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Stereochemistry of Lewis Acid and Fluoride Promoted Intramolecular Cyclization of β-(Alkoxycarbonyl)allylsilane with Enones. Synthesis of Bicyclo[4.3.0]nonanes

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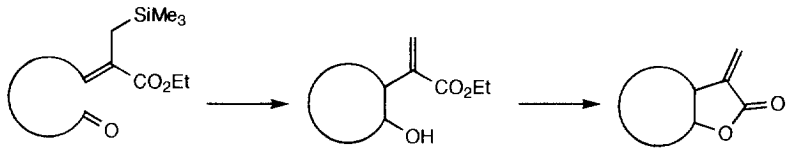
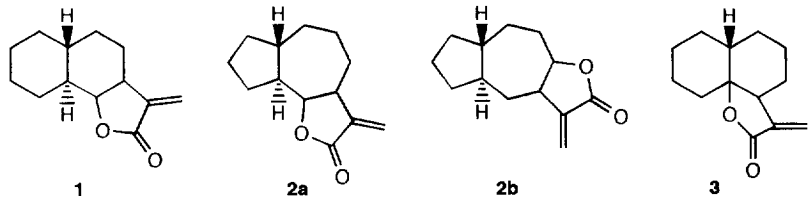
Abstract Treatment of ethyl 10-oxo-2-(trimethylsilylmethyl)undeca-2,8-dienoate with a Lewis acid or fluoride afforded ethyl 2-[2-(2-oxopropyl)cyclohex-1-yl]acrylate and/or 7-acetyl-9-methylenebicyclo-[4.3.0]nonan-8-one. Under these conditions the 2*Z*,8*E*- and 2*Z*,8*Z*-precursors give predominantly *cis*-disubstituted six-membered ring products, while the 2*E*,8*E*- and 2*E*,8*Z*-precursors give primarily *trans*-disubstituted six-membered ring products. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Allylsilanes are versatile allylanion equivalents in organic synthesis.[1] The intramolecular addition of allylsilanes to conjugated ketones[2,3] has allowed the construction of various carbocyclic compounds.[4] In this regard, the use of fuctionalized allylsilanes[5] such as the trimethylenemethane group developed by Trost[6] and the β-(dimethoxymethyl)allylsilane developed by Lee,[7] are useful building blocks for the synthesis of five and seven membered rings. The β-(alkoxycarbonyl)allylsilane is unique among this class of reagent since the γ-position of the allysilane can participate in both nucleophilic and electrophilic reactions. Hosomi *et al.* first reported on the intermolecular reaction of β-(ethoxycarbonyl)allylsilanes with carbonyl compounds to give α-methylene-γ-lactones,[8] a common structural unit of sesquiterpenes.[9] We applied an intramolecular variation of this reaction (Scheme 1) in the synthesis of various natural products containing α-methylene-γ-lactones,[10-12] such as 14,15-bisnor-eudesmanolide **1**,[10a-c] -guaianolides **2a**,[10d] **2b**,[10e] and -cadinanolides **3**[10f] (Chart 1). This approach allowed for the sequential formation of two rings. A carbocyclic ring is formed from the initial 1,2 addition of



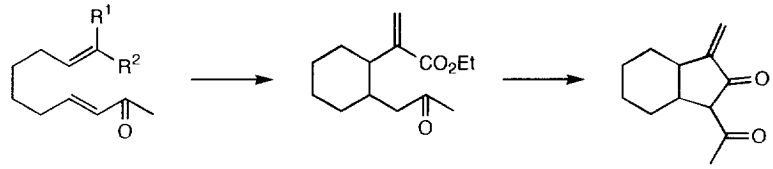
Scheme 1.



1 **2a** **2b** **3**

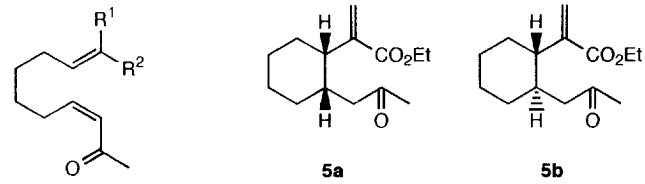
Chart 1.

the allylsilane to the aldehyde carbonyl, and the resulting alcohol then reacts with the ester to give the γ-lactone. In a preliminary communication[13] we reported on an extension of this concept to include the use of α,β-unsaturated ketones providing a new synthetic pathway to the bicyclo[4.3.0]nonane framework (Scheme 2). Here we present the details of this cyclization reaction using all four allylsilane stereoisomers **4a-d** (Chart 2), and discuss the stereochemistry of the products **5a,b** resulting from the use of Lewis acids and fluoride ion.



4a R^1=CH_2SiMe_3, R^2=CO_2Et
4b R^1=CO_2Et, R^2=CH_2SiMe_3

Scheme 2.



5a **5b**

4c R^1=CH_2SiMe_3, R^2=CO_2Et
4d R^1=CO_2Et, R^2=CH_2SiMe_3

Chart 2.

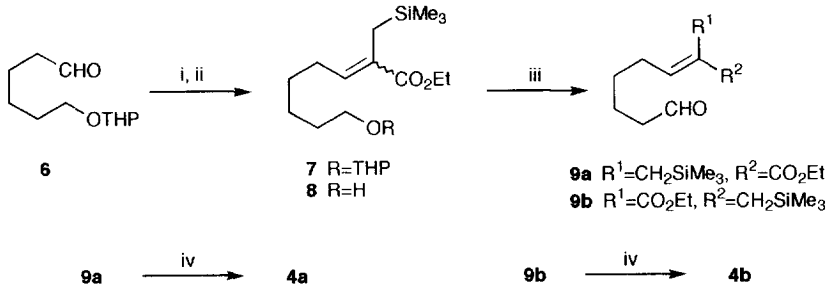
RESULTS AND DISCUSSION

Synthesis of the Cyclization Precursors

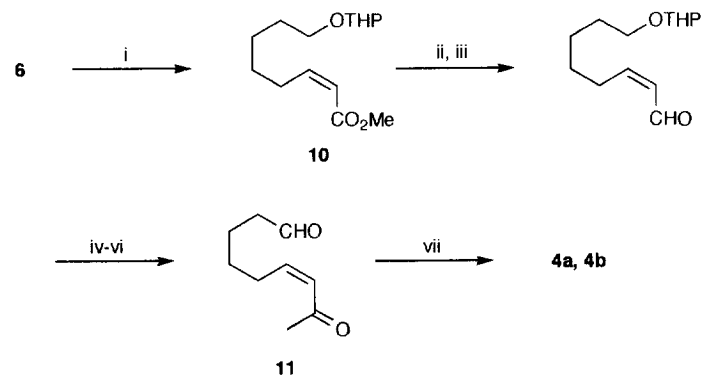
The synthesis of **4a** and **4b** is shown in Scheme 3. Thus, aldehyde **6** was prepared from 1,6-hexanediol according to Nishitani's procedure,[11b] and then converted to a mixture of *Z*- and *E*-isomers **7** using Hoffmann's olefination method[14] (*Z*:*E*=2:1). Deprotection of **7** using aqueous HCl in refluxing THF afforded alcohol **8**,

which was converted to aldehyde **9**[11b] using Swern oxidation conditions. At this point, the separation of the two geometrical isomers **9a** and **9b** was possible by column chromatography using silica-gel. The stereochemistry of each isomer was determined from the chemical shift of the olefinic protons of the ^{1}H NMR spectrum. The proton for the *Z*-isomer resonates at δ 6.55, whereas the proton in the *E*-isomer is found upfield at δ 5.62.[10] The required cyclization precursors **4a** and **4b** were obtained in 91% and 77% yield respectively from **9a** and **9b**, using $(MeO)_2P(O)CH_2COCH_3$ in a Wittig-Horner reaction.[15] The *E*-configuration of the newly formed enone moiety was assigned to both **4a** and **4b** from the observed 16 Hz coupling between the olefinic protons.

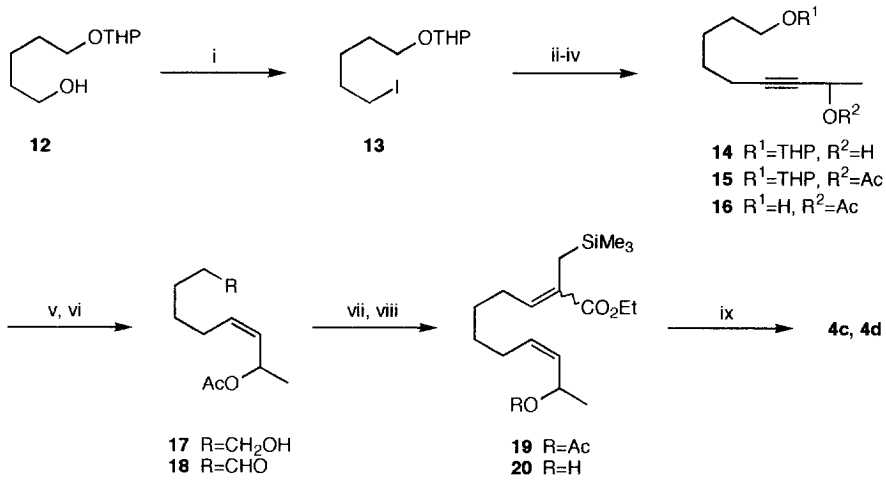
In order to synthesize the corresponding *Z*-isomers **4c** and **4d**, two routes were examined. The first approach depicted in scheme 4 relies upon Still's *cis*-selective Wittig reaction[16] of **6** to give **10**. Although this step worked as planned to give the desired *Z*-isomer **10**, this approach was eventually abandoned due to



Scheme 3. Reagents and conditions: i, $(EtO)_2P(O)CH(CO_2Et)CH_2SiMe_3$, NaH, DME, r.t. (84%); ii, 5% HCl/THF (1:4), reflux (95%); iii, DMSO, $(COCl)_2$, Et_3N, CH_2Cl_2, -60 °C (89%); iv, $(MeO)_2P(O)CH_2COCH_3$, NaH, THF, r.t. (91% **4a**, 77% **4b**).



Scheme 4. Reagents and conditions: i, $(CF_3CH_2O)_2P(O)CH_2CO_2Me$, 18-crown-6, $KN(SiMe_3)_2$, THF, r.t. (57%); ii, DIBAL-H, CH_2Cl_2, -50 °C (99%); iii, MnO_2, CH_2Cl_2, r.t. (77%); iv, MeMgBr, THF, r.t. (92); v, 5% HCl/THF (1:4), reflux (65%); vi, DMSO, $(COCl)_2$, Et_3N, CH_2Cl_2, -60 °C; vii, $(EtO)_2P(O)CH(CO_2Et)CH_2SiMe_3$, NaH, DME, r.t.



Scheme 5. Reagents and conditions: i, I_2, Ph_3P, imidazole, benzene, r.t. (83%); ii, 3-butyn-2-ol, BuLi, THF/DMPU, r.t. (59%); iii, Ac_2O, pyridine, r.t. (96%); iv, PPTS, MeOH, reflux (95%); v, H_2, Lindlar catalyst, EtOH, r.t. (86%); vi, DMSO, $(COCl)_2$, Et_3N, CH_2Cl_2, -60 °C; vii, $(EtO)_2P(O)CH(CO_2Et)CH_2SiMe_3$, NaH, DME, r.t. (65% from **17**); viii, K_2CO_3, EtOH, r.t. (49%); ix, MnO_2, CH_2Cl_2, r.t. (78%).

isomerization of enone **11** during installation of the allylsilane moiety as described in scheme 3. As a result, only **4a** and **4b** were produced from *Z*-enone **11**.

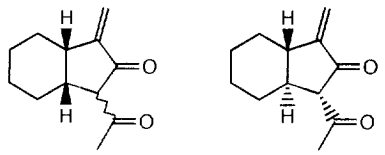
Eventually we were able to obtain **4c** and **4d** by the route shown in scheme 5. In this approach, the required *cis*-double bond was introduced by stereoselective reduction of an alkyne. Thus, 1,5-pentanediol mono-THP ether **12**[11b] was converted to iodide **13** using I_2/Ph_3P/imidazole.[17] The iodide was allowed to react with the dianion of 3-butyn-2-ol[18,19] in THF-DMPU[20] to give alkyne **14** in 59% yield. Acylation of alcohol **14** gave acetate **15** which was hydrolyzed in MeOH with PPTS to afford diol monoacetate **16** in 95% yield. Lindlar reduction[19,21] of alkyne **16** provided alkene **17** in 86% yield with complete *cis*-selectivity. The newly formed double bond was assigned the *cis*-configuration based upon the observed 11 Hz coupling of the olefinic protons. It was also possible to reduce the alkyne to the *cis*-olefin at some other stage of the synthesis, however the overall yield of **4c** and **4d** was lower by this route. Swern oxidation of alcohol **17** afforded aldehyde **18** which was subjected to the previously discussed olefination procedure to give **19** as an inseparable mixture of geometrical isomers in 65% overall yield from **17**. The acetate group was removed using K_2CO_3 in EtOH to give alcohol **20** which was oxidized with MnO_2 to give **4c** and **4d** as a mixture of *Z*- and *E*-allylsilanes. Although it was not possible to isolate **4c** and **4d** in a pure state, several mixtures of different isomer ratios were obtained by column chromatography. These mixtures were used in the cyclization reactions discussed below.

Intramolecular Cyclization Reactions

The intramolecular cyclization of the isomeric allylsilanes **4a-d**, were examined using various Lewis acids and fluoride ion. The results for the *E*-enones **4a** and **4b**, are given in Table 1. All of the Lewis acid promoted cyclizations proceeded in good yield. The stereochemistry of products appeared to be more dependent on the

geometry of the allylsilane rather than the reagent used. Thus, the *Z*-isomer **4a**, afforded the *cis*-product **5a** in favor of the *trans*-isomer **5b** in approximately a 9:1 ratio (entries 1-4), while the corresponding *E*-allylsilane **4b** gave a ratio of **5a** to **5b** of between 3:7 to 1:9 (entries 5-8). In each case, the products **5a,b** were separated by column chromatography and the stereochemistry of the products determined from the magnitude of the *J*-values for the methine protons in the ^{1}H NMR spectra. The value for *cis*-isomer **5a** was found to be 4 Hz while the corresponding protons in the *trans*-isomer **5b** showed an 11Hz coupling. Cyclization of **4a** and **4b** using TBAF as an source of fluoride ion (entries 9-10) afforded **5a** and **5b** along with the bicyclic compounds **21a** and **21b** (Chart 3). Formation of bicyclic compounds **21a** and **21b** can be explained by addition of the ketone enolates of **5a** and **5b**, formed upon 1,4-addition of the allylanion to the enone system, to the adjacent ester group.

It is interesting that the stereochemical outcome of these reactions, as defined by the relative stereochemistry of substituents on the newly formed cyclohexane ring, is independent of the reagent used to promote the reaction. For example, the *cis*:*trans* ratio for $TiCl_4$ mediated reaction (cationic mechanism; entry 1) is 88:12 while that for the fluoride induced pathway (anionic mechanism; entry 9) is 78:22 [(**5a**+**21a**):(**5b**+**21b**)]. In a similar way, the reaction of **4b** with $SnCl_4$ affords a 27:73 ratio of stereoisomers while the corresponding reaction with



21a **21b**

Chart 3.

Table 1. Cyclization of 4a and 4b (*trans*-Enone Precursors)[a]

Entry	Precursor	Reagent	Equiv.	Solvent	Time (h)	Yield (%)	Ratio **5a**	**5b**	**21a**	**21b**
1	**4a**	$TiCl_4$	1.5	CH_2Cl_2	17	89	88	12	0	0
2	**4a**	BF_3OEt_2	1.5	CH_2Cl_2	18	89	95	5	0	0
3	**4a**	$SnCl_4$	1.5	CH_2Cl_2	1	96	94	6	0	0
4	**4a**	$EtAlCl_2$	3	CH_2Cl_2	46	89	86	14	0	0
5	**4b**	$TiCl_4$	1.5	CH_2Cl_2	21	91	10	90	0	0
6	**4b**	BF_3OEt_2	1.5	CH_2Cl_2	24	91	14	86	0	0
7	**4b**	$SnCl_4$	1.5	CH_2Cl_2	1	98	27	73	0	0
8	**4b**	$EtAlCl_2$	3	CH_2Cl_2	45	91	29	71	0	0
9	**4a**	TBAF	3	THF	19	79	57	16	21	6
10	**4b**	TBAF	3	THF	16	83	25	65	2	8

a All reaction were carried out at room temperature.

Table 2. Cyclization of 4c and 4d (*cis*-Enone Precursors)[a]

Entry	Precursor **4c**:**4d**	Reagent	Equiv.	Solvent	Yield (%)	Ratio **5a**	**5b**	**21a**	**21b**
1	39:61	$SnCl_4$	1.5	CH_2Cl_2	74	59	41	0	0
2	51:49	$SnCl_4$	1.5	CH_2Cl_2	62	67	33	0	0
3	67:33	$SnCl_4$	1.5	CH_2Cl_2	84	77	23	0	0
4	87:13	$SnCl_4$	1.5	CH_2Cl_2	75	87	13	0	0
5	39:61	BF_3OEt_2	6	CH_2Cl_2	81	55	45	0	0
6	51:49	BF_3OEt_2	6	CH_2Cl_2	68	63	37	0	0
7	72:28	BF_3OEt_2	6	CH_2Cl_2	70	80	20	0	0
8	87:13	BF_3OEt_2	6	CH_2Cl_2	84	88	12	0	0
9	39:61	TBAF	3	THF	82	53	35	6	6
10	60:40	TBAF	3	THF	85	66	30	1	3
11	67:33	TBAF	3	THF	89	57	22	12	9
12	87:13	TBAF	3	THF	79	63	19	12	6

a All reactions were carried out at room temperature for *ca.* 20 h.

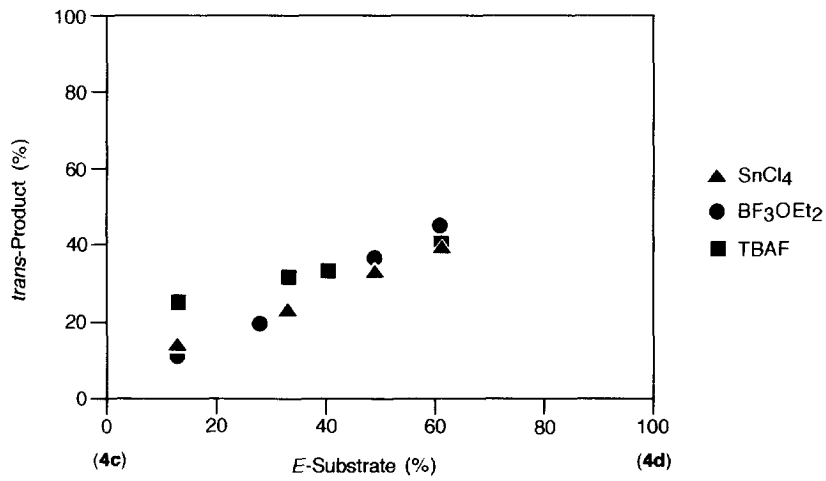


Figure 1. Relation between the ratio of *E*-substrate (**4d**) and the ratio of *trans*-product (**5b** and/or **27b**) in the cyclization of a mixture of **4c** and **4d**.

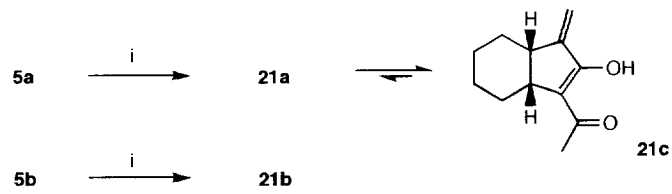
fluoride ion results in the same 27:73 ratio of products. Thus, it appears that the geometry of the allylsilane is the major factor controlling the stereochemical outcome of these reactions.

The inability to separate the isomeric allylsilanes **4c** and **4d** led to the use of various mixtures of these compounds in the cyclization reactions. In this study, the use of Lewis acids was limited to $SnCl_4$ and BF_3OEt_2, and TBAF was again the source of fluoride ion. The results of these experiments are given in Table 2. Comparing the ratio of *cis*- (**5a**) to *trans*- (**5b**) products to the relative amount of *Z*- (**4c**) and *E*- (**4d**) isomers in the starting mixture reveals the same trend in stereochemical dependence observed for **4a** and **4b** (Table 1). In each case, as the percentage of *Z*-isomer **4c** increases relative to **4d**, the amount of *cis*-product **5a** observed in the product mixture also increases. Further, a linear correlation was found between the ratio of **4c/4d** and that of **5a/5b** (Figure 1). Using the data from the $SnCl_4$ mediated reaction, extrapolation to the use of pure **4c** leads to a predicted ratio of **5a** to **5b** of 95:5, while a similar analysis for pure **4d** suggests that a 37:63 ratio of cyclized products would be produced. These results are in complete agreement with the cyclization of **4a** (Table 1, entry 3) under similar conditions and of **4b** (Table 1, entry 7). The same analysis using the experimental data for either the BF_3OEt_2 or TBAF induced reactions yields a similar result. Once again, the geometry of the allylsilane moiety appears to be the major controlling factor determining the stereochemical outcome of these reactions.

Synthesis of Bicyclo[4.3.0]nonanes

The synthesis of bicyclo[4.3.0]nonanes from **5a** and **5b** was performed in two ways. Treatment of **5a** or **5b** with NaH in THF at room temperature afforded **21a** and **21b** in 60% and 77% yield respectively (Scheme 6). Compound **21a** was found to be a 4:1 mixture of stereoisomers having a large enol component (**21c**) in solution. Support for the presence of **21c** came from the observation of an enol proton in the ^1H NMR spectrum at δ 14.0, and a UV absorption at $\lambda_{max} = 318$ nm. In contrast, **21b** was isolated as a single isomer. The α-configuration of the acetyl group in **21b** was assigned from the observation of a 12 Hz coupling of the methine proton flanked by the two carbonyl groups to the adjacent proton at the ring junction.

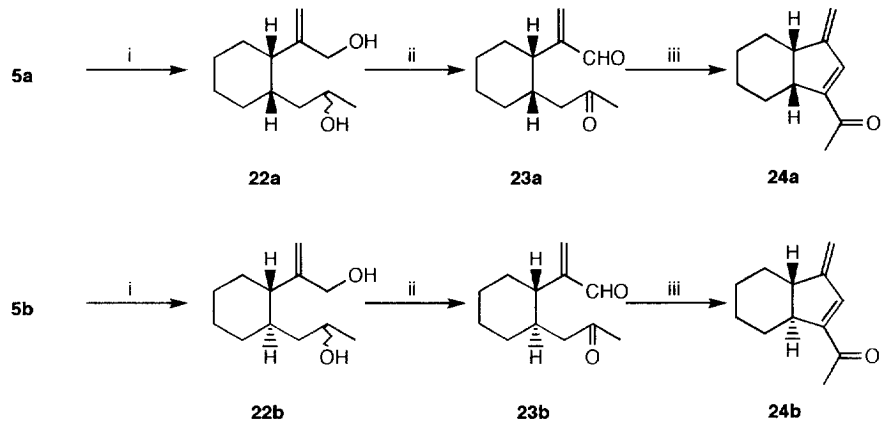
A second route to the bicyclo[4.3.0]nonane ring system was also investigated (Scheme 7). Thus treatment of **5a** with DIBAL-H in CH_2Cl_2 afforded diol **22a** in 98% yield. Oxidation with pyridinium dichromate gave keto-aldehyde **23a** which underwent an intramolecular aldol condensation when exposed to KOH in EtOH to give hydrindane **24a** in 49% yield. In a similar manner, the *trans*-isomer **5b** was converted to *trans*-hydrindane **24b**.



Scheme 6. Reagents and conditions: i, NaH, THF, r.t. (60% **21a**, 77% **21b**).

Stereochemistry of the Cyclization Reaction

The results of the cyclization reactions given in Tables 1 and 2 indicate that the geometry of the allylsilane is the major factor controlling the stereochemistry of the product. Both **4a** and **4c** where the allylysilane is in the *Z*-

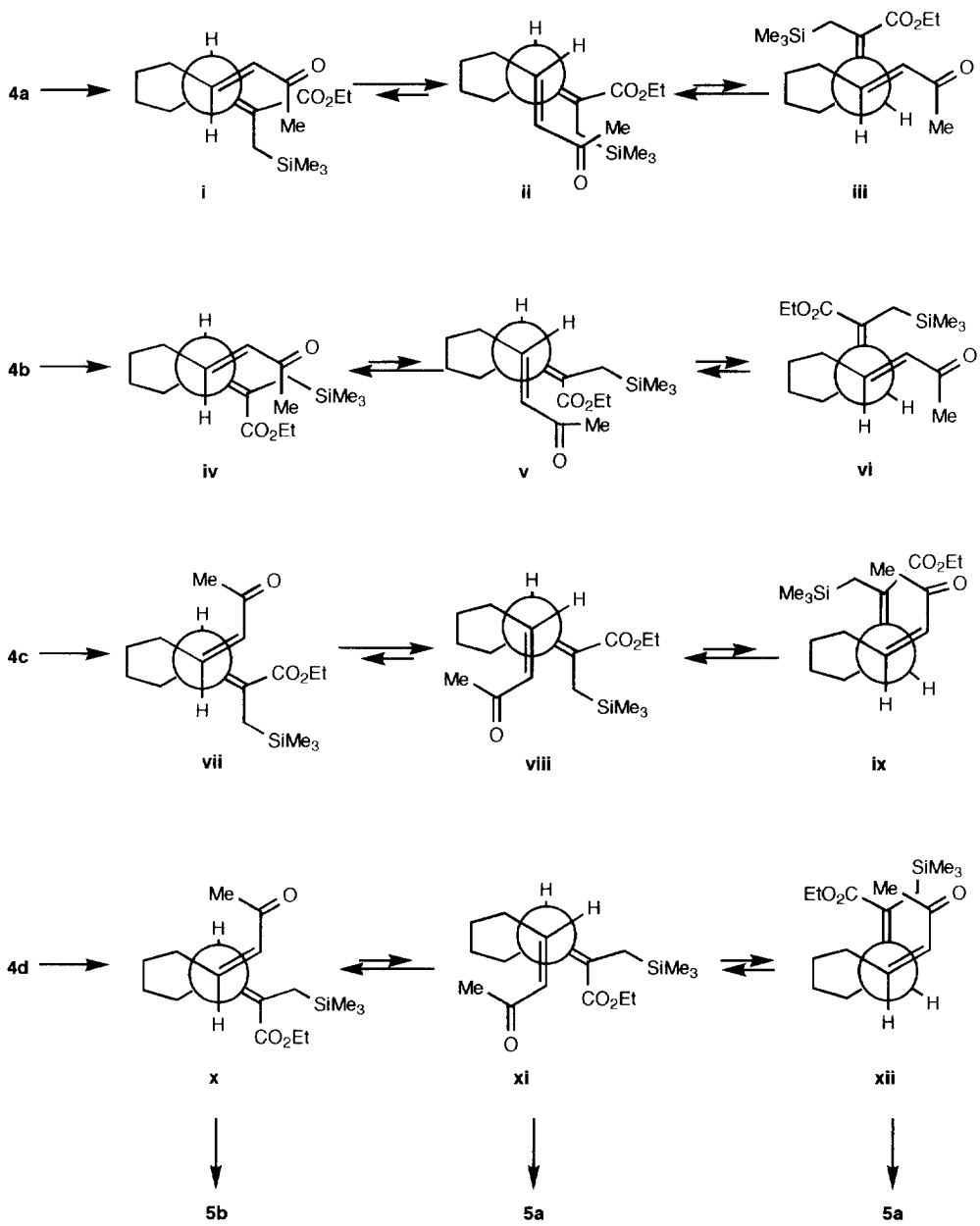


Scheme 7. Reagents and conditions: i, DIBAL-H, CH_2Cl_2, -50 °C (98% **22a**, 80% **22b**); ii, PDC, CH_2Cl_2, r.t. (71% **23a**, 77% **23b**); iii, KOH, EtOH, 75 °C (49% **24a**, 51% **24b**).

configuration give the *cis*-cyclohexane **5a** as the major product. In the same way the *E*-allylsilanes **4b** and **4d** afford the *trans*-cyclohexane **5b** as the major component of the product mixture. Although both the Lewis acid and fluoride mediated reactions give the same stereoselective outcome, the selectivity of the fluoride induced reation is slightly lower. Also, in the fluoride mediated reactions the intermediate tetrabutylammonium enolate is reactive enough to form hydrindanes **21a,b**.

A discussion of the ratio of *cis*-isomer (**5a**) to *trans*-isomer (**5b**) produced in each reaction can be made by examining the Newman projections of the various conformations available to **4a-d** (Scheme 8) with the following assumptions; (1) the six-membered ring is formed via a chair transition-state conformation; (2) and the enone moiety adopts an *s-trans*-conformation prior to cyclization. In each case, two conformations lead to the formation of the *cis*-isomer **5a**, however, one of these conformations places bulky β-(ethoxycarbonyl)allylsilane group in an axial position in the forming six-membered ring. As a result, either the trimethylsilylmethyl or ethoxycarbonyl group occupies a position directly over the forming cyclohexane ring. If these are considered high energy conformations due to developing steric strain, then the reaction stereoselectivity will be a function of the remaining two conformations. Thus, conformations **iii**, **vi**, **ix**, and **xii** may be considered to contribute only a small fraction of the **5a** produced in each case. Of the remaining conformations, consideration of steric interactions[13] and the involvement of secondary orbital overlap, as developed for the reactions of allylstannanes by Denmark[22] and Keck,[23] allows for a rationalization of the observed stereochemical results.

Thus, in the case of **4a**, conformer **i** is disfavored relative to **ii** due to larger steric interactions of the enone carbonyl-Lewis acid complex with the ester group, which is more bulky than trimethylsilylmethyl group since silicon atom is positioned *anti* to the newly forming bond.[24] Also favoring conformer **ii** relative to **i**, is the potential for additional stabilization of the transition state due to the secondary orbital interactions between the HOMO of the allylsilane moiety and the LUMO of the enone as illustrated in Figure 2. As a result, the *cis*-



Scheme 8.

substituted cyclohexane **5a** is predicted to be the major product from **4a** as observed. The same analysis applied to the remaining substrates **4b-d** predicts the major isomer found in each case.

The role of enone isomerization by the Lewis acid prior to cyclization can be considered as a possible mechanism contributing to the loss of stereoselectivity in these reactions. However, if pure **4a** and **4c** each give the same ratio of enone isomers due to equilibration under the reaction conditions (Lewis acid or fluoride), then the similar ratio of products observed from each substrate suggests that it is the geometry of the allylsilane moiety which is most important in controlling the stereochemistry of the products.

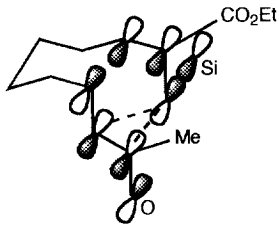


Figure 2.

Conclusions

The intramolecular cyclization of β-(ethoxycarbonyl)allysilanes was shown to be useful in the synthesis of bicyclo[4.3.0]nonanes, a common structural unit present in terpenoid natural products. The stereochemistry of the cyclization reaction was found to be dependent on the geometry of the allylsilane used and gives essentially the same product distribution under cationic (Lewis acid) and anionic (fluoride ion) reaction conditions, although the selectivity of the fluoride induced reation is lower. In addition, these data also indicate that the stereoselectivity is slightly higher for the *Z*-allylsilanes (**4a,c**) relative to the *E*-isomers (**4b,d**), a result consistent with the observations of Keck[23] where the reaction of *Z*-allylstannanes were more selective than the corresponding *E*-isomers.

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EXPERIMENTAL

General Procedures

UV spectra were measured on a JASCO Ubest-50 or a Hitachi U-3210 spectrophotometer. IR spectra were taken on a Hitachi 270-30 spectrometer. Both ^{1}H and ^{13}C NMR spectra were measured on a JEOL GSX-

400 (400 MHz for ^1H, 100 MHz for ^{13}C) or Alpha-500 (500 MHz for ^1H) spectrometer. Chemical shifts are reported on the δ scale (ppm) with tetramethylsilane (TMS=0.00) or chloroform ($CHCl_3$=7.25 for ^1H and $CHCl_3$=77.00 for ^{13}C) as an internal standard. Both low-resolution mass spectra (MS) and high-resolution mass spectra (HRMS) were obtained on a JEOL SX-102A mass spectrometer. Analytical TLC was performed on precoated TLC plates (Kieselgel 60 F_{254}, layer thickness 0.2 mm). Wakogel C-200, C-300 or Florisil (100-200 mesh) were used for column chromatography. Anhydrous Na_2SO_4 or $MgSO_4$ were used for drying of extracted organic layers. For reactions requiring dry solvents, dimethoxyethane (DME) was distilled from $LiAlH_4$; tetrahydrofuran (THF), hexane, pyridine, and CH_2Cl_2 were distilled from CaH_2.

***Ethyl 8-Tetrahydropyranyloxy-2-(trimethylsilylmethyl)oct-2-enoate* (7)**[11b]

NaH (248 mg, 6.20 mmol; 60% in mineral oil) was placed in a 50 cm^3 two-necked flask under Ar, and the mineral oil was removed by washing with dry hexane three times. To this was added dry DME (5 cm^3), then added a solution of $(EtO)_2POCH_2CO_2Et$ (1.12 cm^3, 5.65 mmol) in DME (3 cm^3) dropwise in an ice bath. After being stirred for 30 min at room temperature, a solution of (iodomethyl)trimethylsilane (1.0 cm^3, 6.7 mmol) in DME (2 cm^3) was added, and the mixture was warmed to 70 °C for 4 h. This was cooled to 0 °C again, and a second portion of NaH (203 mg, 5.08 mmol) was added. After being stirred at room temperature for 1.5 h, a solution of **6** (750.4 mg, 3.75 mmol) in DME (5 cm^3) was added at 0 °C, and the reaction mixture was stirred at room temperature over night. Aqueous NH_4Cl was added to quench the reaction, and the resulting aqueous mixture was extracted with Et_2O. The ethereal solution was dried, and the solvent was evaporated to give crude product, which was chromatographed on a silica gel (50 g) using hexane-Et_2O (19:1) as eluent to afford **7** (1.05 g, 79%; *Z*:*E*=2:1) as an oil; UV (EtOH) λ_{max}=233 nm (ε 10000); IR (neat) 1715 (C=O) and 1640 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, ref=$CHCl_3$) -0.04 (9H X1/3, s, $SiMe_3$ of *E*-isomer), -0.03 (9H X2/3, s, $SiMe_3$ of *Z*-isomer), 1.27 (3H X2/3, t, *J*=7Hz, $OCH_2C\underline{H}_3$ of *Z*-isomer), 1.28 (3H X1/3, t, *J*=7Hz, $OCH_2C\underline{H}_3$ of *E*-isomer), 1.3-1.9 (14H, m), 1.70 (2H X1/3, s, $C\underline{H}_2SiMe_3$ of *E*-isomer), 1.78 (2H X2/3, s, $C\underline{H}_2SiMe_3$ of *Z*-isomer), 3.32-3.88 (4H, m, $C\underline{H}_2OTHP$ and OCH_2 in THP), 4.15 (2H, q, *J*=7Hz, $OC\underline{H}_2CH_3$), 4.55 (1H, m, OCHO in THP), 5.64 (1H X1/3, t, *J*=7Hz, CH=C of *E*-isomer), and 6.58 (1H X2/3, t, *J*=7Hz, CH=C of *Z*-isomer); ^{13}C NMR ($CDCl_3$, ref=$CHCl_3$) assigned for *Z*-isomer: -1.09, 60.36, 62.35, 67.44, 98.87, 130.03, 138.35, and 168.39, assigned for *E*-isomer: -1.69, 59.99, 62.27, 67.53, 98.77, 129.26, 138.95, and 168.43; MS *m/z* 356 (M^+, 11%), 341 (50), 272 (100), 185 (100), and 156 (68).

***Ethyl 8-Hydroxy-2-(trimethylsilylmethyl)oct-2-enoate* (8)**[11b]

Compound **7** (296 mg, 0.831 mmol) was dissolved in a mixed solvent of THF and 5% HCl aq (50 cm^3; ratio 4:1). After refluxing for 1 h, the mixture was cooled to room temperature, and a saturated aqueous solution of $NaHCO_3$ was added. This was extracted with Et_2O and the solvent was evaporated. Silica gel (*ca.* 5 g) column chromatography using hexane-AcOEt (4:1) as eluent afforded **8** (215 mg, 95%; *Z*:*E*=2:1) as an oil; IR (neat) 3400 (OH), 1715 (C=O), and 1640 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, ref=$CHCl_3$) -0.07 (9H X1/3, s, $SiMe_3$ of *E*-isomer), -0.06 (9H X2/3, s, $SiMe_3$ of *Z*-isomer), 1.24 (3H X2/3, t, *J*=7Hz, $OCH_2C\underline{H}_3$ of *Z*-isomer), 1.24 (3H X1/3, t, *J*=7Hz, $OCH_2C\underline{H}_3$ of *E*-isomer), 1.3-1.6 (6H, m), 1.67 (2H X1/3, s, $C\underline{H}_2SiMe_3$ of *E*-isomer), 1.75 (2H X2/3, s, $C\underline{H}_2SiMe_3$ of *Z*-isomer), 2.05 (2H X2/3, q, *J*=7Hz, $C\underline{H}_2CH$=C of *Z*-isomer), 2.15 (1H, br, OH), 2.35 (2H X1/3, q, *J*=7Hz, $C\underline{H}_2CH$=C of *E*-isomer), 3.57 (2H, m, $C\underline{H}_2OH$), 4.11 (2H, q, *J*=7Hz, $OC\underline{H}_2CH_3$), 5.60 (1H X1/3, t, *J*=7Hz, CH=C of *E*-isomer), and 6.55 (1H X2/3, t, *J*=7Hz, CH=C of *Z*-isomer); ^{13}C NMR ($CDCl_3$, ref=$CHCl_3$) assigned for Z-isomer: -1.19, 60.33, 62.53, 130.01, 138.23, and 168.39, assigned for *E*-isomer: -1.79, 59.98, 62.63, 129.29, 138.73, and 168.45; MS *m/z* 272 (M^+, 39%), 252 (37), 227 (24), 211 (16), 200 (28), 185 (52), 85 (61), and 73 (100).

***Ethyl 8-Oxo-2-(trimethylsilylmethyl)oct-2(Z)-enoate* (9a) *and Ethyl 8-Oxo-2-(trimethylsilylmethyl)oct-2(E)-enoate* (9b)**[11b]

To a stirred solution of $(COCl)_2$ (0.33 cm^3, 3.8 mmol) in dry CH_2Cl_2 (15 cm^3) was added dropwise a solution of dry DMSO (0.57 cm^3, 8.0 mmol) in CH_2Cl_2 at -50 °C under N_2. After being stirred for 10 min, a

solution of **8** (722.4 mg, 2.66 mmol) in CH_2Cl_2 (8 cm^3) was added slowly, and the mixture was further stirred for 40 min. Et_3N (1.8 cm^3, 13 mmol) was added, and the mixture was allowed to warm to room temperature with stirring. The reaction was quenched by the addition of water, and the resultant suspension was extracted with CH_2Cl_2. After evaporation of the solvent, the crude product was purified by silica gel (15 g) column chromatography using hexane-AcOEt (49:1) as eluent. Chromatography was repeated several times until *Z*-isomer **9a** (476.5 mg, 66%) and *E*-isomer **9b** (164.7 mg, 23%) were separated. **9a**: an oil; IR (neat) 2730 (CHO), 1725 (C=O), 1715 (C=O), and 1640 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, ref=$CHCl_3$) -0.02 (9H, s, $SiMe_3$), 1.27 (3H, t, *J*=7Hz, $OCH_2C\underline{H}_3$), 1.47 (2H, m, CH_2), 1.66 (2H, m, CH_2), 1.79 (2H, s, $C\underline{H}_2SiMe_3$), 2.10 (2H, q, *J*=7Hz, $C\underline{H}_2CH{=}C$), 2.44 (2H, dt, *J*=2, 7Hz, $C\underline{H}_2CHO$), 4.15 (2H, q, *J*=7Hz, $OC\underline{H}_2CH_3$), 6.55 (1H, t, *J*=7Hz, CH=C), and 9.76 (1H, t, *J*=2Hz, CHO); ^{13}C NMR ($CDCl_3$, ref=$CHCl_3$) -1.09 (3C), 14.25, 17.35, 21.82, 28.31, 28.75, 43.70, 60.43, 130.60, 137.37, 168.25, and 202.30; MS *m/z* 270 (M^+, 10%), 255 (18), 242 (14), 227 (21), 209 (18), 185 (100), and 73 (98). **9b**: IR (neat) 2725 (CHO), 1725 (C=O), 1715 (C=O), and 1635 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, ref=$CHCl_3$) -0.04 (9H, s, $SiMe_3$), 1.28 (3H, t, *J*=7Hz, $OCH_2C\underline{H}_3$), 1.43 (2H, m, CH_2), 1.64 (2H, m, CH_2), 1.71 (2H, s, $C\underline{H}_2SiMe_3$), 2.42 (4H, m, $C\underline{H}_2CH{=}C$ and $C\underline{H}_2CHO$), 4.15 (2H, q, *J*=7Hz, $OC\underline{H}_2CH_3$), 5.62 (1H, t, *J*=7Hz, CH=C), and 9.74 (1H, t, *J*=1.5Hz, CHO); ^{13}C NMR ($CDCl_3$, ref=$CHCl_3$) -1.70 (3C), 14.24, 21.66, 24.08, 29.14, 29.19, 43.64, 60.06, 129.91, 138.00, 168.28, and 202.58; MS *m/z* 270 (M^+, 11%), 255 (27), 242 (11), 227 (20), 200 (15), 185 (100), and 73 (72).

***Ethyl 10-Oxo-2-(trimethylsilylmethyl)undeca-2(Z),8(E)-dienoate* (4a)**

To a stirred suspension of NaH (141 mg, 3.5 mmol; 60% in mineral oil which was removed by washing with dry hexane) in dry THF (40 cm^3) under Ar was added dimethyl 2-(oxopropyl)phosphonate (0.60 cm^3, 4.3 mmol). After being stirred at room temperature for 2.3 h, the reaction mixture was cooled to 0 °C, a solution of **9a** (476.5 mg, 1.76 mmol) in THF (9 cm^3) was added, and the stirring was continued at room temperature over night. Water was added and the product was extracted with Et_2O. After evaporation of the solvent, the residual oil was chromatographed on silica gel (12 g) using hexane-AcOEt (49:1) as eluent to afford **4a** (500.0 mg, 91%) as an oil; IR (neat) 1715 (C=O), 1680 (C=O), and 1635 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, ref=$CHCl_3$) -0.03 (9H, s, $SiMe_3$), 1.27 (3H, t, *J*=7Hz, $OCH_2C\underline{H}_3$), 1.47 (4H, m, CH_2CH_2), 1.78 (2H, s, $C\underline{H}_2SiMe_3$), 2.09 (2H, q, *J*=7Hz, $C\underline{H}_2CH{=}CCO_2Et$), 2.22 (3H, s, $COCH_3$), 2.22 (2H, m, $C\underline{H}_2CH{=}CHCO$), 4.15 (2H, q, *J*=7Hz, $OC\underline{H}_2CH_3$), 6.05 (1H, dt, *J*=16, 1.5Hz, $CH{=}C\underline{H}CO$), 6.55 (1H, t, *J*=7Hz, $CH{=}CCO_2Et$), and 6.76 (1H, dt, *J*=16, 7Hz, $C\underline{H}{=}CHCO$); ^{13}C NMR ($CDCl_3$, ref=$CHCl_3$) -1.10 (3C), 14.23, 17.31, 26.83, 27.80, 28.31, 28.72, 32.24, 60.40, 130.45, 131.43, 137.59, 147.88, 168.26, and 198.56; MS *m/z* 310 (M^+, 14%), 295 (21), 279 (14), 267 (8), 185 (14), 169 (34), and 73 (100); HRMS [Found: M^+, 310.1937. Calc for $C_{17}H_{30}O_3Si$: M, 310.1965].

***Ethyl 10-Oxo-2-(trimethylsilylmethyl)undeca-2(E),8(E)-dienoate* (4b)**

By the same procedure described above, **9b** (78.4 mg, 0.290 mmol) was converted into **4b** (69.7 mg, 77%); an oil; IR (neat) 1715 (C=O), 1680 (C=O), and 1635 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, ref=$CHCl_3$) -0.04 (9H, s, $SiMe_3$), 1.28 (3H, t, *J*=7Hz, $OCH_2C\underline{H}_3$), 1.45 (4H, m, CH_2CH_2), 1.71 (2H, s, $C\underline{H}_2SiMe_3$), 2.21 (2H, m, $C\underline{H}_2CH{=}CHCO$), 2.22 (3H, s, $COCH_3$), 2.40 (2H, q, *J*=7Hz, $C\underline{H}_2CH{=}CCO_2Et$), 4.15 (2H, q, *J*=7Hz, $OC\underline{H}_2CH_3$), 5.61 (1H, tt, *J*=1, 7Hz, $CH{=}CCO_2Et$), 6.04 (1H, dt, *J*=16, 1.5Hz, $CH{=}C\underline{H}CO$), and 6.77 (1H, dt, *J*=16, 7Hz, $C\underline{H}{=}CHCO$); ^{13}C NMR ($CDCl_3$, ref=$CHCl_3$) -1.69 (3C), 14.23, 24.07, 26.80, 27.68, 29.19 (2C), 32.21, 60.03, 129.75, 131.33, 138.26, 148.27, 168.30, and 198.68; MS *m/z* 310 (M^+, 16%), 295 (15), 269 (9), 265 (8), 185 (14), 169 (41), and 73 (100); HRMS [Found: M^+, 310.1949. Calc for $C_{17}H_{30}O_3Si$: M, 310.1965].

***5-(Tetrahydropyranyloxy)pentyl Iodide* (13)**

To a stirred solution of **12** (2.60 g, 13.8 mmol) in benzene (140 cm^3) was added imidazole (2.33 g, 34.3 mmol), triphenylphosphine (9.11 g, 34.8 mmol) and iodine (6.60 g, 26.0 mmol) successively. After being stirred at room temperature for 1.5 h, an aqueous solution of Na_2SO_3 was added, and the mixture was extracted

with Et_2O. Evaporation of the solvent followed by silica gel (50 g) column chromatography using hexane-AcOEt (49:1) as eluent afforded **13** (3.43 g, 83%) as an oil; IR (neat) 1035 (C-O) cm^{-1}; ^1H NMR ($CDCl_3$, ref=TMS) 1.4-1.9 (12H, m), 3.20 (2H, t, *J*=7Hz, CH_2I), 3.39 (1H, dt, *J*=10, 6Hz, C<u>H</u>HOTHP), 3.51 (1H, m, OC<u>H</u>H in THP), 3.75 (1H, dt, *J*=10, 7Hz, CH<u>H</u>OTHP), 3.87 (1H, m, OCH<u>H</u> in THP), and 4.58 (1H, dd, *J*=3, 4Hz, OCHO in THP); ^{13}C NMR ($CDCl_3$, ref=TMS) 6.91, 19.67, 25.48, 27.31, 28.67, 30.75, 33.36, 62.39, 67.21, and 98.91; MS *m/z* 298 (M^+, 31%), 240 (26), 198 (32), 169 (77), 153 (81), and 74 (100); HRMS [Found: M^+, 298.0391. Calc for $C_{10}H_{19}O_2I$: M, 298.0431].

***9-(Tetrahydropyranyloxy)non-3-yn-2-ol* (14)**

In a 100 cm^3 two-necked flask, a solution of 3-butyn-2-ol (0.70 cm^3, 8.9 mmol) in dry THF (15 cm^3) was prepared with stirring under Ar, and the flask was cooled in an ice bath. To this was added BuLi (14 cm^3, 22.4 mmol; 1.6 mol dm^{-3} solution in hexane) and the stirring was continued for 10 min. Dry 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU; 25 cm^3; distilled from CaH_2) was added, and after 15 min of additional stirring, a solution of **13** (2.24 g, 7.52 mmol) in THF (5 cm^3) was added. The reaction mixture was allowed to warm to room temperature and stirred over night. An aqueous solution of NH_4Cl was added, and the product was extracted with Et_2O. After evaporation of the solvent, the crude product was chromatographed on silica gel (50 g) using hexane-AcOEt (19:1) as eluent to give **14** (1.00 g, 55%) as an oil; IR (neat) 3440 (OH), 2250 (C≡C), 1080 (C-O), and 1030 (C-O) cm^{-1}; ^1H NMR ($CDCl_3$, ref=TMS) 1.4-1.9 (13H, m), 1.43 (3H, d, *J*=7Hz, CH(OH)C<u>H</u>$_3$), 2.22 (2H, dt, *J*=2, 7Hz, $CH_2C{\equiv}C$), 3.40 (1H, dt, *J*=10, 6Hz, C<u>H</u>HOTHP), 3.51 (1H, m, OC<u>H</u>H in THP), 3.75 (1H, dt, *J*=10, 7Hz, CH<u>H</u>OTHP), 3.87 (1H, m, OCH<u>H</u> in THP), 4.51 (1H, tq, *J*=2, 7Hz, C<u>H</u>OH), and 4.58 (1H, dd, *J*=3, 4Hz, OCHO in THP); ^{13}C NMR ($CDCl_3$, ref=TMS) 18.60, 19.69, 24.75, 25.49, 25.50, 28.42, 29.23, 30.77, 58.55, 62.40, 67.43, 82.43, 84.46, and 98.91; MS *m/z* 241 (M+H, 46%), 223 (35), 195 (43), and 157 (100); HRMS [Found: M+H, 241.1852. Calc for $C_{14}H_{25}O_3$: M+H, 241.1805].

***9-(Tetrahydropyranyloxy)non-3-yn-2-yl Acetate* (15)**

To a stirred solution of **14** (1.08 g, 4.50 mmol) in dry pyridine (6.5 cm^3) was added acetic anhydride (3.5 cm^3) at 0 °C, and the mixture was stirred at room temperature for 19 h. Water was added, and the product was extracted with Et_2O. Evaporation of the solvent followed by silica gel (60 g) column chromatography using hexane-AcOEt (19:1 and 9:1) as eluent gave **15** (1.22 g, 96%) as an oil; IR (neat) 2250 (C≡C), 1745 (C=O), 1240 (C-O), and 1025 (C-O) cm^{-1}; ^1H NMR ($CDCl_3$, ref=TMS) 1.4-1.9 (12H, m), 1.44 (3H, d, *J*=7Hz, CH(OAc)C<u>H</u>$_3$), 2.05 (3H, s, $COCH_3$), 2.20 (2H, dt, *J*=2, 7Hz, $CH_2C{\equiv}C$), 3.37 (1H, dt, *J*=10, 6Hz, C<u>H</u>HOTHP), 3.48 (1H, m, OC<u>H</u>H in THP), 3.72 (1H, dt, *J*=10, 7Hz, CH<u>H</u>OTHP), 3.85 (1H, m, OCH<u>H</u> in THP), 4.56 (1H, dd, *J*=3, 4Hz, OCHO in THP), and 5.42 (1H, tq, *J*=2, 7Hz, C<u>H</u>OAc); ^{13}C NMR ($CDCl_3$, ref=TMS) 18.65, 19.69, 21.17, 21.83, 25.52 (2C), 28.32, 29.25, 30.78, 60.83, 62.34, 67.39, 78.74, 85.37, 98.87, and 169.97; MS *m/z* 283 (M+H, 11%), 240 (14), 223 (35), 199 (100), and 86 (72); Analysis [Found: C, 68.15; H, 9.09%. Calc for $C_{16}H_{26}O_4$: C, 68.06; H, 9.28%].

***9-Hydroxynon-3-yn-2-yl Acetate* (16)**

A solution of **15** (185.3 mg, 0.657 mmol) in MeOH (45 cm^3), together with a small amount of PPTS, was refluxed for 2 h. After being cooled to room temperature, water was added, and the solvent was evaporated to about half of the original volume. This was extracted with AcOEt and the solvent was evaporated. The crude product was chromatographed on silica gel (5 g) using hexane-AcOEt (19:1 and 9:1) as eluent to obtain **16** (123.9 mg, 95%) as an oil; IR (neat) 3410 (OH), 2250 (C≡C), 1740 (C=O), 1240 (C-O), and 1060 (C-O) cm^{-1}; ^1H NMR ($CDCl_3$, ref=TMS) 1.4-1.6 (6H, m), 1.46 (3H, d, *J*=7Hz, CH(OAc)C<u>H</u>$_3$), 1.91 (1H, br, OH), 2.07 (3H, s, $COCH_3$), 2.22 (2H, dt, *J*=2, 7Hz, $CH_2C{\equiv}C$), 3.64 (2H, t, *J*=6Hz, C<u>H</u>$_2$OH), 5.42 (1H, tq, *J*=2, 7Hz, C<u>H</u>OAc); ^{13}C NMR ($CDCl_3$, ref=TMS) 18.62, 21.17, 21.74, 24.94, 28.16, 32.16, 60.89, 62.65, 78.82, 85.30, and 170.14; MS *m/z* 199 (M+H, 100%), 181 (8), 156 (34), 139 (83), and 121 (94); HRMS [Found: M+H, 199.1324. Calc for $C_{11}H_{19}O_3$: M+H, 199.1335].

***9-Hydroxynon-3(Z)-en-2-yl Acetate* (17)**

To a stirred solution of **16** (328.0 mg, 1.66 mmol) in EtOH (10 cm^3) was added a Lindlar catalyst (117.4 mg) and the reaction atmosphere was replaced by hydrogen. After being stirred at room temperature over night, the mixture was filtered through Celite. Evaporation of the solvent followed by silica gel (5 g) column chromatography using hexane-AcOEt (9:1) as eluent afforded **17** (284.9 mg, 86%) as an oil; IR (neat) 3410 (OH), 1740 (C=O), 1665 (C=C), 1250 (C-O), and 1040 (C-O) cm^{-1}; ^1H NMR ($CDCl_3$, ref=TMS) 1.27 (3H, d, *J*=6Hz, CH(OAc)C<u>H</u>$_3$), 1.3-1.6 (6H, m), 1.89 (1H, br, OH), 2.02 (3H, s, $COCH_3$), 2.13 (2H, m, CH_2C=C), 3.63 (2H, t, *J*=6Hz, C<u>H</u>$_2$OH), 5.36 (1H, ddt, *J*=9, 11, 1.5Hz, CH=C<u>H</u>CHOAc), 5.48 (1H, ddt, *J*=1, 11, 7Hz, C<u>H</u>=CHCHOAc), and 5.64 (1H, ddq, *J*=1, 9, 6Hz, C<u>H</u>OAc); ^{13}C NMR ($CDCl_3$, ref=TMS) 20.90, 21.40, 25.29, 27.58, 29.17, 32.53, 62.79, 67.14, 129.48, 132.82, and 170.53; MS *m/z* 201 (M+H, 100%), 183 (16), 157 (81), 142 (99), and 124 (95); HRMS [Found: M+H, 201.1514. Calc for $C_{11}H_{21}O_3$: M+H, 201.1491].

***8-Acetoxynon-6(Z)-enal* (18)**

Swern oxidation of **17** (1185.3 mg, 5.92 mmol) was carried out as described for the preparation of **9a** and **9b** to give crude product **18**, the amount of which was not measured and was used in the next step without purification. **18**: an oil; IR (neat) 2730 (CHO), 1735 (C=O), 1665 (C=C), and 1250 (C-O) cm^{-1}; ^1H NMR ($CDCl_3$, ref=TMS) 1.27 (3H, d, *J*=6Hz, CH(OAc)C<u>H</u>$_3$), 1.42 (2H, m, CH_2), 1.65 (2H, quint, *J*=8Hz, CH_2), 2.02 (3H, s, $COCH_3$), 2.16 (2H, m, CH_2C=C), 2.45 (2H, dt, *J*=1.5, 7Hz, C<u>H</u>$_2$CHO), 5.35-5.51 (2H, m, CH=CH), 5.63 (1H, m, C<u>H</u>OAc), and 9.76 (1H, t, *J*=1.5Hz, CHO); ^{13}C NMR ($CDCl_3$, ref=TMS) 20.86, 21.36, 21.57, 27.38, 28.89, 43.67, 66.89, 129.89, 132.22, 170.33, and 202.46; MS *m/z* 199 (M+H, 100%), 181 (9), 155 (9), 137 (91), and 109 (70); HRMS [Found: M+H, 199.1333. Calc for $C_{11}H_{19}O_3$: M+H, 199.1335].

***Ethyl 10-Acetoxy-2-(trimethylsilylmethyl)undeca-2,8(Z)-dienoate* (19)**

The crude **18** obtained above was subjected to the Wittig reaction, as described for the preparation of **7**, to yield **19** (1352.8 mg, 65% from **17**) as a mixture of 2*Z*- and 2*E*-isomers; an oil; IR (neat) 1740 (C=O), 1715 (C=O), 1640 (C=C), and 1250 (C-O) cm^{-1}; ^1H NMR ($CDCl_3$, ref=$CHCl_3$) -0.04 (9H X1/3, s, $SiMe_3$ of 2*E*-isomer), -0.03 (9H X2/3, s, $SiMe_3$ of 2*Z*-isomer), 1.24 (3H X1/3, d, *J*=6Hz, CH(OAc)C<u>H</u>$_3$ of 2*E*-isomer), 1.24 (3H X2/3, d, *J*=6Hz, CH(OAc)C<u>H</u>$_3$ of 2*Z*-isomer), 1.26 (3H X1/3, t, *J*=7Hz, OCH$_2$C<u>H</u>$_3$ of 2*E*-isomer), 1.26 (3H X2/3, t, *J*=7Hz, OCH$_2$C<u>H</u>$_3$ of 2*Z*-isomer), 1.39 (4H, m, CH_2CH_2), 1.70 (2H X1/3, br s, C<u>H</u>$_2$SiMe$_3$ of 2*E*-isomer), 1.77 (2H X2/3, br s, C<u>H</u>$_2$SiMe$_3$ of 2*Z*-isomer), 1.99 (3H X2/3, s, $COCH_3$ of 2*Z*-isomer), 1.99 (3H X1/3, s, $COCH_3$ of 2*E*-isomer), 2.09 (2H and 2H X2/3, m, C<u>H</u>$_2$CH=CHCHOAc and C<u>H</u>$_2$CH=CCO$_2$Et of 2*Z*-isomer), 2.37 (2H X1/3, m, C<u>H</u>$_2$CH=CCO$_2$Et of 2*E*-isomer), 4.14 (2H, q, *J*=7Hz, OC<u>H</u>$_2$CH$_3$), 5.34 (1H, m, CH=C<u>H</u>CHOAc), 5.44 (1H, dt, *J*=11, 7Hz, C<u>H</u>=CHCHOAc), 5.60 (1H, m, C<u>H</u>OAc), 5.62 (1H X1/3, t, *J*=7Hz, C<u>H</u>=CCO$_2$Et of 2*E*-isomer), and 6.56 (1H X2/3, t, *J*=7Hz, C<u>H</u>=CCO$_2$Et of 2*Z*-isomer); ^{13}C NMR ($CDCl_3$, ref=$CHCl_3$) assigned for 2*Z*-isomer: -1.16 (3C), 14.19, 17.19, 20.78, 21.26, 27.48, 28.31, 28.84, 29.18, 60.27, 66.86, 129.29, 129.47, 132.56, 138.04, 168.24, and 170.17, assigned for 2*E*-isomer: -1.76 (3C), 22.55, 23.97, 27.53, 29.09, 29.29, 29.39, 31.49, 34.57, 59.92, 66.92, 129.34, 130.10, 132.78, 138.65, and 168.28; MS *m/z* 354 (M^+, 4%), 339 (23), 295 (100), 280 (88), 267 (62), 223 (46), 179 (79), and 157 (80); HRMS [Found: M^+, 354.2197. Calc for $C_{19}H_{34}O_4Si$: M, 354.2227]. The ratio of the two isomers was determined to be 2*Z*-isomer : 2*E*-isomer=1.8:1 from the ^1H NMR spectrum.

***Ethyl 10-Hydroxy-2-(trimethylsilylmethyl)undeca-2,8(Z)-dienoate* (20)**

To a stirred solution of **19** (139.6 mg, 0.394 mmol) in EtOH (50 cm^3) was added K_2CO_3 (1.24 g) and the mixture was stirred at room temperature over night. Water was added and the solvent was evaporated to about half of the original volume. After extraction with Et_2O and drying, the solvent was evaporated off. The residual oil was chromatographed on silica gel (2 g) using hexane-AcOEt (9:1 and 4:1) as eluent to afford **20** (59.9 mg, 49%) as an oil; IR (neat) 3420 (OH), 1710 (C=O), 1640 (C=C), and 1250 (C-O) cm^{-1}; ^1H NMR ($CDCl_3$,

ref=$CHCl_3$) -0.05 (9H X1/3, s, $SiMe_3$ of 2*E*-isomer), -0.04 (9H X2/3, s, $SiMe_3$ of 2Z-isomer), 1.20 (3H X1/3, d, *J*=6Hz, $CHCH_3$ of 2*E*-isomer), 1.21 (3H X2/3, d, *J*=6Hz, $CHCH_3$ of 2*Z*-isomer), 1.26 (3H X1/3, t, *J*=7Hz, OCH_2CH_3 of 2*E*-isomer), 1.27 (3H X2/3, t, *J*=7Hz, OCH_2CH_3 of 2*Z*-isomer), 1.3-1.5 (5H, m), 1.69 (2H X1/3, br s, CH_2SiMe_3 of 2*E*-isomer), 1.77 (2H X2/3, br s, CH_2SiMe_3 of 2*Z*-isomer), 2.07 (2H and 2H X2/3, m, CH_2CH=CHCHOH and CH_2CH=CCO_2Et of 2*Z*-isomer), 2.36 (2H X1/3, m, CH_2CH=CCO_2Et of 2*E*-isomer), 4.13 (2H, q, *J*=7Hz, OCH_2CH_3), 4.60 (1H, m, CHOH), 5.38 (2H, m, CH=CH), 5.62 (1H X1/3, t, *J*=8Hz, CH=CCO_2Et of 2*E*-isomer), and 6.55 (1H X2/3, t, *J*=7Hz, CH=CCO_2Et of 2*Z*-isomer); ^{13}C NMR ($CDCl_3$, ref=$CHCl_3$) assigned for 2*Z*-isomer: -1.12 (3C), 14.22, 17.22, 23.59, 27.33, 28.34, 28.84, 29.41, 60.37, 63.76, 130.15, 130.69, 134.02, 138.10, and 168.34, assigned for 2*E*-isomer: -1.73 (3C), 14.18, 23.48, 23.99, 27.14, 29.09, 29.16, 29.25, 60.03, 63.68, 129.34, 130.82, 133.97, and 138.88; MS *m/z* 312 (M^+, 3%), 297 (7), 279 (27), 267 (22), 251 (19), 185 (100), and 149 (63); HRMS [Found: M^+, 312.2148. Calc for $C_{17}H_{32}O_3Si$: M, 312.2122].

***Ethyl 10-Oxo-2-(trimethylsilylmethyl)undeca-2,8(Z)-dienoate* (4c and 4d)**

To a stirred solution of **20** (313.0 mg, 1.00 mmol) in dry CH_2Cl_2 (60 cm^3) was added a large excess of activated MnO_2 (10.8 g). $CaCl_2$ drying tube was attached and the mixture was stirred at room temperature for 24 h. MnO_2 was filtered off through Celite, and the solvent was evaporated to give a residual oil which was chromatographed on silica gel (8 g) using hexane-AcOEt (49:1) as eluent to give a mixture of **4c** and **4d** (243.9 mg, 78%). The same chromatography was repeated several times to obtain several samples of different *Z*/*E* ratio, as described in the text. A mixture of **4c** and **4d**: an oil; IR (neat) 1710 (C=O), 1700 (C=O), 1640 (C=C), 1620 (C=C), and 1250 (C-O) cm^{-1}; ^1H NMR ($CDCl_3$, ref=$CHCl_3$) -0.06 (9H X1/3, s, $SiMe_3$ of **4d**), -0.05 (9H X2/3, s, $SiMe_3$ of **4c**), 1.25 (3H X2/3, t, *J*=7Hz, OCH_2CH_3 of **4c**), 1.26 (3H X1/3, t, *J*=7Hz, OCH_2CH_3 of **4d**), 1.37-1.46 (4H, m, CH_2CH_2), 1.69 (2H X1/3, d, *J*=1Hz, CH_2SiMe_3 of **4d**), 1.76 (2H X2/3, br s, CH_2SiMe_3 of **4c**), 2.06 (2H X2/3, m, CH_2CH=CCO_2Et of **4c**), 2.17 (3H X1/3, s, $COCH_3$ of **4d**), 2.17 (3H X2/3, s, $COCH_3$ of **4c**), 2.37 (2H X1/3, m, CH_2CH=CCO_2Et of **4d**), 2.59 (2H, m, CH_2CH=CHCO), 4.13 (2H X2/3, q, *J*=7Hz, OCH_2CH_3 of **4c**), 4.13 (2H X1/3, q, *J*=7Hz, OCH_2CH_3 of **4d**), 5.61 (1H X1/3, t, *J*=7Hz, CH=CCO_2Et of **4d**), 5.98-6.14 (2H, m, CH=CH), and 6.55 (1H X2/3, t, *J*=7Hz, CH=CCO_2Et of **4c**); ^{13}C NMR ($CDCl_3$, ref=$CHCl_3$) assigned for **4c**: -1.10 (3C), 14.25, 17.25, 28.40, 28.81, 28.88, 29.09, 31.58, 60.36, 127.20, 130.22, 138.04, 148.13, 168.35, and 199.21, assigned for **4d**: -1.70 (3C), 14.23, 24.04, 28.84, 29.22, 29.40 (2C), 31.55, 60.01, 127.12, 129.48, 138.56, 148.38, 168.39, and 199.21; MS *m/z* 310 (M^+, 42%), 296 (25), 265 (37), 221 (53), 163 (67), and 43 (100); HRMS [Found: M^+, 310.1951. Calc for $C_{17}H_{30}O_3Si$: M, 310.1965].

***Ethyl 2-[cis-2-(2-Oxopropyl)cyclohex-1-yl]acrylate* (5a) *and Ethyl 2-[trans-2-(2-Oxopropyl)-cyclohex-1-yl]acrylate* (5b)**

Cyclization with $TiCl_4$. To a stirred solution of **4a** (13.5 mg, 0.0435 mmol) in dry CH_2Cl_2 (5 cm^3) was added a solution of $TiCl_4$ (0.065 cm^3, 0.065 mmol; 1 mol dm^{-3} solution in CH_2Cl_2) and the mixture was stirred at room temperature for 17 h. Water was added and the solution was extracted with Et_2O. Evaporation of the solvent followed by silica gel (1 g) column chromatography using hexane-AcOEt (9:1) as eluent afforded a mixture of **5a** and **5b** (9.2 mg, 89%). Separation of two isomers was performed by repeated the same column chromatography.

Cyclization with BF_3OEt_2. To a stirred solution of **4a** (15.6 mg, 0.0503 mmol) in dry CH_2Cl_2 (5 cm^3) was added BF_3OEt_2 (0.010 cm^3, 0.081 mmol) and the mixture was stirred at room temperature for 18 h. Water was added and the solution was extracted with Et_2O. A mixture of **5a** and **5b** (10.6 mg, 89%) was obtained after chromatography.

Cyclization with $SnCl_4$. To a stirred solution of **4a** (21.4 mg, 0.0690 mmol) in dry CH_2Cl_2 (5 cm^3) was added a solution of $SnCl_4$ (0.10 cm^3, 0.10 mmol; 1 mol dm^{-3} solution in CH_2Cl_2) and the mixture was stirred at

room temperature for 1 h. Water was added and the solution was extracted with Et_2O A mixture of **5a** and **5b** (15.8 mg, 96%) was obtained after chromatography.

Cyclization with $EtAlCl_2$. To a stirred solution of **4a** (29.3 mg, 0.0945 mmol) in dry CH_2Cl_2 (6 cm^3) was added a solution of $EtAlCl_2$ (0.30 cm^3, 0.29 mmol; 0.95 mol dm^{-3} solution in hexane) and the mixture was stirred at room temperature for 46 h. Water was added and the solution was extracted with Et_2O. A mixture of **5a** and **5b** (20.0 mg, 89%) was obtained after chromatography.

Cyclization with TBAF. To a stirred solution of TBAF[25] (103 mg, 0.39 mmol) in dry THF (10 cm^3) was added a solution of **4a** (41.0 mg, 0.132 mmol) in THF (12 cm^3) at 0 °C under Ar. After being stirred at room temperature for 15 h, an aqueous solution of NH_4Cl was added, and the mixture was extracted with Et_2O. Evaporation of the solvent afforded a mixture of **5a**, **5b**, **21a**, and **21b** (23.5 mg, 79%; ratio 57:16:21:6) as an oil.

5a: an oil; IR (neat) 1720 (C=O) and 1630 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, ref=$CHCl_3$) 1.29 (3H, t, *J*=7Hz, $OCH_2C\underline{H}_3$), 1.3-1.8 (8H, m), 2.03 (3H, s, $COCH_3$), 2.23 (1H, dd, *J*=5, 16Hz, C<u>H</u>HCO), 2.30 (1H, dd, *J*=8, 16Hz, CH<u>H</u>CO), 2.57 (1H, d quint, *J*=8, 4Hz, C<u>H</u>CH_2CO), 2.78 (1H, br dt, *J*=11, 4Hz, CHC=C), 4.20 (1H, dq, *J*=11, 7Hz, OC<u>H</u>HCH_3), 4.21 (1H, dq, *J*=11, 7Hz, OCH<u>H</u>CH_3), 5.34 (1H, t, *J*=1.5Hz, C=C<u>H</u>H), and 6.17 (1H, t, *J*=1Hz, C=CH<u>H</u>); ^{13}C NMR ($CDCl_3$, ref=$CHCl_3$; DEPT) 14.19 (CH_3), 20.43 (CH_2), 25.07 (CH_2), 26.14 (CH_2), 30.08 (CH_3), 30.08 (CH_2), 31.24 (CH), 41.15 (CH), 41.18 (CH_2), 60.70 (CH_2), 123.43 (CH_2), 144.30 (C), 167.04 (CO), and 208.56 (CO); MS *m/z* 238 (M^+, 10%), 220 (7), 192 (80), 181 (100), and 135 (91); HRMS [Found: M^+, 238.1557. Calc for $C_{14}H_{22}O_3$: M, 238.1570]. **5b**: an oil; IR (neat) 1720 (C=O) and 1630 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, ref=$CHCl_3$) 0.9-1.9 (8H, m), 1.30 (3H, t, *J*=7Hz, $OCH_2C\underline{H}_3$), 2.01 (1H, tq, *J*=3, 10Hz, C<u>H</u>CH_2CO), 2.06 (3H, s, $COCH_3$), 2.11 (1H, dd, *J*=10, 16Hz, C<u>H</u>HCO), 2.28 (1H, dt, *J*=3, 11Hz, CHC=C), 2.42 (1H, dd, *J*=3, 16Hz, CH<u>H</u>CO), 4.20 (2H, q, *J*=7Hz, $OC\underline{H}_2CH_3$), 5.55 (1H, br s, C=C<u>H</u>H), and 6.20 (1H, d, *J*=1Hz, C=CH<u>H</u>); ^{13}C NMR ($CDCl_3$, ref=$CHCl_3$; DEPT), 14.17 (CH_3), 25.98 (CH_2), 26.48 (CH_2), 30.55 (CH_3), 32.96 (CH_2), 34.32 (CH_2), 37.33 (CH), 44.38 (CH), 48.62 (CH_2), 60.71 (CH_2), 124.28 (CH_2), 144.57 (C), 167.46 (CO), and 208.88 (CO); MS *m/z* 238 (M^+, 10%), 220 (7), 192 (80), 181 (100), 135 (90), and 43 (99); HRMS [Found: M^+, 238.1557. Calc for $C_{14}H_{22}O_3$: M, 238.1570].

***7-Acetyl-9-methylene-*cis*-bicyclo[4.3.0]nonan-8-one* (21a)**

NaH (4.2 mg, 0.18 mmol; 55% in mineral oil which was removed by washing with dry hexane) was placed under Ar as a suspension in dry THF (1 cm^3). To this was added a solution of **5a** (14.1 mg, 0.059 mmol) in THF (3 cm^3) at room temperature. After being refluxed for 1.3 h, water was added, and the mixture was extracted with Et_2O. Evaporation of the solvent afforded **21a** (6.8 mg, 60%), which was partly purified by silica gel column chromatography using hexane-Et_2O (19:1) as eluent. **21a**: an oil; UV (EtOH, c=1.5X10^{-4} mol dm^{-3}) λ_{max}=245 (ε 3000) and 318 (ε 9000) nm; IR (neat) 1730 (C=O), 1710 (C=O), and 1630 (C=C) cm^{-1}; ^1H NMR (C_6D_6, ref=TMS) 0.6-1.8 (8H, m), 1.69 (3H X4/5, s, $COCH_3$ of the major isomer), 2.00 (3H X1/5, s, $COCH_3$ of the minor isomer), 2.22 (1H X4/5, ddd, *J*=5.5, 6, 11Hz, C<u>H</u>C=COH of the major isomer), 2.45 (1H X4/5, tq, *J*=6, 3Hz, C<u>H</u>C=CH_2 of the major isomer), 2.54 (1H X1/5, ddt, *J*=6, 10, 4.5Hz, C<u>H</u>CHCO of the minor isomer), 2.75 (1H X1/5, tq, *J*=3, 6Hz, C<u>H</u>C=CH_2 of the minor isomer), 2.91 (1H X1/5, d, *J*=4.5Hz, COCHCO of the minor isomer), 4.80 (1H X1/5 dd, *J*=1, 3Hz, C=C<u>H</u>H of the minor isomer), 4.96 (1H X4/5, d, *J*=3Hz, C=C<u>H</u>H of the major isomer), 6.00 (1H X4/5, d, *J*=3.5Hz, C=CH<u>H</u> of the major isomer), and 6.05 (1H X1/5, br d, *J*=3Hz, C=CH<u>H</u> of the minor isomer), 14.0 (1H X4/5, br, OH of the major isomer); MS *m/z* 192 (M^+, 100%), 177 (32), 149 (99), and 57 (72); HRMS [Found: M^+, 192.1138. Calc for $C_{12}H_{16}O_2$: M, 192.1151].

***7-Acetyl-9-methylene*-trans-*bicyclo[4.3.0]nonan-8-one* (21b)**

By the same procedure, **5b** (5.0 mg, 0.021 mmol) was treated with NaH to yield **21b** (3.1 mg, 77%) as an oil; UV (EtOH, c=1.5X10^{-4} mol dm^{-3}) λ_{max}=230 (ε 7000) and 320 (ε 500) nm; IR (neat) 1730 (C=O), 1710 (C=O), and 1645 (C=C) cm^{-1}; ^{1}H NMR (C_6D_6, ref=TMS), 0.7-1.9 (10H, m), 2.12 (3H, s, $COCH_3$), 2.48 (1H, d, *J*=12Hz, COCHCO), 4.71 (1H, dd, *J*=1, 3Hz, C=C<u>H</u>H), and 5.87 (1H, dd, *J*=1, 3Hz, C=CH<u>H</u>); ^{13}C NMR ($CDCl_3$, ref=$CHCl_3$) 25.66, 25.91, 26.64, 28.40, 30.38, 43.34, 45.56, 67.30, 104.21, 115.36, 200.11, and 203.85; MS *m/z* 192 (M$^+$, 73%), 149 (94), 121 (47), and 73 (100); HRMS [Found: M$^+$, 192.1191. Calc for $C_{12}H_{16}O_2$: M, 192.1151].

***2-[*cis-*2-(2-Hydroxypropyl)cyclohex-1-yl]prop-2-en-1-ol* (22a)**

To a stirred solution of **5a** (59.8 mg, 0.251 mmol) in dry CH_2Cl_2 (12 cm^3) was added diisobutylaluminium hydride (DIBAL-H; 1.3 cm^3; 1.0 mol dm^{-3} solution in hexane) under Ar at -50 °C. After being stirred for 2.5 h, MeOH (1.0 cm^3) was added, and the stirring was continued for 10 min. A saturated aqueous solution of Rochelle salt was added, and the mixture was stirred at room temperature for 1.2 h. Extraction with Et_2O and subsequent evaporation of the solvent gave crude product, which was chromatographed on silica gel (1 g) column chromatography using Et_2O as eluent to yield **22a** (48.7 mg, 98%) as an oil; IR (neat) 3350 (OH) and 1650 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, ref=$CHCl_3$) 1.09 (3H X2/5, d, *J*=6Hz, CH(OH)C<u>H</u>$_3$ of the minor isomer), 1.1-2.2 (12H, m), 1.14 (3H X3/5, d, *J*=6Hz, CH(OH)C<u>H</u>$_3$ of the major isomer), 2.70 (2H, br, OH), 3.75 (1H, m, C<u>H</u>(OH)CH_3), 4.04 (2H, br s, C<u>H</u>$_2$OH), 4.77 (1H, br s, C=C<u>H</u>H), 5.09 (1H X2/5, br s, C=CH<u>H</u> of the minor isomer), and 5.14 (1H X3/5, br s, C=CH<u>H</u> of the major isomer); ^{13}C NMR ($CDCl_3$, ref=$CHCl_3$; assigned for the major isomer) 20.45, 24.78, 25.08, 26.38, 29.33, 31.65, 34.87, 44.46, 66.09, 66.29, 111.09, and 151.73; MS *m/z* 180 ([M-H_2O]$^+$, 22%), 165 (21), 151 (21), 147 (27), 137 (40), and 122 (100); HRMS [Found: M-H_2O, 180.1520. Calc for $C_{12}H_{20}O$: M-H_2O, 180.1515]. The ratio of the two isomers were determined to be 3:2 from the ^{1}H NMR spectrum.

***2-[*trans-*2-(2-Hydroxypropyl)cyclohex-1-yl]prop-2-en-1-ol* (22b)**

By the same procedure, **5b** (24.0 mg, 0.101 mmol) was treated with DIBAL-H (0.5 cm^3) to afford **22b** (16.0 mg, 80%) as an oil; IR (neat) 3370 (OH) and 1650 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, ref=$CHCl_3$) 1.1-2.3 (14H, m), 1.12 (3H X2/5, d, *J*=6Hz, CH(OH)C<u>H</u>$_3$ of the minor isomer), 1.14 (3H X3/5, d, *J*=6Hz, CH(OH)C<u>H</u>$_3$ of the major isomer), 3.90 (1H, m, C<u>H</u>OH), 4.04 (1H X3/5, d, *J*=14Hz, C<u>H</u>HOH of the major isomer), 4.07 (2H X2/5, br s, C<u>H</u>$_2$OH of the minor isomer), 4.11 (1H X3/5, d, *J*=14Hz, CH<u>H</u>OH of the major isomer), 4.88 (1H X2/5, br s, C=C<u>H</u>H of the minor isomer), 4.91 (1H X3/5, br s, C=C<u>H</u>H of the major isomer), 5.07 (1H X2/5, q, *J*=1.5Hz, C=CH<u>H</u> of the minor isomer), and 5.08 (1H X3/5, q, *J*=1.5Hz, C=CH<u>H</u> of the major isomer); MS *m/z* 180 ([M-H_2O]$^+$, 16%), 165 (16), 151 (18), 147 (20), 137 (29), and 122 (100); HRMS [Found: M-H_2O, 180.1531. Calc for $C_{12}H_{20}O$: M-H_2O, 180.1515]. The ratio of two isomers were determined to be 3:2 from the ^{1}H NMR spectrum.

***2-[*cis-*2-(2-Oxopropyl)cyclohex-1-yl]acrolein* (23a)**

To a stirred solution of **22a** (41.8 mg, 0.211 mmol) in dry CH_2Cl_2 (6 cm^3) was added pyridinium dichromate (325 mg) at once. $CaCl_2$ drying tube was attached and the mixture was stirred at room temperature for 24 h. Et_2O was added and the resultant suspension was filtered through Florisil (5 g) short column with Et_2O as eluent. Evaporation of the solvent afforded **23a** (29.0 mg, 71%) which showed one spot on the TLC and was not purified. **23a**: an oil; IR (neat) 1715 (C=O), 1700 (C=O), and 1630 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, ref=$CHCl_3$) 1.2-1.8 (8H, m), 2.02 (3H, s, $COCH_3$), 2.16 (1H, dd, *J*=5, 16Hz, C<u>H</u>HCOCH$_3$), 2.29 (1H, dd, *J*=8, 16Hz, CH<u>H</u>COCH$_3$), 2.53 (1H, d quint, *J*=8, 4Hz, C<u>H</u>CH_2COCH$_3$), 2.80 (1H, br dt, *J*=11, 4Hz, C<u>H</u>C=CH_2), 5.99 (1H, s, C=C<u>H</u>H), 6.08 (1H, s, C=CH<u>H</u>), and 9.45 (1H, s, CHO); ^{13}C NMR ($CDCl_3$, ref=$CHCl_3$) 20.64, 24.68, 25.82, 30.00, 30.07, 31.02, 38.07, 41.85, 133.50, 152.94, 194.28, and 208.38; MS *m/z* 194 (M$^+$, 100%), 176 (M-H_2O, 5), and 136 (3); HRMS [Found: M$^+$, 194.1342. Calc for $C_{12}H_{18}O_2$: M, 194.1307].

***2-[trans-2-(2-Oxopropyl)cyclohex-1-yl]acrolein* (23b)**

Similarly, **22b** (19.0 mg, 0.096 mmol) was converted to **23b** (14.4 mg, 77%); an oil; IR (neat) 1720 (C=O), 1700 (C=O), and 1630 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, ref=$CHCl_3$) 0.9-1.9 (8H, m), 2.01 (1H, m, C<u>H</u>CH_2CO), 2.04 (3H, s, $COCH_3$), 2.10 (1H, dd, *J*=9, 16Hz, C<u>H</u>HCO), 2.22 (1H, dd, *J*=3, 16Hz, CH<u>H</u>CO), 2.35 (1H, dt, *J*=3, 11Hz, C<u>H</u>C=CH_2), 6.04 (1H, s, C=C<u>H</u>H), 6.30 (1H, s, C=CH<u>H</u>), and 9.52 (1H, s, CHO); MS *m/z* 195 (M+H, 17%), 176 (M-H_2O, 9), 136 (100), and 108 (69); HRMS [Found: M+H, 195.1413. Calc for $C_{12}H_{19}O_2$: M, 195.1386].

***7-Acetyl-9-methylene*-cis-*bicyclo[4.3.0]non-7-ene* (24a)**

To a stirred solution of **23a** (10.3 mg, 0.053 mmol) in EtOH (5 cm^3) was added a pellet of KOH (60 mg), and the mixture was heated to 75 °C for 1.5 h. After being cooled to room temperature, the reaction was quenched by the addition of ice-cooled dilute HCl aq (0.2 cm^3). The mixture was extracted with CH_2Cl_2, and the solvent was evaporated. Silica gel (1 g) column chromatography using pentane as eluent yielded **24a** (4.6 mg, 49%) as an oil; UV (EtOH) λ_{max}=287 nm (ε 14000); IR (neat) 1670 (C=O) and 1560 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, ref=$CHCl_3$) 0.8-2.1 (8H, m), 2.36 (3H, s, $COCH_3$), 2.75 (1H, tq, *J*=6, 3Hz, C<u>H</u>C=CH_2), 2.91 (1H, ddd, *J*=6, 7, 11Hz, CHC(CO)=C), 5.06 (1H, d, *J*=3Hz, C=C<u>H</u>H), 5.32 (1H, d, *J*=3Hz, C=CH<u>H</u>), and 6.88 (1H, s, CH=CCO); ^{13}C NMR ($CDCl_3$, ref=$CHCl_3$) 21.40, 22.64, 24.78, 26.83, 29.57, 42.25, 42.42, 110.64, 142.06, 153.65, 154.88, and 196.73; MS *m/z* 176 (M^+, 44%), 161 (8), 133 (100), 105 (20), and 91 (36); HRMS [Found: M^+, 176.1207. Calc for $C_{12}H_{16}O$: M, 176.1202].

***7-Acetyl-9-methylene*-trans-*bicyclo[4.3.0]non-7-ene* (24b)**

Similarly, **23b** (14.4 mg, 0.074 mmol) was treated with KOH to give **24b** (6.7 mg, 51%) as an oil; UV (EtOH) λ_{max}=282 nm (ε 7000); IR (neat) 1670 (C=O) and 1580 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, ref=$CHCl_3$) 0.8-2.3 (8H, m), 2.32 (3H, s, $COCH_3$), 2.55 (2H, m, C<u>H</u>C=CH_2 and CHC(CO)=C), 5.00 (1H, m, C=C<u>H</u>H), 5.12 (1H, d, *J*=2.5Hz, C=CH<u>H</u>), and 6.85 (1H, d, *J*=2.5Hz, CH=CCO); ^{13}C NMR ($CDCl_3$, ref=$CHCl_3$) 26.17, 26.63, 26.91, 27.29, 29.72, 50.63, 52.30, 107.71, 142.96, 150.00, 153.64, and 197.84; MS *m/z* 176 (M^+, 26%), 133 (100), 105 (27), and 91 (51); HRMS [Found: M^+, 176.1187. Calc for $C_{12}H_{16}O$: M, 176.1202].

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