An Acylative C–C Single-Bond Cleavage and a Self-Cyclization of Ethyl 2-(Trimethylsilylmethyl)penta-2,4-dienoate or Its Free Acid under Ritter Condition

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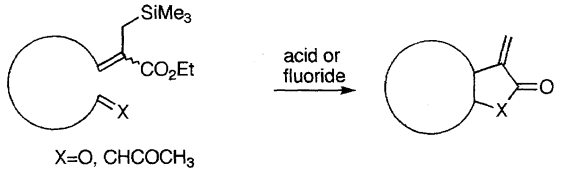
An acylative C(3)–C(4)-bond cleavage of ethyl 4,5-disubstituted 2-(trimethylsilylmethyl)penta-2,4-dienoate occurred to give an ethyl 2-(2-oxoalkyl)acrylate by treatment with trifluoromethanesulfonic acid in nitriles. A self-cyclization also occurred to give a 5,5-disubstituted 3-methylenetetrahydrofuran-2-one when the reactions were carried out in bulky nitriles. Only self-cyclization proceeded when the corresponding 4,5-disubstituted 2-(trimethylsilylmethyl)penta-2,4-dienoic acid was treated in acetonitrile. The reaction mechanism is described.

Functionalized allylsilanes are useful building blocks in organic syntheses.[1] Among these, alkyl 2-(trimethylsilylmethyl)acrylate has a unique structure which can react with either a nucleophile (as Michael acceptor) or an electrophile (as allylsilane). We are studying the synthetic utility of ethyl 2-(trimethylsilylmethyl)acrylate; we have reported intramolecular reaction of this unit with aldehyde or α,β-unsaturated ketone producing fused α-methylene-γ-lactone[2,3] or carbocycle,[4] respectively (Eq. 1). Applications of this chemistry to the synthesis of 10-epi-frullanolide[5] and of spiro[4.5]decanes[6] were also reported.



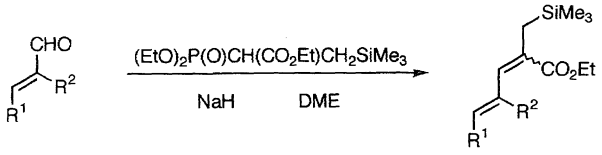
(1)

We now focus on ethyl 2-(trimethylsilylmethyl)alka-2,4-dienoate (general structure **1**), which has a further conjugated double bond (Chart 1). However, **1** is not a simple extension of the corresponding ethyl 2-(trimethylsilylmethyl)acrylate **2**, because **1** has both a nucleophilic center and an electrophilic center in appropriate positions to form a five-membered ring by self-cyclization, whereas **2** has no such possibility. The synthesis of ethyl 2-(trimethylsilylmethyl)-alka-2,4-dienoate unit was reported by Pornet et al.,[7] however the nature is not known so far. We recently reported[8] that an acylative C–C single bond cleavage and a self-cyclization giving α-methylene-γ-lacones occur when ethyl 4,5-disubstituted 2-(trimethylsilylmethyl)penta-2,4-dienoates were treated under Ritter conditions.[9] Here we report the details of this reaction as well as self-cyclization of corresponding carboxylic acids and the reaction mechanisms.

Chart 1.

Results and Discussion

We chose three substrates: **3**, **4**, and **5**, for this study (Chart 2). These compounds were prepared from the corresponding aldehydes by Hoffmann-Wittig reactions (Eq. 2).[2,4] Thus, **3**, **4**, and **5** were obtained from (*E*)-2-methylbut-2-enal (tiglic aldehyde), cyclohex-1-ene-1-carbaldehyde, and perillaldehyde, respectively. ^{1}H NMR spectra showed that **3**, **4**, and **5** contain *Z*- and *E*-isomers with the ratios 18 : 1, 6.5 : 1, and 5 : 1, respectively. These mixtures of geometrical isomers were used in the following study without separation.



(2)

The results of the treatment of **3**, **4**, and **5** under Ritter conditions are summarized in Table 1. When **3** was treated with 3 molar amounts of trifluoromethanesulfonic acid (TfOH) in acetonitrile, ethyl 2-acetonylacrylate **6a**,[10] was obtained (Entry 1) (Chart 3). Similarly, treatment of **3** in propiononitrile and isobutyronitrile afforded **6b** and **6c**, respectively (Entries 2 and 3). Their structures could be determined from

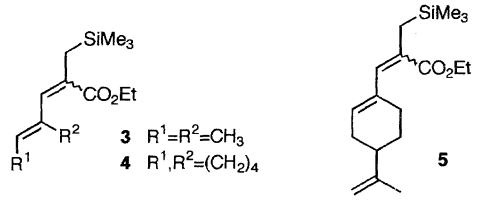


Chart 2.

Table 1. Reaction of Ethyl 2-(Trimethylsilylmethyl)penta-2,4-dienoates under Ritter Condition[a)]

Entry	Substrate	Acid	Solvent	Time/h	Product(s)	Yield/%	
1	**3**	TfOH	MeCN	17	**6a**	57	
2	**3**	TfOH	EtCN	20	**6b**	67	
3	**3**	TfOH	*i*-PrCN	20	**6c**	93	
4	**3**	TfOH	*t*-BuCN	20	**6d**+**7**	74	(**6d** : **7**=1 : 1.2)[b)]
5	**4**	TfOH	MeCN	21	**6a**	43	
6	**4**	TfOH	EtCN	18	**6b**	91	
7	**4**	TfOH	*i*-PrCN	22	**6c**+**8**	52	(**6c** : **8**=1 : 1.4)[c,d)]
8	**4**	TfOH	*t*-BuCN	22	**6d**+**8**	55	(**6d** : **8**=1 : 1.8)[c,d)]
9	**5**	TfOH	MeCN	1	**9a**	88	(*E* : *Z*=2.4 : 1)[b,d)]
10	**5**	TsOH	MeCN	20	**9a**	61	(*E* : *Z*=1.8 : 1)[d)]
11	**5**	TfOH	EtCN	1	**9b**	78	(*E* : *Z*=2.3 : 1)[d)]
12	**5**	TfOH	*i*-PrCN	1	**9c**	89	(*E* : *Z*=2.2 : 1)[d)]
13	**5**	TfOH	*t*-BuCN	1	See text		

a) The reactions were carried out at room temperature with 3 molar amounts of acid. b) Products were separated by column chromatography. c) Products were inseparable. d) The ratio was determined from ^{1}H NMR spectrum of the product mixture.

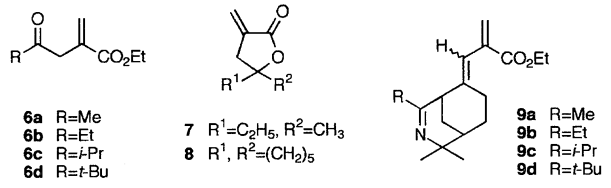


Chart 3.

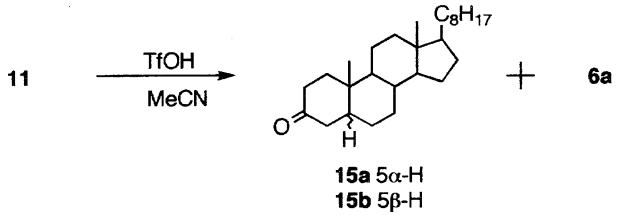
spectral data by comparison with that of the known **6a**. A different result was obtained when the reaction was carried out in pivalonitrile. Then 5-ethyl-5-methyl-3-methylenetetrahydrofuran-2-one **7**[11] was afforded as the major product, in addition to the corresponding ethyl 2-(3,3-dimethyl-2-oxobutyl)acrylate **6d** (Entry 4). The reaction of **4** showed almost parallel results (Entries 5 to 8), except that 3-methylene-1-oxaspiro[4.5]decan-2-one **8**[11,12] was also produced in isobutyronitrile as solvent.

On the other hand, the behavior of **5** under Ritter conditions was completely different from that of either **3** or **4**. When **5** was treated with TfOH in acetonitrile, the bicyclic compound **9a** was afforded as a sole product and no 2-(2-oxoalkyl)-acrylate nor α-methylene-γ-lactone was detected (Entry 9). Two geometrical isomers of **9a** were separated by silica-gel column chromatography (*E* : *Z*=2.4 : 1) and the geometry of two isomers were determined from δ-values of allylic protons (δ=2.80 for *E*-isomer and δ=3.30 for *Z*-isomer). The same reaction also proceeded slowly by TsOH treatment, with the *E*/*Z* ratio slightly different (Entry 10). Treatment of **5** in propiononitrile or isobutyronitrile showed parallel results (Entries 11 and 12); however, treatment in pivalonitrile gave only a complex mixture in which the corresponding compound **9d** was not detected (Entry 13).

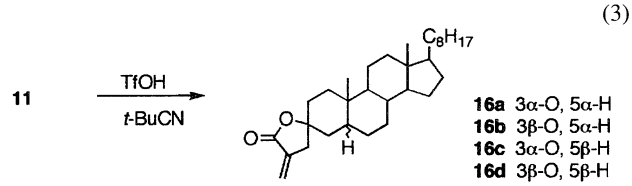
We proposed a possible reaction mechanism of the formation of ethyl 2-(2-oxoalkyl)acrylates **6**, or α-methylene-γ-lactones **7** and **8**, as illustrated in Scheme 1.[8)] Here, protonation first occurred at olefinic terminal position giving a stable tertiary cation (**i**) which also can be stabilized by silicon atom (**ii**).[13)] Attack of nitrile (route a) followed by cyclization of allylsilane gives strained four-membered ring **iii**. Cleavage of this ring and subsequent hydrolysis of **iv** gives ethyl 2-(2-oxoalkyl)acrylates **6**. When R^3 group is bulky, intramolecular attack of ester oxygen takes place (route b), in addition to the nitrile attack, to give α-methylene-γ-lactones **7** and **8** after protiodesilylation and hydrolysis. The *E*/*Z* isomerization of allylsilane moiety at the stage **i** or **ii** must happen via the route shown in Scheme 2 since lactones, which cannot be produced from (**Z**)-**i**, were obtained as the major product from both **3** and **4** in which *Z*-isomer was the major.

The formation of 3-azabicyclo[3.3.1]non-2-ene derivative **9** from **5** can be easily explained (Scheme 3). Here protonation occurred at isopropenyl group giving tertiary cation **v**, to which the nitrile attack of Ritter type takes place. Compound **9** is the result of intramolecular cyclization of pentadienylsilane **vi**. This indicates that ester-conjugated pentadienylsilane is less reactive than isopropenyl group against protonic acid.

From the mechanisms shown in Scheme 1, ketone **10** must be obtained as well as ethyl 2-(2-oxoalkyl)acrylate **6** by hydrolysis of imine **iv**; however, we could not detect any of this ketone in the above experiments. Therefore, in order to establish this reaction mechanism, we next examined the reaction of **11**, since it must be easier to detect a ketone of a relatively larger molecule. Compound **11** was synthesized



(3)



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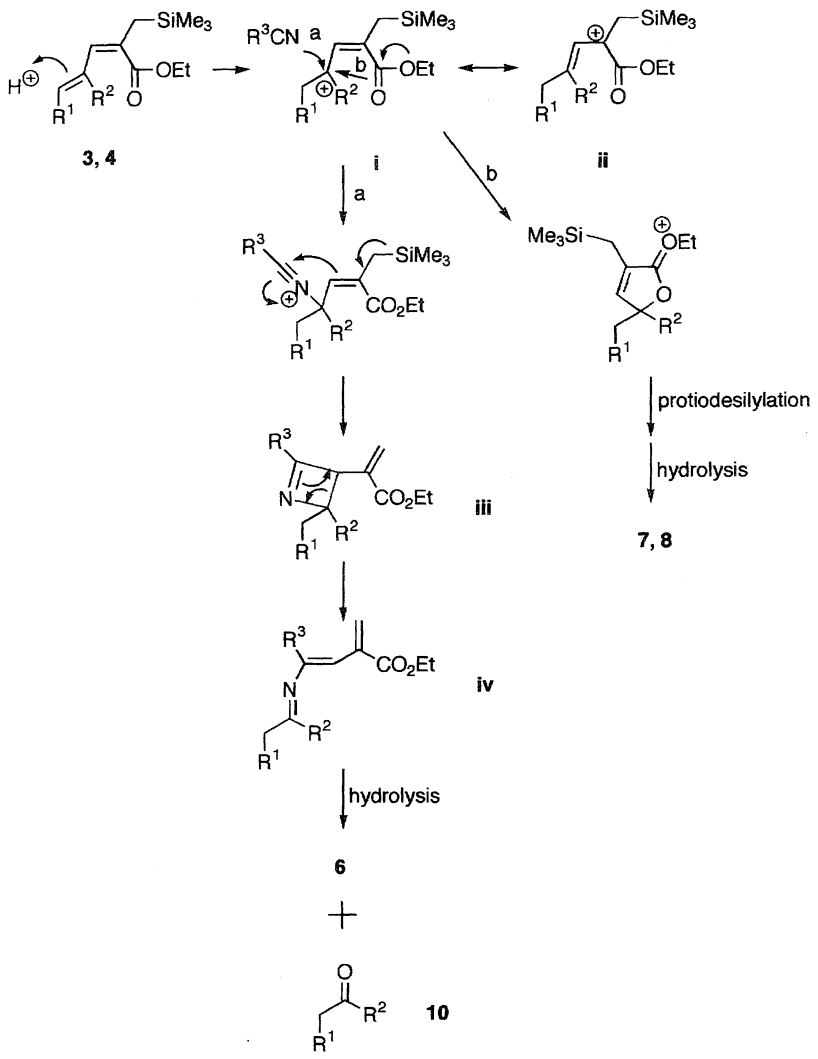
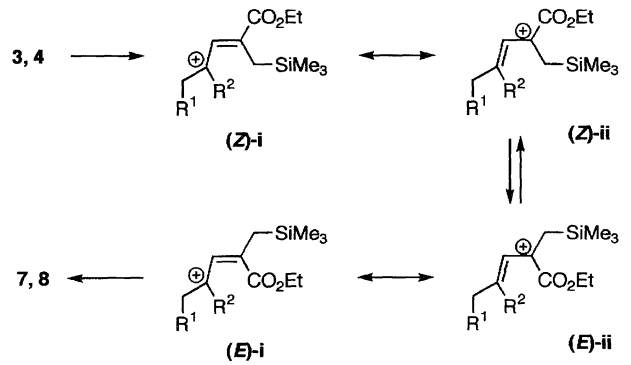


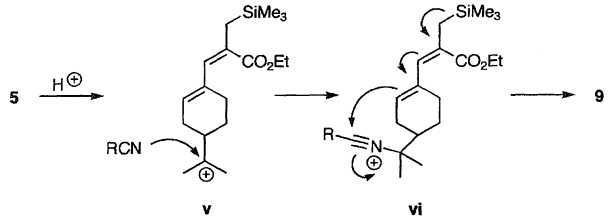
Scheme 1.

as an inseparable mixture of two diastereoisomers, **11a** and **11b**, from cholest-4-en-3-one **12**, as shown in Scheme 4. The ratio of two isomers was found to be **11a** : **11b**=1 : 3 from the ^{1}H NMR spectrum including NOE, which was observed between 19-Me (δ=0.97) and C(5β)-H (δ=2.14) of the major isomer (**11b**). It should be noted that no *E*-isomer of **11**, with respect to the double bond of allylsilane, was obtained by Wittig reaction[2,4] of **14**. Reaction of **11** under Ritter condition was carried out with TfOH in acetonitrile, giving a mixture of cholestanones **15** (**15a** : **15b**=1 : 3) in 61% yield, along with 55% of 2-acetonylacrylate **6a** (Eq. 3). This results strongly support the reaction mechanism described above, even though the intermediate **iii** or **iv** could not be detected.

Spiro-α-methylene-γ-lactone annulation of **11** was also examined by treatment with TfOH in pivalonitrile (Eq. 4). The spirolactone **16** was obtained in 39% yield, along with cholestanone (39%) and keto ester **6d** (12%). The ^{1}H NMR spectrum showed that **16** consists of four stereoisomers with the ratio of **16a** : **16b** : **16c** : **16d**=16 : 9 : 31 : 44. Two of these four isomers, **16a** and **16b**, are known compounds,[14] and



Scheme 2.

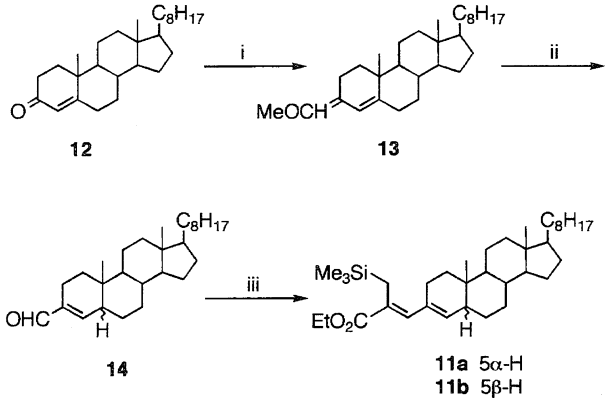


Scheme 3.

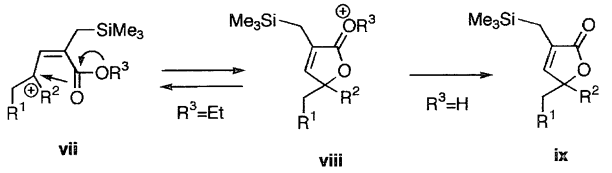
Table 2. ^{1}H NMR Data of Lactones **16** in $CDCl_3$[a)]

Compound	18-Me [lit[b)]]	19-Me [lit[b)]]	β-CH_2 of lactone [lit[b)]]
16a	0.64 (s)	0.79 (s)	2.66 (t, J=2.5 Hz)
	[0.65 (s)]	[0.80 (s)]	[2.67 (t, J=2.6 Hz)]
16b	0.65 (s)	0.85 (s)	2.78 (m)[c)]
	[0.65 (s)]	[0.85 (s)]	[2.79 (t, J=2.4 Hz)]
16c	0.64 (s)	0.96 (s)	2.79 (AB, J=17 Hz, each t, J=2.5 Hz)
16d	0.65 (s)	0.97 (s)	2.69 (t, J=3 Hz)

a) Internal $CHCl_3$ (δ=7.26) as reference. b) Me_4Si as reference; see Ref. 14. c) The multiplicity could not be determined due to overlap with signals of **16c**.



Scheme 4. Reagents and conditions: i, $Ph_2P(O)CH_2OMe$, LDA, THF, r.t.; ii, 5% HCl, THF, reflux; iii, $(EtO)_2P(O)CH(CO_2Et)CH_2SiMe_3$, NaH, DME, r.t.

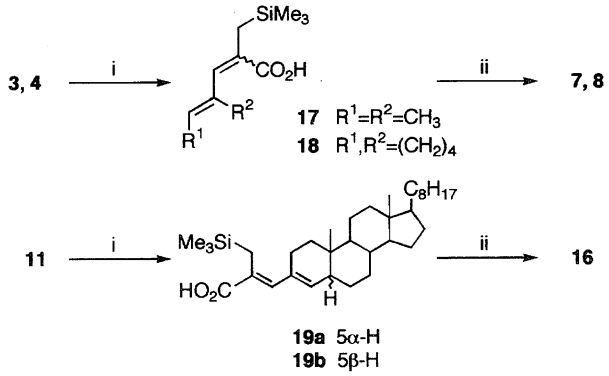


Scheme 5.

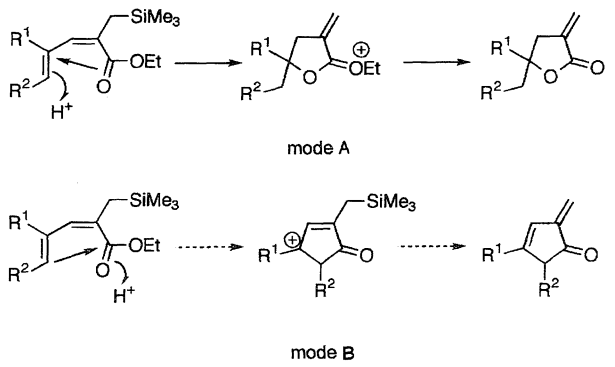
the structures of **16c** and **16d** were deduced from chemical shifts of ^{1}H NMR signals listed in Table 2. Thus the chemical shifts of β-methylene protons of **16c** and **16d** showed similar values to those of **16b** and **16a**, respectively. This indicates that the orientations of β-methylene of **16c** and **16d** against steroidal A-ring are similar to that of **16b** (axial) and of **16a** (equatorial), respectively.

The α-methylene-γ-lactone moiety is often found in natural terpenoids as a part of a biologically important structural unit,[15)] and a number of syntheses are reported.[16)] The spiro-α-methylene-γ-lactone annulation described here is a unique entry since this new method includes construction of a lactone moiety from a single oxygen function. However, the products are always accompanied with Ritter type of acylated product **6** (for example, Entries 4, 7, and 8 in Table 1). From the reaction mechanism described in Scheme 1, we assumed that the self-cyclization proceeds more effectively if ethyl group is replaced by hydrogen (Scheme 5); i.e. loss of proton from intermediate **viii** would occur easily to give **ix** when R^3=H, while Et^+ does not eliminate from **viii**, and therefore, **vii** and **viii** must be in equilibrium when R^3=Et. Ethyl group eliminates as EtOH after hydrolysis. Based on this hypothesis, the ester group of **3**, **4**, and **11** was hydrolyzed to give **17**, **18**, and **19**, respectively. Compounds **17** and **18** consisted of mostly *Z*-isomer after chromatographic purification. Even though the yields of hydrolysis were not good enough, the cyclization proceeded in acetonitrile, not in bulky nitrile, to obtain spiro-α-methylene-γ-lactones **7**, **8**, and **16** in 78, 95, and 97% yields, respectively, without accompanying 2-acetonylacrylate **6a**, as expected (Scheme 6). The compound **16** was a mixture of four stereoisomers; the ratio was **16a** : **16b** : **16c** : **16d**=13 : 16 : 46 : 25. Interestingly, the major isomer of lactones has 3-equatorial oxygen for both 5α-H and 5β-H steroids, while the major isomer has 3-axial oxygen for cyclization of ester **11**, as mentioned above.

In conclusion, we found two new type of reactions: a C–C single bond cleavage and a self-cyclization reaction of 4,5-disubstituted 2-(trimethylsilylmethyl)penta-2,4-dienoate and/or -dienoic acid under Ritter condition. The results obtained in this study can be classified as follows. Thus (1) ethyl 2-(trimethylsilylmethyl)penta-2,4-dienoate gives 2-(2-oxoalkyl)acrylates by Ritter type of acylative C–C single-bond cleavage in less-bulky nitriles; (2) the same ester gives two types of reaction products: C–C single-bond cleavage and self-cyclization, in bulky nitriles; (3) 2-(trimethylsilylmethyl)penta-2,4-dienoic acid gives only self-cyclization product. Moreover it was found that the ethoxycarbonyl-conjugated pentadienylsilane moiety is less reactive than isopropenyl group. As for self-cyclization, we originally expected that



Scheme 6. Reagents and conditions: i, KOH, MeOH aq, reflux; ii, TfOH, MeCN, reflux.



Scheme 7.

the reaction would proceed via "mode B" of Scheme 7, in which pentadienylsilane acts as nucleophile and carbonyl carbon acts as electrophile. However the actual cyclization proceeded via "mode A", in which carbonyl oxygen acts as nuclephile. Interestingly, the roles of the two double bonds, terminal C=C and carbonyl C=O, are opposite in these two modes.

Experimental

General Procedures. Melting points were collected on a Mel-temp capillary melting point apparatus (Laboratory Devices) and are uncorrected. 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) spectrometer. Chemical shifts are reported on the δ scale (ppm) with chloroform as an internal standard ($CHCl_3$=7.26 for ^{1}H and $CDCl_3$=77.00 for ^{13}C). Both low-resolution and high-resolution mass spectra were obtained on an SX-102A mass spectrometer. Analytical TLC was performed on precoated TLC plates (Kieselgel 60 F_{254}, layer thickness 0.2 mm). Wakogel C-200 and C-300, Florisil (100—200 mesh), or ICN Alumina N Act 1 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, tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were distilled from $LiAlH_4$; hexane was distilled form CaH_2.

Ethyl 4-Methyl-2-(trimethylsilylmethyl)hexa-2,4-dienoate (3). Sodium hydride (225 mg, 5.63 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. To this was added dry DME (7 cm^3), then a solution of $(EtO)_2P(O)CH_2CO_2Et$ (1.0 cm^3, 5.04 mmol) in DME (5 cm^3) dropwise in an ice bath. After this was stirred for 40 min at room temperature, a solution of (iodomethyl)trimethylsilane (0.9 cm^3, 6.07 mmol) in DME (7 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 (183 mg, 4.58 mmol) was added. After this was stirred at room temperature for 1.5 h, a solution of (*E*)-2-methylbut-2-enal (0.40 cm^3, 4.14 mmol) was added at 0 °C, and the reaction mixture was stirred at room temperature for 15 h. Aqueous NH_4Cl was then added to quench the reaction and the resulting aqueous mixture was extracted with Et_2O. Evaporation of the solvent gave a crude product which was chromatographed on a silica gel (30 g) using pentane–Et_2O (99 : 1 and 98 : 2) as eluent to afford **3** (96.0 mg, 10%) as an oil; IR (neat) 1705 (C=O), 1625 (C=C), and 1250 cm^{-1} (C–O); ^{1}H NMR ($CDCl_3$) δ=0.00 (9H, s, $SiMe_3$), 1.30 (3H, t, *J*=7 Hz, $OCH_2C\underline{H}_3$), 1.73 (3H, br d, *J*=6 Hz, C=CHMe), 1.82 (3H, br s, C=CMe), 2.06 (2H, s, $C\underline{H}_2SiMe_3$), 4.18 (2H, q, *J*=7 Hz, $OC\underline{H}_2CH_3$), 5.69 (1H, tq, *J*=1, 7 Hz, C=C$\underline{H}$Me), 5.91 (1H, s, C$\underline{H}$=CCO_2Et of *E*-isomer), and 7.00 (1H, s, C$\underline{H}$=CCO_2Et of *Z*-isomer); the *E*/*Z* ratio was determined to be 1 : 18 from signals due to C$\underline{H}$=CCO_2Et; ^{13}C NMR ($CDCl_3$) assigned for *Z*-isomer: δ=−0.96 (3C), 13.86, 14.29, 16.00, 17.76, 60.52, 127.72, 129.50, 133.31, 139.17, and 169.46; MS *m*/*z* (rel intensity) 240 (M$^+$; 99), 225 (100), 211 (86), and 195 (50). Found: C, 64.73; H, 9.80%. Calcd for $C_{13}H_{24}O_2Si$: C, 64.95; H, 10.06%.

Ethyl 3-(Cyclohex-1-en-1-yl)-2-(trimethylsilylmethyl)prop-2-enoate (4). Similarly, cyclohex-1-ene-1-carbaldehyde (394.7 mg, 3.58 mmol) was converted into **4** (396.6 mg, 42%); an oil, IR (neat) 1710 (C=O), 1620 (C=C), and 1250 cm^{-1} (C–O); ^{1}H NMR ($CDCl_3$) δ=0.00 (9H, s, $SiMe_3$), 1.29 (3H, t, *J*=7 Hz, $OCH_2C\underline{H}_3$), 2.06 (2H, s, $C\underline{H}_2SiMe_3$), 4.17 (2H, q, *J*=7 Hz, $OC\underline{H}_2CH_3$), 5.62 (1H, m, $CH_2C\underline{H}$=C of *E*-isomer), 5.82 (1H, s, C$\underline{H}$=CCO_2Et of *E*-isomer), 5.89 (1H, m, $CH_2C\underline{H}$=C of *Z*-isomer), and 6.93 (1H, s, C$\underline{H}$=CCO_2Et of *Z*-isomer); the *E*/*Z* ratio was determined to be 1 : 6.5 from signals due to C$\underline{H}$=CCO_2Et; ^{13}C NMR ($CDCl_3$) assigned for *Z*-isomer: δ=−0.94 (3C), 14.30, 18.01, 21.86, 22.73, 25.93, 28.66, 60.52, 127.74, 132.08, 135.10, 138.03, and 169.46; MS *m*/*z* (rel intensity) 266 (M$^+$; 92), 252 (100), 238 (100), 223 (98), 177 (98), and 103 (98). Found: C, 67.67; H, 9.78%. Calcd for $C_{15}H_{26}O_2Si$: C, 67.72; H, 9.84%.

Ethyl 3-(4-Isopropenylcyclohex-1-en-1-yl)-2-(trimethylsilylmethyl)prop-2-enoate (5). By the same procedure as that described for **3**, **5** was prepared from perillaldehyde (1.0 cm^3, 6.42 mmol). **5** (1.08 g, 55%): and oil; IR (neat) 1715 (C=O), 1650 (C=C), 1620 (C=C), and 1250 cm^{-1} (C–O); ^{1}H NMR ($CDCl_3$) δ=0.01 (9H, s, $SiMe_3$), 1.30 (3H, t, *J*=7 Hz, $OCH_2C\underline{H}_3$), 1.72 (3H, s, C=CMe of *E*-isomer), 1.75 (3H, s, C=CMe of *Z*-isomer), 2.07 (2H, s, $C\underline{H}_2SiMe_3$), 4.18 (2H, q, *J*=7 Hz, $OC\underline{H}_2CH_3$), 4.72 (2H, m, $C=C\underline{H}_2$), 5.65 (1H, m, $CH_2C\underline{H}$=C of *E*-isomer), 5.84 (1H, s, C$\underline{H}$=CCO_2Et of *E*-isomer), 5.91 (1H, m, $CH_2C\underline{H}$=C of *Z*-isomer), and 6.95 (1H, s, C$\underline{H}$=CCO_2Et of *Z*-isomer); the *E*/*Z* ratio was determined to be 1 : 5 from signals due to C$\underline{H}$=CCO_2Et; ^{13}C NMR ($CDCl_3$) assigned for *Z*-isomer: δ=−0.94 (3C), 14.30, 18.06, 20.76, 27.58, 28.95, 31.36, 40.36, 60.56, 108.85, 128.02, 131.55, 134.76, 137.44, 149.33, and 169.39; MS *m*/*z* (rel intensity) 306 (M$^+$; 27), 291 (12), 261 (8), 187 (14), 159 (17), 119 (19), and 73 (100). Found: C, 70.55; H, 9.77%. Calcd for $C_{18}H_{30}O_2Si$: C, 70.53; H, 9.86%.

General Procedure of Acid Treatment of 3, 4, and 5 (Table 1). To a stirred solution of substrate (0.1 mmol) in nitrile (2 cm^3) was added a solution of TfOH (3 molar amounts; 0.23 mol cm^{-3} in the same nitrile) at room temperature. After this had been stirred for an appropriate time, aqueous $NaHCO_3$ was added, and the mixture was extracted with Et_2O and dried. The product(s) was purified by silica-gel column chromatography using hexane–AcOEt as eluent.

Ethyl 2-Acetonylacrylate (6a). An oil; IR (neat) 1725 (C=O), 1720 (C=O), and 1640 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ=1.29 (3H, t, *J*=7 Hz, $OCH_2C\underline{H}_3$), 2.21 (3H, s, $COCH_3$), 3.41 (2H, br s, $-CH_2-$), 4.20 (2H, q, *J*=7 Hz, $OC\underline{H}_2CH_3$), 5.64 (1H, q, *J*=1 Hz, C=C$\underline{H}$H), and 6.34 (1H, d, *J*=1 Hz, C=CH$\underline{H}$) [lit,[10a] 1.26 (t), 2.09 (s), 3.25 (br s), 4.13 (q), 5.51 (br s), and 6.18 (br s); measured in CCl_4]; ^{13}C NMR ($CDCl_3$) δ=14.08, 29.72, 46.53, 61.04, 128.49, 134.50, 166.28, and 205.26; MS *m*/*z* (rel intensity) 156 (M$^+$; 11), 114 (100), and 86 (84).

Ethyl 2-(2-Oxobutyl)acrylate (6b). An oil; IR (neat) 1725 (C=O), 1720 (C=O), and 1640 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ=1.07 (3H, t, *J*=7 Hz, $COCH_2C\underline{H}_3$), 1.28 (3H, t, *J*=7 Hz, $OCH_2C\underline{H}_3$), 2.52 (2H, q, *J*=7 Hz, $COC\underline{H}_2CH_3$), 3.39 (2H, d, *J*=1 Hz, $-CH_2-$), 4.19 (2H, q, *J*=7 Hz, $OC\underline{H}_2CH_3$), 5.63 (1H, q, *J*=1 Hz, C=C$\underline{H}$H), and 6.33 (1H, d, *J*=1 Hz, C=CH$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ=7.74,

14.10, 35.82, 45.35, 60.99, 128.37, 134.56, 166.35, and 207.89; MS *m/z* (rel intensity) 170 (M^+; 33), 141 (21), 125 (71), and 57 (100). Found: *m/z* 170.0944 (M^+). Calcd for $C_9H_{14}O_3$: M, 170.0943.

Ethyl 2-(3-Methyl-2-oxobutyl)acrylate (6c). An oil; IR (neat) 1725 (C=O), 1720 (C=O), and 1640 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=1.13 (6H, d, J=7 Hz, COCH ($C\underline{H}_3$)$_2$), 1.27 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.70 (1H, sept, J=7 Hz, $COC\underline{H}(CH_3)_2$), 3.45 (2H, d, J=1 Hz, $-CH_2-$), 4.18 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.61 (1H, q, J=1 Hz, C=C$\underline{H}$H), and 6.34 (1H, d, J=1 Hz, C=CH$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ=14.08, 18.17 (2C), 40.78, 43.45, 60.93, 128.35, 134.63, 166.34, and 211.03; MS *m/z* (rel intensity) 184 (M^+; 10), 139 (41), 113 (39), 86 (67), and 71 (100). Found: *m/z* 184.1149 (M^+). Calcd for $C_{10}H_{16}O_3$: M, 184.1100.

Ethyl 2-(3,3-Dimethyl-2-oxobutyl)acrylate (6d). An oil; IR (neat) 1725 (C=O), 1720 (C=O), and 1645 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=1.20 (9H, s, *t*-Bu), 1.27 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 3.52 (2H, d, J=1 Hz, $-CH_2-$), 4.18 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.57 (1H, q, J=1 Hz, C=C$\underline{H}$H), and 6.33 (1H, d, J=1 Hz, C=CH$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ=14.13, 26.48 (3C), 40.15, 44.28, 60.84, 128.18, 135.03, 166.40, and 212.35; MS *m/z* (rel intensity) 153 ([M−OEt]$^+$; 47), 141 (58), 114 (72), 85 (92), and 57 (100). Found: *m/z* 153.0884 ([M−OEt]$^+$). Calcd for $C_9H_{13}O_2$: M, 153.0916.

5-Ethyl-5-methyl-3-methylenetetrahydrofuran-2-one (7). An oil; IR (neat) 1765 (C=O) and 1670 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=0.95 (3H, t, J=7 Hz, $CH_2C\underline{H}_3$), 1.39 (3H, s, CH_3), 1.71 (2H, q, J=7 Hz, $C\underline{H}_2CH_3$), 2.67 (1H, dt, J=17, 2.5 Hz, C=C–C$\underline{H}$H–C), 2.79 (1H, dt, J=17, 2.5 Hz, C=C–CH$\underline{H}$–C), 5.60 (1H, t, J=2.5 Hz, C=C$\underline{H}$H), and 6.22 (1H, t, J=3 Hz, C=CH$\underline{H}$) [lit,[11] 0.96 (t), 1.36 (s), 1.70 (q), 5.50 (m), and 6.10 (t)]; ^{13}C NMR ($CDCl_3$) δ=7.99, 26.07, 33.99, 38.95, 84.06, 121.98, 136.01, and 169.99.

3-Methylene-1-oxaspiro[4.5]decan-2-one (8). Since this compound could not be separated from acylated product **6c** or **6d** (see Table 1), the following spectral data were collected from the product of the cyclization of **18**. IR (neat) 1765 (C=O) and 1670 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=2.71 (2H, t, J=2.5 Hz, $-CH_2-$), 5.60 (1H, t, J=2.5 Hz, C=C$\underline{H}$H), and 6.22 (1H, t, J=3 Hz, C=CH$\underline{H}$) [lit,[12] 2.75 (t, J=3 Hz), 5.65 (t, J=2.7 Hz), and 6.25 (t, J=2.7 Hz)]; ^{13}C NMR ($CDCl_3$) δ=22.47 (2C), 24.73, 37.44 (2C), 39.52, 83.38, 122.15, 135.56, and 166.90; MS *m/z* (rel intensity) 166 (M^+; 100), 149 (53), and 123 (100). Found: *m/z* 166.1015 (M^+). Calcd for $C_{10}H_{14}O_2$: M, 166.0994.

Ethyl 2-[(2,4,4-Trimethyl-3-azabicyclo[3.3.1]non-2-en-8-ylidene)methyl]acrylate (9a). Two isomers were separated by silica-gel column chromatography using hexane–AcOEt (4 : 1) as eluent. The ratio of the two isomers was determined to be Z:E= 1 : 2.4 (see text).

Z-Isomer: an oil; IR (neat) 1725 (C=O) and 1655 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=1.19 (3H, s, C–Me), 1.30 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.30 (3H, s, C–Me), 1.80 (3H, s, N=C–Me), 3.30 (1H, br s, N=C–CH–C=C), 4.22 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.59 (1H, t, J=1.5 Hz, C=C$\underline{H}$H), 5.97 (1H, br s, C=CH), and 6.33 (1H, d, J=2 Hz, C=CH$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ=14.20 (CH_3), 26.25 (CH_3), 27.23 (CH_3), 29.28 (CH_2), 30.35 (CH_2), 31.17 (CH_2 or CH_3), 31.24 (CH_3 or CH_2), 35.52 (CH), 39.23 (CH), 57.60 (C), 60.94 (CH_2), 118.84 (CH), 126.25 (CH_2), 136.73 (C), 143.53 (C), 165.59 (C), and 166.92 (C); MS *m/z* (rel intensity) 275 (M^+; 28), 234 (90), 191 (76), 145 (100), and 117 (49). Found: *m/z* 275.1869 (M^+). Calcd for $C_{17}H_{25}NO_2$: M, 275.1885.

E-Isomer: an oil; IR (neat) 1725 (C=O) and 1660 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=1.19 (3H, s, C–Me), 1.29 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.30 (3H, s, C–Me), 1.89 (3H, s, N=C–Me), 2.47 (1H, dd, J=5, 14 Hz, C=C–C$\underline{H}$H), 2.80 (1H, br s, N=C–CH–C=C), 4.21 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.49 (1H, br s, C=C$\underline{H}$H), 6.04 (1H, br s, C=CH), and 6.28 (1H, d, J=2 Hz, C=CH$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ=14.14 (CH_3), 24.14 (CH_2), 25.73 (CH_3), 27.09 (CH_3), 29.13 (CH_2), 29.23 (CH_2), 31.19 (CH_3), 35.46 (CH), 47.46 (CH), 57.57 (C), 60.84 (CH_2), 119.73 (CH), 126.42 (CH_2), 136.47 (C), 143.44 (C), 166.12 (C), and 166.93 (C); MS *m/z* (rel intensity) 275 (M^+; 100), 234 (75), 191 (78), and 117 (80). Found: *m/z* 275.1869 (M^+). Calcd for $C_{17}H_{25}NO_2$: M, 275.1885.

Ethyl 2-[(2-Ethyl-4,4-dimethyl-3-azabicyclo[3.3.1]non-2-en-8-ylidene)methyl]acrylate (9b). An oil; IR (neat) 1725 (C=O) and 1650 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) assigned for *Z*-isomer: δ=0.98 (3H, t, J=8 Hz, CH_3CH_2C=N), 1.18 (3H, s, C–Me), 1.30 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.31 (3H, s, C–Me), 3.39 (1H, br s, N=C–CH–C=C), 4.21 (2H, m, $OC\underline{H}_2CH_3$), 5.58 (1H, t, J=1.5 Hz, C=C$\underline{H}$H), 5.94 (1H, br s, C=CH), and 6.33 (1H, d, J=1.5 Hz, C=CH$\underline{H}$); assigned for *E*-isomer: δ=1.05 (3H, t, J=8 Hz, $C\underline{H}_3CH_2C$=N), 1.19 (3H, s, C–Me), 1.30 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.31 (3H, s, C–Me), 2.48 (1H, dd, J=5, 15 Hz, C=C–C$\underline{H}$H), 2.90 (1H, br s, N=C–CH–C=C), 4.21 (2H, m, $OC\underline{H}_2CH_3$), 5.49 (1H, t, J=1.5 Hz, C=C$\underline{H}$H), 6.04 (1H, br s, C=CH), and 6.28 (1H, d, J=2 Hz, C=CH$\underline{H}$); the *E*/*Z* ratio was determined to be 2.3 : 1 from signals due to N=C–CH–C=C; MS *m/z* (rel intensity) 289 (M^+; 29), 234 (91), 191 (78), and 145 (100). Found: *m/z* 289.2025 (M^+). Calcd for $C_{18}H_{27}NO_2$: M, 289.2043.

Ethyl 2-[(2-Isopropyl-4,4-dimethyl-3-azabicyclo[3.3.1]non-2-en-8-ylidene)methyl]acrylate (9c). An oil; IR (neat) 1725 (C=O) and 1650 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) assigned for *Z*-isomer: δ=1.05 (6H, d, J=7 Hz, $CH\underline{Me}_2$), 1.17 (3H, s, C–Me), 1.30 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.31 (3H, s, C–Me), 2.29 (1H, sept, J=7 Hz, $C\underline{H}Me_2$), 3.45 (1H, br s, N=C–CH–C=C), 4.21 (2H, m, $OC\underline{H}_2CH_3$), 5.56 (1H, br s, C=C$\underline{H}$H), 5.92 (1H, br s, C=CH), and 6.35 (1H, br s, C=CH$\underline{H}$); assigned for *E*-isomer: δ=1.05 (6H, d, J=8 Hz, $CH\underline{Me}_2$), 1.18 (3H, s, C–Me), 1.30 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.31 (3H, s, C–Me), 2.47 (2H, m, C=C–C$\underline{H}$H and $C\underline{H}Me_2$), 2.98 (1H, br s, N=C–CH–C=C), 4.21 (2H, m, $OC\underline{H}_2CH_3$), 5.47 (1H, br s, C=C$\underline{H}$H), 6.03 (1H, br s, C=CH), and 6.27 (1H, br s, C=CH$\underline{H}$); the *E*/*Z* ratio was determined to be 2.2 : 1 from signals due to N=C–CH–C=C; MS *m/z* (rel intensity) 303 (M^+; 19), 288 (6), 274 (6), 261 (23), 234 (87), 191 (88), and 145 (100). Found: *m/z* 303.2181 (M^+). Calcd for $C_{19}H_{29}NO_2$: M, 303.2200.

3-(Methoxymethylene)cholest-4-ene (13). Lithium diisopropylamide (LDA) was generated in a 200 cm^3 three-necked flask by mixing diisopropylamine (3.5 cm^3) and BuLi (10.2 cm^3, 16.3 mmol; 1.6 mol dm^{-3} solution in hexane) in dry THF (12 cm^3) at 0 °C under Ar. To this was added dropwise a solution of $Ph_2P(O)CH_2OMe$ (2.93 g, 11.9 mmol) in THF (70 cm^3) with stirring and the mixture was further stirred at 0 °C for 20 min. A solution of cholest-4-en-3-one (3.15 g, 8.19 mmol) in THF (10 cm^3) was added at −50 °C and the mixture was allowed to warm to room temperature. After it was stirred for 19 h, the reaction was quenched by addition of saturated aqueous NH_4Cl, and the mixture was extracted with Et_2O. After evaporation of the solvent, the crude product was chromatographed on silica gel (15 g) using hexane as eluent to afford **13** (1.48 g, 44%) as a viscous oil; IR (neat) 1660 (C=C), 1620 (C=C), and 1210 cm^{-1} (C–O); ^1H NMR ($CDCl_3$) δ=3.59 (3H, s, OMe), 5.68 (1H, s, 4-H), and 6.12 (1H, s, C=C$\underline{H}$OMe).

3-Formycholest-3-ene (14). Compound **13** (671.2 mg, 1.63 mmol) was dissolved in 5% HClaq–THF (50 cm^3; 1 : 4 ratio) and the solution was refluxed for 3 h. After this was cooled to room temperature, aqueous $NaHCO_3$ was added slowly and the mixture was extracted with Et_2O. Evaporation of the solvent followed

by silica-gel (15 g) column chromatography using hexane–AcOEt (19 : 1 and 9 : 1) as eluent afforded **14** (530.6 mg, 82%); mp 98—100 °C (recryst from MeOH); IR (neat) 2730 (CHO), 1685 (C=O), and 1645 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=6.43 (1H, q, J=1 Hz, 4-H of one isomer), 6.53 (1H, br s, 4-H of the other isomer), 9.41 (1H, s, CHO of one isomer), and 9.45 (1H, s, CHO of the other isomer); the ratio of two isomers was found to be 1 : 1 from these signals; ^{13}C NMR ($CDCl_3$) δ=139.68, 141.63, 155.51, 156.97, 194.11, and 194.36.

Ethyl 3-(Cholest-3-en-3-yl)-2-(trimethylsilylmethyl)prop-2-enoate (11). By the same procedure as that described for the preparation of **3**, compound **14** (747.6 mg, 1.88 mmol) was converted into **11** (550 mg, 53%); mp 65—68 °C (recryst from MeOH); IR (Nujol) 1715 (C=O), 1620 (C=C), and 1250 cm^{-1} (C–O); ^1H NMR ($CDCl_3$) δ=0.00 (9H, s, $SiMe_3$), 1.30 (3H, t, J=7 Hz, OCH_2CH_3), 2.11 (2H, s, CH_2SiMe_3), 4.18 (2H, q, J=7 Hz, OCH_2CH_3), 5.55 (1H, s, 4-H of **11a**), 5.62 (1H, s, 4-H of **11b**), 6.92 (1H, s, CH=CCO_2Et of **11a**), and 6.96 (1H, s, CH=CCO_2Et of **11b**); the ratio of two isomers was determined to be 1 : 3 from signals due to CH=CCO_2Et; ^{13}C NMR ($CDCl_3$) assigned for **11b**: δ=127.49, 134.95, 137.61, 138.56, and 169.52; MS m/z (rel intensity) 554 (M^+; 76), 539 (98), 522 (100), 508 (73), 447 (90), 414 (64), and 211 (64).

Treatment of 11 with TfOH in MeCN. A solution of **11** (78.4 mg, 0.141 mmol) in MeCN (2.5 cm^3) was treated with TfOH for 14 h as described for **3**, **4**, and **5**. The products were separated by silica-gel (3 g) column chromatography using pentane–Et_2O (19 : 1) as eluent to afford cholestanone (33.3 mg, 61%) and **6a** (12.1 mg, 55%).

Treatment of 11 with TfOH in *t*-BuCN. A solution of **11** (42.5 mg, 0.0766 mmol) was treated with TfOH in *t*-BuCN (3 cm^3) as described above. The products were roughly separated into four groups (Groups I—IV) by silica-gel (ca. 2 g) column chromatography using pentane–Et_2O (99 : 1, 98 : 2, and 9 : 1) as eluent. Group I (8.3 mg) is cholestanone; Group II (3.8 mg) contains cholestanone and **16d**; Group III (11.0 mg) contains mostly **6d**, **16a**, and **16d**; Group IV (3.9 mg) contains mostly **16b** and **16c**. The total contribution of each product was cholestanone (0.0300 mmol, 39%), **6d** (0.00904 mmol, 12%), and **16a—d** (0.0300 mmol, 39%); these values were determined from ^1H NMR spectra of each group. The ratio of four lactones was **16a** : **16b** : **16c** : **16d**=16 : 9 : 31 : 44. For characterization of **16a—d**, see later.

4-Methyl-2-(trimethylsilylmethyl)hexa-2,4-dienoic Acid (17). To a solution of **3** (41.7 mg, 0.173 mmol) in MeOH (8 cm^3) was added H_2O (2 cm^3) and KOH aq (1 cm^3; 1 mol dm^{-3} solution) successively with stirring. After being refluxed for 8 h, the mixture was cooled to room temperature, and acidified by addition of dilute HCl aq to pH ca. 5. This was extracted with Et_2O and dried, and the solvent was evaporated off. The residual oil was chromatographed on silica-gel (2 g) using hexane–AcOEt (9 : 1) as eluent to afford **17** (9.6 mg, 26%) as an oil; IR (neat) 3400 (OH), 1680 (C=O), and 1250 cm^{-1} (C–O); ^1H NMR ($CDCl_3$) assigned for *Z*-isomer: δ=0.02 (9H, s, $SiMe_3$), 1.74 (3H, br d, J=7 Hz, C=CHMe), 1.84 (3H, br s, C=CMe), 2.06 (2H, s, CH_2SiMe_3), 5.77 (1H, br q, J=7 Hz, C=CHMe), and 7.15 (1H, s, CH=CCO_2H); ^{13}C NMR ($CDCl_3$) assigned for *Z*-isomer: δ=−0.95 (3C), 13.99, 14.11, 15.87, 17.54, 126.65, 131.17, 133.44, 141.51, and 174.92; MS m/z (rel intensity) 212 (M^+; 20), 197 (31), 181 (29), 122 (45), 107 (34), and 73 (100). Found: m/z 212.1215 (M^+). Calcd for $C_{11}H_{20}O_2Si$: M, 212.1233.

3-(Cyclohex-1-en-1-yl)-2-(trimethylsilylmethyl)prop-2-enoic Acid (18). By the same procedure, **4** (32.1 mg, 0.120 mmol) gave **18** (8.8 mg, 31%); mp 65—68 °C; IR (Nujol) 2400—3400 (OH), 1680 (C=O), and 1620 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) assigned for *Z*-isomer: δ=0.02 (9H, s, $SiMe_3$), 1.56—1.70 (4H, m, CH_2CH_2), 2.06 (2H, s, CH_2SiMe_3), 2.15—2.26 (4H, m, CH_2CH=CCH_2), 5.97 (1H, m, CH_2CH=C), and 7.08 (1H, s, CH=CCO_2H); ^{13}C NMR ($CDCl_3$) assigned for *Z*-isomer: −0.94 (3C), 17.76, 21.79, 22.70, 26.08, 28.53, 126.63, 133.73, 135.18, 140.35, and 175.00; MS m/z (rel intensity) 238 (M^+; 32), 223 (34), 148 (80), 120 (58), 91 (53), and 73 (100). Found: m/z 238.1408 (M^+). Calcd for $C_{17}H_{18}O$: M, 238.1358.

3-(Cholest-3-en-3-yl)-2-(trimethylsilylmethyl)prop-2-enoic Acid (19). Compound **11** (247.8 mg, 0.447 mmol) was hydrolyzed by the same procedure except EtOH was used in place of MeOH to afford **19** (58.4 mg, 25%) after silica-gel (18 g) column chromatography using hexane–Et_2O (96 : 4) as eluent. **19**: a viscous oil; IR (neat) 2400—3600 (OH), 1685 (C=O), 1585 (C=C), 1580 (C=C), and 1250 cm^{-1} (C–O); ^1H NMR ($CDCl_3$) δ=0.04 (9H, s, $SiMe_3$), 2.10 (2H, s, CH_2SiMe_3), 5.63 (1H, br s, 4-H of **19a**), 5.68 (1H, s, 4-H of **19b**), and 7.09 (1H, s, CH=CCO_2H); MS m/z (rel intensity) 526 (M^+; 16), 511 (15), 369 (100), and 81 (94). Found: m/z 526.4166 (M^+). Calcd for $C_{34}H_{58}O_2Si$: M, 526.4208.

Treatment of 17, 18, and 19 with TfOH in MeCN. To a stirred solution of **17** (21.0 mg, 0.0989 mmol) in MeCN (3.6 cm^3) was added a solution of TfOH in MeCN (1.2 cm^3, 0.312 mmol; 0.26 mol dm^{-3} solution) at room temperature. The mixture was heated to reflux for 20 min, cooled to room temperature again, and an aqueous solution of $NaHCO_3$ was added. After extraction with Et_2O and drying, the solvent was evaporated off. The resulting residue was chromatographed on silica-gel (ca. 2 g) using hexane–Et_2O (19 : 1) as eluent to afford **7** (10.8 mg, 78%). Similarly, **18** (6.5 mg, 0.027 mmol) gave **8** (4.3 mg, 95%) and **19** (19.8 mg, 0.0376 mmol) gave **16** (16.6 mg, 97%). The product **16** was roughly separated into two groups (Group I and Group II) by silica-gel (6 g) column chromatography using hexane–Et_2O (96 : 4) as eluent.

Group I consists of **16a** and **16d**; R_f 0.39 (hexane/AcOEt; 9 : 1); mp 115—119 °C; IR (Nujol) 1765 (C=O), 1670 (C=C), and 1260 cm^{-1} (C–O); ^1H NMR ($CDCl_3$) δ=0.86 (6H, dd, J=2, 6 Hz, 25-Me_2), 0.90 (3H, d, J=6 Hz, 20-Me), 5.59 (1H, t, J=2.5 Hz, C=CHH) and 6.22 (1H, t, J=3 Hz, C=CHH), see Table 2 for 18-Me, 19-Me, and β-CH_2 [lit,[14] 5.58 (t, J=2.4 Hz) and 6.20 (t, J=2.4 Hz) for **16a**]; MS m/z (rel intensity) 454 (M^+; 18), 429 (8), 355 (8), 299 (13), 223 (13), 205 (20), and 149 (100). Found: m/z 454.3832 (M^+). Calcd for $C_{31}H_{50}O_2$: M, 454.3813.

Group II consists mostly of **16b** and **16c**; R_f 0.32 (hexane/AcOEt; 9 : 1); mp 129—133 °C; IR (Nujol) 1755 (C=O), 1670 (C=C), and 1265 cm^{-1} (C–O); ^1H NMR ($CDCl_3$) δ=0.86 (6H, dd, J=2, 6 Hz, 25-Me_2), 0.90 (3H, d, J=6 Hz, 20-Me), 5.59 (1H, t, J=2.5 Hz, C=CHH) and 6.22 (1H, t, J=3 Hz, C=CHH), see Table 2 for 18-Me, 19-Me, and β-CH_2 [lit,[14] 5.58 (t, J=2.6 Hz) and 6.20 (t, J=2.6 Hz) for **16b**]; MS m/z (rel intensity) 454 (M^+; 79), 439 (11), 369 (13), 299 (22), 236 (28), and 43 (100). Found: m/z 454.3763 (M^+). Calcd for $C_{31}H_{50}O_2$: M, 454.3813. The ratio of four isomers was determined to be **16a** : **16b** : **16c** : **16d**=13 : 16 : 46 : 25 from the signal of β-CH_2 in the ^1H NMR spectra.

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