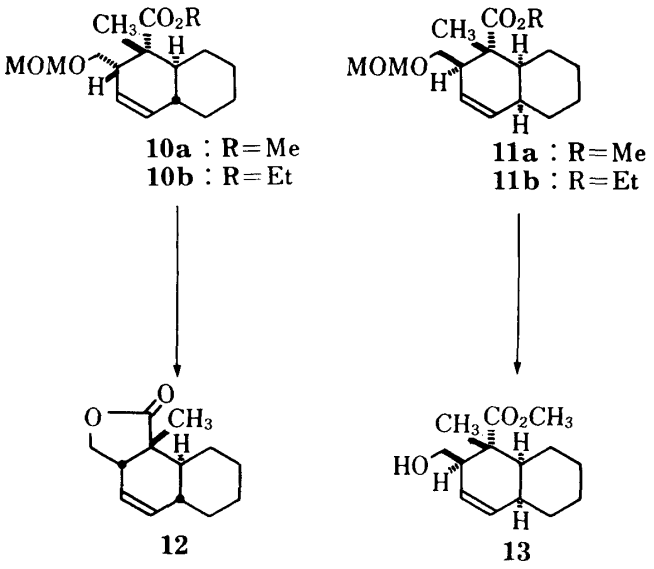


Chart 4

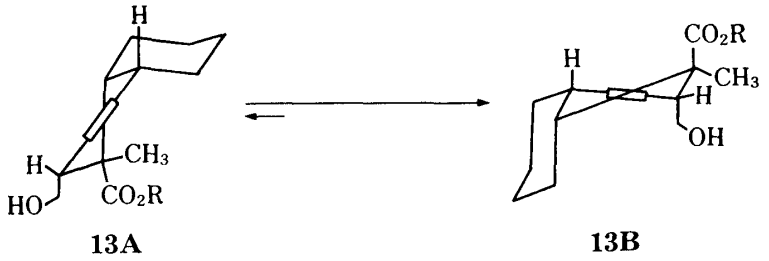


Chart 5

as employed for **4a**, affording a mixture of *trans* and *cis* products (**10b** and **11b**, ratio=48:52) in a combined yield of 86%. The *trans–cis* ratio obtained here is the same as that observed with the methyl ester **4a** within the limits of experimental error. In order to increase the relative amount of the desired *trans* isomer, we attempted Lewis acid-catalyzed cycloaddition using ethylaluminum dichloride,[4b] but only decomposition of the substrate trienoate occurred.[4a]

Recently, Roush and Hall[4a] reported a survey of the intramolecular Diels–Alder reactions of methyl undeca-2,8,10-trienoates, indicating that *cis*-fused cycloadducts are major products and that a parent unsubstituted trienoate shows least *cis*-selectivity giving a *cis*/*trans* ratio of *ca.* 1. More recently, Funk and Zeller[4b] observed high *trans*-selectivity in intramolecular cycloaddition of methyl (*E*, *E*, *E*)-4-hydroxy-2,8,10-dodecatrienoate. Even when these precedents and our own present result are taken into consideration, it remains uncertain whether *trans*-selectivity is realizable in a further functionalized precursor of **3**, but we are satisfied to have been able to construct the basic framework of the bottom half of **1** with desired stereochemistry. Compound **10a** and/or **12** will be employed in a model synthetic study of the 14-membered macrolide framework of **1**.

Experimental

Infrared (IR) spectra were recorded on a Jasco IRA-1 grating spectrophotometer. ^{1}H NMR spectra were taken on a Varian EM-390 or XL-200 spectrometer. Chemical shifts were expressed in ppm downfield from internal tetramethylsilane. Low- and high-resolution mass spectra (MS) were obtained on a Jeol D-300

NII-Electronic Library Service

spectrometer at an ionization potential of 70 eV. Analytical thin-layer chromatography was performed on Merck precoated silica gel 60 F_{254} plates. Column chromatography was performed by using Merck silica gel 60 (70—230 mesh). Gas-liquid partition chromatography (GLC) was done with a Shimadzu GC-6A gas chromatograph. High-performance liquid chromatography (HPLC) was performed with a Waters Model 6000A on μPorasil columns. A Büchi Kugelrohr apparatus was used for vacuum distillation and all boiling points are uncorrected. Melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of this university. Dry tetrahydrofuran (THF) was obtained by distillation from lithium aluminum hydride under argon. Hexamethylphosphoric triamide (HMPA) and dimethyl sulfoxide (DMSO) were dried by distillation from calcium hydride at reduced pressure. Dry dichloromethane was obtained by distillation from phosphorus pentoxide. Other solvents were purified by using standard procedures. All organic solvent extracts were dried with anhydrous magnesium sulfate and the solvents were removed with a rotary evaporater at reduced pressure.

6-(Tetrahydropyran-2-yl)oxyhexanal (**6**)——A stirred solution of oxalyl chloride (49.36 g, 0.389 mol) in dry CH_2Cl_2 (540 ml) was cooled to −60°C and a solution of dry DMSO (61.1 g, 0.783 mol) in dry CH_2Cl_2 (155 ml) was added over a 30 min period. Then, a solution of 6-(tetrahydropyran-2-yl)oxyhexan-1-ol (**5**) (71.4 g, 0.353 mol) in dry CH_2Cl_2 (340 ml) was introduced into the mixture, and after 1 h, triethylamine (225 ml) was added. The reaction mixture was allowed to warm to room temperature during 1.5 h, and then poured into water. The organic layer was separated and it was successively washed with cold 5% HCl, cold saturated $NaHCO_3$ and brine, and dried. Removal of the solvent afforded an oil, which was subjected to distillation to give 37.2 g (53%) of **6**, bp 99°C (1.3 Torr). IR (neat): 1730 cm^{-1}. ^1H NMR (CCl_4) δ: 4.52 (1H, diffused t, O-CH-O), 9.77 (1H, t, J=1.5 Hz, CHO).

Methyl (2*E*,4*E*)-10-(Tetrahydropyran-2-yl)oxy-2,4-decadienoate (**7**)——A solution of the aldehyde **6** (4.5 g, 22.5 mmol) and methyl diethylphosphonocrotonate (5.85 g, 24.8 mmol) in dry THF (90 ml) was added at −50 to −60°C under an Ar atmosphere to a stirred lithium diisopropyl amide (LDA)-HMPA solution prepared by reacting diisopropylamine (2.98 g, 29.5 mmol) in dry THF (28 ml) with *n*-BuLi (13.3 ml of 10% hexane solution, 20.8 mmol) followed by addition of HMPA (28 ml). After being stirred for 4 h at 0°C, the reaction mixture was poured into 0.5 M aqueous $NaHCO_3$ (200 ml) and extracted with a 1 : 1 mixture of ether and hexane. The organic extract was washed with brine, dried, and concentrated. The residual oil was subjected to distillation to give **7** (2.75 g, 43.4%), bp 130—140°C (0.25 Torr). IR (neat): 1725, 1650, 1620 cm^{-1}. ^1H NMR (CCl_4) δ: 3.63 (3H, s, OCH_3), 4.50 (1H, diffused t, O-CH-O), 5.70 (1H, d, J=15 Hz, 2-H), 5.9—6.3 (2H, m, 4- and 5-H), 7.17 (1H, ddd, J=15, 6, 3 Hz, 3-H). MS *m/e*: 282.1865 (M^+, calcd. for $C_{16}H_{26}O_4$: 282.1832), 198.1275 ($M^+-C_5H_8O$, calcd. 198.1255).

(2*E*,4*E*)-1-Methoxymethoxy-10-(tetrahydropyran-2-yl)oxy-2,4-decadiene (**8**)——A mixture of **7** (1.25 g, 4.43 mmol) and dry toluene (12.5 ml) maintained under an Ar atmosphere was cooled with ice-water, and diisobutylaluminum hydride (25 w/v % hexane solution, 5.54 ml, 9.75 mmol) was added by means of a syringe with stirring. After 1 h, the reaction was quenched by addition of MeOH and the mixture was concentrated under reduced pressure. The residue was extracted with ether, and the ether solution was dried and concentrated to give (2*E*,4*E*)-10-(tetrahydropyran-2-yl)oxy-2,4-decadien-1-ol (1.09 g, 96%) which was sufficiently pure for the next step as judged from the spectral data and TLC results. ^1H NMR ($CDCl_3$) δ: 1.25—1.8 (12H, m), 1.9—2.3 (2H, m), 2.57 (1H, s, OH), 3.2—3.8 (4H, m), 4.05 (2H, d, J=6 Hz, OCH_2), 4.53 (1H, diffused t, O-CH-O), 5.4—6.4 (4H, m, vinyl H), MS *m/e*: 255 (M^++1), 254 (M^+), 253 (M^+−1), 152, 86.

Chloromethyl methyl ether (1.1 g, 13.7 mmol) was added with a syringe to a stirred and refluxing solution of the above alcohol (0.87 g, 3.43 mmol) and diisopropylethylamine (3.53 g, 27.4 mmol) in dry CH_2Cl_2 (5.8 ml). After 20 min, the reaction mixture was allowed to cool and water (70 ml) was added. The mixture was extracted with ether, and the ether extract was briefly washed with cold 5% HCl and then with saturated $NaHCO_3$ and brine. The extract was dried, and the organic solvent was removed to give essentially pure **8** (0.964 g, 94%). ^1H NMR (CCl_4) δ: 1.25—1.8 (12H, m), 2.0—2.2 (2H, m), 3.32 (3H, s, OCH_3), 3.15—3.8 (4H, m), 4.00 (2H, d, J=5.5 Hz, OCH_2), 4.51 (1H, diffused t, O-CH-O), 4.53 (2H, s, OCH_2O), 5.3—6.4 (4H, m, vinyl H). MS *m/e*: 152 (M^+−146), 101, 85, 66, 45.

(6*E*,8*E*)-10-Methoxymethoxy-6,8-decadienal (**9**)——A solution of **8** (4.12 g, 13.8 mmol) and pyridinium *p*-toluenesulfonate (348 mg, 1.38 mmol) in dry EtOH (110 ml) was heated at 55°C. After 20 h, the solution was concentrated under reduced pressure and the residue was extracted with ether. The ether solution was washed with brine, dried, and concentrated to give an oil, which was subjected to column chromatography eluting with ether-hexane (5: 2) to give (6*E*,8*E*)-10-methoxymethoxy-6,8-decadien-1-ol (2.70 g, 77%), bp 130—155°C (0.4 Torr). ^1H NMR (CCl_4) δ: 1.80 (6H, m), 1.9—2.3 (2H, m), 2.72 (1H, s, OH), 3.33 (3H, s, OCH_3), 3.40—3.7 (2H, m, CH_2OH), 4.02 (2H, d, J=5.5 Hz, CH_2O), 4.57 (2H, s, OCH_2O), 5.4—6.35 (4H, m, vinyl H).

This alcohol was subjected to oxidation by Swern's technique as described for the preparation of **6**. The aldehyde **9** was obtained as an oil (68—80% yield), bp 116°C (0.6 Torr). IR (neat): 1730 cm^{-1}. ^1H NMR (CCl_4) δ: 2.38 (2H, td, J=7, 1.5 Hz, 2-H), 3.32 (3H, s, OCH_3), 4.02 (2H, d, J=5.5 Hz, OCH_2), 4.55(2H, s, OCH_2O), 5.3—6.4 (4H, m, vinyl H), 9.77 (1H, t, J=1.5 Hz, CHO). MS *m/e*: 212 (M^+), 168, 151, 150

NII-Electronic Library Service

Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.92; H, 9.43. Found: C, 67.38; H, 9.20.

Methyl (2*E*,8*E*,10*E*)-12-Methoxymethoxy-2-methyl-2,8,10-dodecatrienoate (4a)——A solution of **9** (4.26 g, 20.1 mmol) and 1-(methoxycarbonyl)ethylidenetriphenylphosphorane (11.9 g, 32.9 mmol) in benzene (200 ml) was refluxed for 2 h. The reaction mixture was allowed to cool and filtered. The filtrate was concentrated, and ether was added for further precipitation of triphenylphosphine oxide. The filtered solution was concentrated and the residual oil was subjected to column chromatography eluting with hexane–AcOEt (7: 1) to give **4a** (3.41 g, 57.4%). ^{1}H NMR (CCl_4) δ: 1.3—1.7 (4H, m), 1.82 (3H, s, C–CH_3), 1.95—2.35 (4H, m), 3.32 (3H, s, OCH_3), 3.72 (3H, s, $COOCH_3$), 4.03 (2H, d, J=5.5 Hz, OCH_2), 4.55 (2H, s, OCH_2O), 5.35—6.4 (4H, m, vinyl H), 6.71 (1H, diffused t, J=7.5 Hz, 3-H). MS *m/e*: 282.1809 (M^+, calcd for $C_{16}H_{26}O_4$: 282.1830.

Ethyl (2*E*,8*E*,10*E*)-12-Methoxymethoxy-2-methyl-2,8,10-dodecatrienoate (4b)——This ethyl ester was prepared by the reaction of **9** with 1-(ethoxycarbonyl)ethylidenetriphenylphosphorane according to the procedure described above. ^{1}H NMR (CCl_4) δ: 1.37 (3H, t, J=6 Hz, $CH_2C\underline{H}_3$), 1.80 (3H, s, C–CH_3), 3.30 (3H, s, OCH_3), 3.98 (2H, d, J=5.5 Hz, OCH_2), 4.15 (2H, q, J=6 Hz, $C\underline{H}_2CH_3$), 4.53 (2H, s, OCH_2O), 5.35—6.3 (4H, m, vinyl H), 6.65 (1H, diffused t, J=7.5 Hz, 3-H). MS *m/e*: 296.2012 (M^+, calcd for $C_{17}H_{28}O_4$: 296.1987), 251.1615 ($M^+-C_2H_5O$, calcd for 251.1645).

Methyl (1*R,2*S**,4a*R**,8a*S**)-2-Methoxymethoxymethyl-1-methyl-1,2,4a,5,6,7,8,8a-octahydronaphthalene-1-carboxylate (10a) and Methyl (1*R**,2*R**,4a*S**,8a*S**)-2-Methoxymethoxymethyl-1-methyl-1,2,4a,5,6,7,8,8a-octahydronaphthalene-1-carboxylate (11a)**——A solution of **4a** (3.4 g) in dry *p*-xylene (55 ml) was heated under reflux for 45 h. The solvent was then removed under reduced pressure and the residual oil was subjected to column chromatography eluting with hexane–ether (5: 1) to give a 55: 45 mixture of **10a** and **11a** (2.7 g, 80%) which showed a single spot on TLC with various solvent systems. The mixture could be separated by GLC [retention times: 13.1 min for **10a** and 18.5 min for **11a** (5% OV-17 on Shimalite, 3 mm×3 m, 210°C)]. Analytical samples were obtained by preparative GLC.

10a: IR (neat): 1730 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.16 (3H, s, C–CH_3), 2.28 (1H, m, allylic H), 3.35 (3H, s, OCH_3), 3.42 (2H, m, OCH_2), 3.36 (3H, s, $COOCH_3$), 4.52 (2H, s, OCH_2O), 5.50 (2H, br s, vinyl H). MS *m/e*: 282 (M^+), 252, 220, 192, 161, 147, 119, 105, 45. *Anal.* Calcd for $C_{16}H_{26}O_4$: C, 68.09; H, 9.22. Found: C, 68.07; H, 9.22.

11a: IR (neat): 1730 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.09 (3H, s, C–CH_3), 3.07 (1H, m, allylic H), 3.35 (3H, s, OCH_3), 3.44 (1H, t, J=8 Hz, OC$\underline{H}$H), 3.68 (3H, s, $COOCH_3$), 4.58 (2H, s, OCH_2O), 5.5—5.65 (2H, m, vinyl H). MS *m/e*: 282 (M^+), 251, 220, 192, 161, 147, 119, 105, 45. *Anal.* Calcd for $C_{16}H_{26}O_4$: C, 68.09; H, 9.22. Found: C, 68.11; H, 9.15.

Ethyl (1*R,2*S**,4a*R**,8a*S**)-2-Methoxymethoxymethyl-1-methyl-1,2,4a,5,6,7,8,8a-octahydronaphthalene-1-carboxylate (10b) and Ethyl (1*R**,2*R**,4a*S**,8a*S**)-2-Methoxymethoxymethyl-1-methyl-1,2,4a,5,6,7,8,8a-octahydronaphthalene-1-carboxylate (11b)**——These compounds were obtained from **4b** in a ratio of 48: 52 (86% yield) according to the procedure described above for **4a**, and were separated by GLC or HPLC. Retention times: GLC, 6.5 min for **10b** and 8.5 min for **11b** (5% SE-30 on Shimalite 3 mm×3 m, 220°C); HPLC, 9.4 min for **10b** and 9.6 min for **11b** (AcOEt–hexane=1: 20).

10b: ^{1}H NMR ($CDCl_3$) δ: 1.16 (3H, s, C–CH_3), 1.26 (3H, t, J=7 Hz, $CH_2C\underline{H}_3$), 2.17 (1H, m, allylic H), 3.13 (3H, s, OCH_3), 3.43 (2H, d, J=6 Hz, OCH_2), 4.10 (2H, q, J=7 Hz, $C\underline{H}_2CH_3$), 4.52 (2H, s, OCH_2O), 5.51 (2H, s, vinyl H). MS *m/e*: 296 (M^+), 266, 234, 192, 161, 147, 119, 105, 45.

11b: ^{1}H NMR ($CDCl_3$) δ: 1.16 (3H, s, C–CH_3), 1.21 (3H, t, J=7 Hz, $CH_2C\underline{H}_3$), 3.05 (1H, m, allylic H), 3.14 (3H, s, OCH_3), 3.41 (1H, t, J=6 Hz, OC$\underline{H}$H), 3.49 (1H, t, J=6 Hz, OC$\underline{H}$H), 4.12 (2H, q, J=7 Hz, $C\underline{H}_2CH_3$), 4.56 (2H, s, OCH_2O), 5.52 (1H, dt, J=10, 2 Hz, vinyl H), 5.60 (1H, dt, J=10, 2 Hz, vinyl H). MS *m/e*: 296 (M^+), 266, 265, 234, 205, 161, 147, 119, 105, 45.

(3a*R,5a*S**,9a*R**,9b*S**)-9b-Methyl-1,3,3a,5a,6,7,8,9,9a,9b-decahydronaphtho[1,2-*c*]furan-1-one (12)**——Three drops of 12 N HCl were added to a solution of **10a** or **10b** (115 mg) in MeOH (8 ml), and the solution was refluxed for 15 min. It was then concentrated and the residue was extracted with ether. The ether extract was washed with 5% $NaHCO_3$ and brine, and dried. Removal of the solvent afforded an oil which was subjected to distillation, bp 117°C (3—5 Torr), mp 93.5—95°C after crystallization from hexane. IR (KBr): 1755 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.60 (3H, s, CH_3), 2.65—2.85 (1H, m, allylic H), 3.86 (1H, dd, J= 9, 8 Hz, OC$\underline{H}$H), 4.42 (1H, t, J=9 Hz, OC$\underline{H}$H), 3.5—3.7 (2H, m, vinyl H). MS *m/e*: 206 (M^+), 161, 133, 119, 105, 91. *Anal.* Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: 75.65; H, 8.56.

Methyl (1*R,2*R**,4a*S**,8a*S**)-2-Hydroxymethyl-1-methyl-1,2,4a,5,6,7,8,8a-octahydronaphthalene-1-carboxylate (13)**——Treatment of **11a** with methanolic HCl as described above afforded **13** as an oil. An analytical sample was obtained by preparative GLC. IR (neat): 3440, 1725 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.19 (3H, s, C–CH_3), 2.9—3.2 (1H, m, allylic H), 3.55—3.65 (2H, m, OCH_2), 3.67 (3H, s, $COOCH_3$), 5.65 (2H, s, vinyl H). MS *m/e*: 238 (M^+), 179, 161, 119, 105, 91. *Anal.* Calcd for $C_{14}H_{22}O_3$: C, 70.59; H, 9.24. Found: C, 70.61; H, 9.00.

References and Notes

1) N. Hirayama, M. Kasai, K. Shirahata, Y. Ohashi, and Y. Sasada, *Tetrahedron Lett.*, **1980**, 2559.
2) A.K. Mallams, M.S. Puar, R.R. Rossman, A.T. PcPhail, and R.D. Macfarlane, *J. Am. Chem. Soc.*, **103**,

NII-Electronic Library Service

3940 (1981).
3) G. Brieger and J.N. Bennett, *Chem. Rev.*, **80**, 63 (1980); W. Oppolzer, *Angew. Chem. Int. Ed. Engl.*, **16**, 10 (1977).
4) During the present investigation the following two articles dealing with the same subject have appeared. *a*) W.R. Roush and S.E. Hall, *J. Am. Chem. Soc.*, **103**, 5200 (1981); *b*) R.L. Funk and W.E. Zeller, *J. Org. Chem.*, **47**, 180 (1982).
5) O.P. Vig, A.K. Vig, J.S. Mann, and K.G. Gupta, *J. Indian Chem. Soc.*, **52**, 538 (1975).
6) A.J. Mancuso, S-L. Huang, and D. Swern, *J. Org. Chem.*, **43**, 2480 (1978).
7) K. Sato, S. Mizuno, and M. Hirayama, *J. Org. Chem.*, **32**, 177 (1967).
8) M. Miyashita, A. Yoshikoshi, and P.A. Grieco, *J. Org. Chem.*, **42**, 3772 (1977).
9) O. Isler, H. Gutmann, M. Montavon, R. Ruegg, G. Ryser, and P. Zeller, *Helv. Chim. Acta*, **40**, 1247 (1957).
10) By using this difference in chemical reactivities, the isomers **10a** and **11a** could have been readily separated as the γ-lactone (**12**) and γ-hydroxy ester (**13**) by silica gel chromatography.

NII-Electronic Library Service