Stereoselective Syntheses of α-Substituted Cyclic Ethers and *syn*-1,3-Diols

Koichi HOMMA, Haruhiro TAKENOSHITA,† and Teruaki MUKAIYAMA*,†
Organic Chemistry Research Laboratory, Tanabe Seiyaku Co., Ltd.,
2-2-50, Kawagishi, Toda-shi, Saitama 335
†Department of Applied Chemistry, Faculty of Science,
Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162
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In the presence of a catalytic amount of triphenylmethylium hexachloroantimonate or a catalyst system of antimony pentachloride, chlorotrimethylsilane and tin(II) iodide, α-substituted cyclic ethers are stereoselectively prepared from lactones by successive treatment with 1-(*t*-butyldimethylsiloxy)-1-ethoxyethene and silyl nucleophiles such as triethylsilane, allyltrimethylsilane and trimethylsilyl cyanide.[1,2] These catalysts also promote the reaction of γ-, δ-, and ε-trimethylsiloxy carbonyl compounds with silyl nucleophiles resulting in the formation of α-substituted cyclic ethers.[3] The former procedure is effectively applied to short syntheses of (−)-*cis*-rose oxide and (*cis*-6-methyltetrahydro-2-pyranyl)acetic acid, a constitutent of civet.[2] Furthermore, *syn*-1,3-diols are also stereoselectively prepared from lactone analogue, 6-*cis*-substituted 2-trichloromethyl-1,3-dioxan-4-ones, easily prepared from β-hydroxy carboxylic acids.[4]

In recent years, much attention has been focused on α-substituted cyclic ethers, because cyclic ethers constitute a characteristic structural feature of many natural products including important *C*-glycosides.[5] Several methods for the preparation of α-substituted cyclic ethers have already been reported, for example, a direct α-substitution of cyclic ethers with organometallic compounds or silyl nucleophiles,[6,7] cyclization of hydroxy olefins,[8] and the Diels–Alder reaction of dienes and carbonyl compounds, α,β-unsaturated carbonyl compounds and dienophiles, or α-substituted furans and dienophiles.[9] Concerning the α-substitution of cyclic ethers such as lactols, cyclic hemiacetals, activated substrates such as α-halo, α-alkoxy, α-acyloxy, α-alkylthio or α-sulfonyl substituted cyclic ethers are usually required.[6] In the cases of several nucleophilic substitutions of unactivated cyclic hemiacetals, a large excess of $BF_3 \cdot Et_2O$ or trifluoroacetic acid was necessary to complete the reaction.[7] In previous papers, we have reported that the siloxyl group of silylated hemiacetals, generated in situ from aldehyde and alkoxytrialkylsilane, was smoothly replaced by a hydrogen atom or an allyl group originated from the corresponding silyl derivatives to give the acyclic ethers by the promotion of a catalytic amount of $TrClO_4$ or $Ph_2BOSO_2CF_3$.[10] Although the aldol type addition of silyl enol ethers to aldehydes and ketones are well known, little is yet known about the addition of silyl enol ethers to lactones. In the course of our study on the acid-catalyzed nucleophilic substitution of silylated hemiacetals, we were interested in the above mentioned reactions. Thus, we attempted first to prepare cyclic ethers from lactones by the successive treatment with silyl ketene acetal and silyl nucleophiles (Et_3SiH, allyltrimethylsilane, Me_3SiCN, etc.), and also from siloxy carbonyl compounds by the treatment with silyl nucleophiles in the presence of a catalytic amount of Lewis acid.

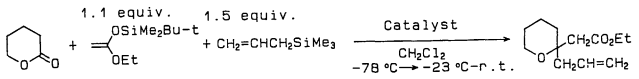
The effect of Lewis acids was examined in the former reaction, and it was found that triphenylmethylium salts such as $TrSbCl_6$, $TrSbF_6$, and $TrClO_4$, and combined use of $SbCl_5$, Me_3SiCl, and SnI_2 are quite effective[1] and that nucleophilic substitution of most of silylated cyclic hemiacetals with silyl nucleophiles proceeds in a highly stereoselective manner except in the cases of γ-butyrolactones and 2-substituted δ-valerolactone.[2] In the presence of the above mentioned catalysts, the cyclic ethers were also stereoselectively prepared from siloxy carbonyl compounds.[3]

The above procedure is effectively applied to short syntheses of (−)-*cis*-rose oxide and (*cis*-6-methyltetrahydro-2-pyranyl)acetic acid, the glandular secretion of the civet cat (*Viverra civetta*).[2]

syn-1,3-Diols are also stereoselectively prepared from 6-*cis*-substituted 2-trichloromethyl-1,3-dioxan-4-ones (**12**), a lactone analogue, by (i) the successive treatment of **12** with silyl ketene acetal (**2**) by use of $TrSbCl_6$ as a catalyst,[11] (ii) reduction of siloxyl group of initially formed silylated cyclic hemiacetals (**21** and **22**) with Et_3SiH by use of $TiCl_4$ as a promoter,[12] (iii) reduction of trichloromethyl group with *n*-Bu_3SnH, and (iv) deprotection of ethylidene group with EtSH by use of $TiCl_4$ as a promoter. The stereochemistry of the silylated cyclic hemiacetals, formed in the first step, is dependent on both the substituent at the 5-position of 2-trichloromethyl-1,3-dioxan-4-ones (**20**) and the amount of the catalyst.[11]

Results and Discussion

Preparation of Cyclic Ethers from Lactones. In the present study, an extensive screening of Lewis acids in the reaction of δ-valerolactone (**1d**), 1-(*t*-butyldimethylsiloxy)-1-ethoxyethene (**2**) and allyltrimethylsilane was tried in order to realize a one-pot procedure for the preparation of corresponding cyclic ethers (**3d**$_2$)



1d **2** **3d$_2$**

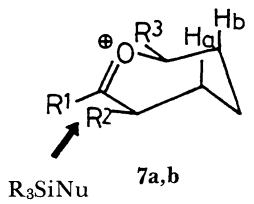
Scheme 1.

Table 1. The Effect of Catalyst

Entry	Catalyst (equiv)	Yield/%
1	$SbCl_5$(0.05)–Me_3SiCl(0.1)–SnF_2(0.1)	2
2	$SbCl_5$(0.05)–Me_3SiCl(0.1)–$SnCl_2$(0.1)	64
3	$SbCl_5$(0.05)–Me_3SiCl(0.1)–$SnBr_2$(0.1)	77
4	$SbCl_5$(0.05)–Me_3SiCl(0.1)–SnI_2(0.1)	84
5	Me_3SiCl(0.1)–SnI_2(0.1)	0
6	$SbCl_5$(0.05)–SnI_2(0.1)	75
7	$SbCl_5$(0.05)–Me_3SiCl(0.1)	0
8	$SnCl_4$(0.05)–Me_3SiCl(0.1)–SnI_2(0.1)	69
9	$TrClO_4$(0.05)	83
10	$TrSbF_6$(0.05)	82
11	$TrSbCl_6$(0.05)	87

(Table 1). Of several Lewis acid screened, $SbCl_5$, $SnCl_4$, $TiCl_4$, and $AlCl_3$ proved to be effective for the addition of **2** to lactones, while $BF_3 \cdot Et_2O$ did not promote the reaction. These Lewis acids do not promote the second step of the nucleophilic substitution reaction of in situ formed intermediate silylated cyclic hemiacetals (**4**) with silyl nucleophiles. Then, we investigated the above reaction by combined use of several Lewis acids. The results showed that both the first and second steps were smoothly promoted when the combination of $SbCl_5$, Me_3SiCl, and SnI_2 or the combination of $SnCl_4$, Me_3SiCl, and SnI_2 was employed as a catalyst system (Entries 4 and 8). On the other hand, $TiCl_4$ and $AlCl_3$ combined with Me_3SiCl and SnI_2 afforded the desired cyclic ethers in poor yields along with several unseparable by-products whose structure remained undetermined. In the case of $SbCl_5$, the combination with SnX_2 (X: Cl, Br, and I) is essential for the promotion of the reaction, and further addition of Me_3SiCl improved the yield (Entries 2—7). Triphenylmethylium salts such as $TrSbCl_6$, $TrSbF_6$, and $TrClO_4$ also effectively promote the reaction (Entries 9, 10, and 11). The counter anions of these triphenylmethylium salts make little difference on the yield. Several examples of the preparation of cyclic ethers from lactones are demonstrated in Table 2 using $TrSbCl_6$ alone or a combination of $SbCl_5$, Me_3SiCl, and SnI_2 as a catalyst. Although Et_3SiH, allyltrimethylsilane and Me_3SiCN could be successfully employed as silyl nucleophiles in the second step, while silyl enol ethers and silyl ketene acetals were not used effectively.

Tetrahydropyrans and oxepanes were stereoselectively prepared from δ-valerolactones and ε-caprolactones, respectively. In the cases of δ-valerolactones, silyl nucleophiles mainly attack the oxonium intermediate (**5**), a major conformer initially formed from the



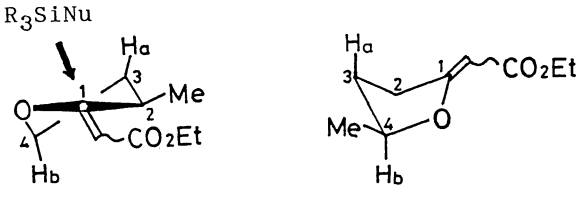
7a,b

a: R^1=CH_2CO_2Et, R^2=Me, R^3=H
b: R^1=CH_2CO_2Et, R^3=Me, R^2=H

Fig. 1.

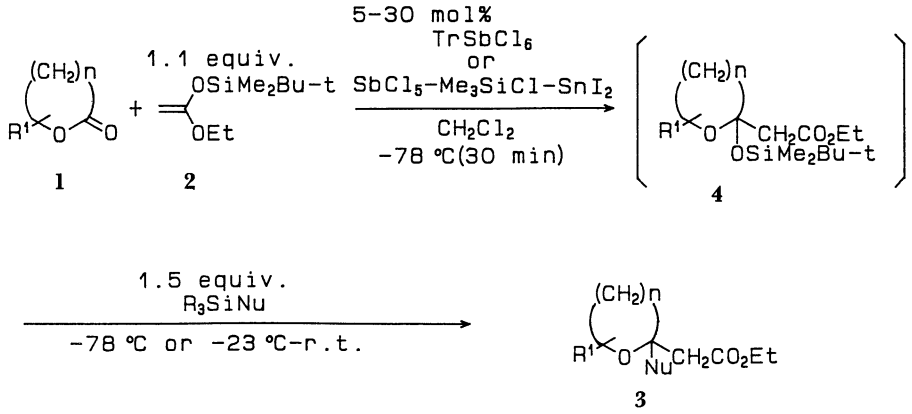
lactone and **2**, from α-side due to tortional strain (Scheme 3). The stereoselectivity is especially high in the cases of 3- and 5-methyl-δ-valerolactones (**1f** and **1h**) (Entries 10, 12, and 13), because silyl nucleophiles attack from α-side of the initially formed oxonium intermediate (**6**), a minor conformer, as well, due to 1,3-diaxial interaction. On the other hand, in the cases of 2- and 4-methyl-δ-valerolactones (**1e** and **1g**) (Entries 8, 9, and 11), the nucleophilic attack takes place mainly from α-side of the intermediate (**5**). However, the decrease in the selectivity may be caused by the competitive β-side attack of nucleophiles to the intermediate (**6**). When 2-methyl-δ-valerolactone was employed, it was expected that cis isomer should mainly be obtained because conformer (**6**) preferred to conformer (**5**) due to allylic strain.[13] Surprisingly, however, the trans isomer was preferentially obtained probably due to a small allylic strain associated with conformer (**5**).

As for ε-caprolactones, the β-side of the oxonium intermediate (**7a** and **7b**) is blocked by the axial hydrogens H_a and H_b, located at the 4- and 6-position, respectively, like the endo side of norbornylene (Fig. 1).[14] Therefore, the silyl nucleophile attacks from the α-side to results in the formation of cis isomers starting from 2- and 6-methyl-ε-caprolactones (**1j** and **1k**) (Entries 17 and 18). In the cases of γ-butyrolactones, the elimination of *t*-butyldimethylsilanol from silylated cyclic hemiacetal took place readily to give ethyl (tetrahydro-2-furylidene)acetates. Accordingly, we suppose that the silyl nucleophile attacks the intermediate, α,β-unsaturated esters (**8** and **9**) derived respectively from 2- and 4-methyl-γ-butyrolactones (**1b** and **1c**) (Fig. 2).[15] In the former case (Entry 2), the trans isomer was obtained in preference to the cis



8 **9**

Fig. 2.



Scheme 2.

Table 2. Preparation of Cyclic Ethers from Lactones

Entry	1[a]	R_3SiNu	Yield/% (cis/trans)[b]	
			Method A[c]	Method B[d]
1	**1a**	Et_3SiH	75	72
2	**1b**	Et_3SiH	71 (36:64)	56 (31:69)
3	**1c**	Et_3SiH	59 (53:47)	39 (48:52)
4	**1d**	Et_3SiH	91[g]	95[e]
5	**1d**	CH_2=$CHCH_2SiMe_3$	87[e]	84[e]
6	**1d**	Me_3SiCN	83[e,g]	66
7	**1d**	$Me_3SiSCH_2C_6H_5$	51	46
8	**1e**	Et_3SiH	84 (12:88)	83 (10:90)[e]
9	**1e**	CH_2=$CHCH_2SiMe_3$	40 (17:83)	45 (26:74)
10	**1f**	Et_3SiH	82 (>99:1)	89 (>99:1)[e]
11	**1g**	Et_3SiH	87 (7:93)	82 (4:96)[e]
12	**1h**	Et_3SiH	82 (>99:1)	79 (>99:1)[e]
13	**1h**	CH_2=$CHCH_2SiMe_3$	86 (>99:1)	76 (>99:1)
14	**1i**	Et_3SiH	87	90
15	**1i**	CH_2=$CHCH_2SiMe_3$	45[f]	67[f]
16	**1i**	Me_3SiCN	70[e,g]	62[f]
17	**1j**	Et_3SiH	91 (>99:1)	86 (>99:1)
18	**1k**	Et_3SiH	85 (>99:1)	81 (>99:1)

a) **1a**=γ-butyrolactone; **1b**=2-methyl-γ-butyrolactone; **1c**=γ-valerolactone; **1d**=δ-valerolactone; **1e**=2-methyl-δ-valerolactone; **1f**=3-methyl-δ-valerolactone; **1g**=4-methyl-δ-valerolactone; **1h**=5-methyl-δ-valerolactone; **1i**=ε-caprolactone; **1j**=2-methyl-ε-caprolactone; **1k**=6-methyl-ε-caprolactone. b) The stereochemistry was determined by 400-MHz ^1H NMR. c) $TrSbCl_6$ was used as a catalyst. d) $SbCl_5$ combined with Me_3SiCl (10 mol%) and SnI_2 (10 mol%) was used as a catalyst. e) 5 mol% of $TrSbCl_6$ or $SbCl_5$ was used. f) 30 mol% of $TrSbCl_6$ or $SbCl_5$ was used. g) At the second step, the reaction was performed at −78 °C: In all other cases, 10 mol% of $TrSbCl_6$ or $SbCl_5$ was used and at the second step, the reaction was performed in the temperature range at −23 °C—r.t.

isomer due to the 1,3-diaxial interaction because H_b is closer to C^1 than H_a in **8**. In the latter case (Entry 3), the nucleophile would attack from both α- and β-sides because there is little difference in the distances C^1–H_a and C^1–H_b in **9**.

Except for ethyl (*cis*-3-methyl-2-oxepanyl)acetate (**3j**), the configuration of cyclic ethers was determined by the NOE analysis (400-MHz ^1H NMR spectrum) and/or by the spin–spin coupling constants for the ring protons. The stereochemistry of **3j** was determined by X-ray analysis for *N*-(1-naphthyl)carbamate (**11**) of *cis*-2-(2-hydroxyethyl)-3-methyloxepane (**10**), derived from **3j** by reduction with lithium aluminum hydride (Fig. 3).

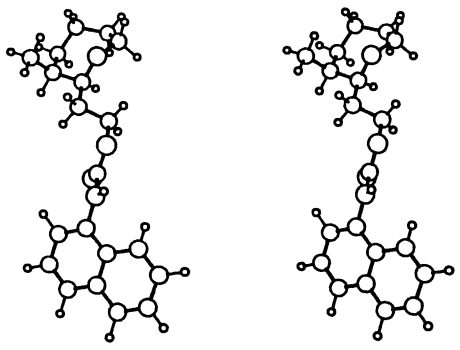
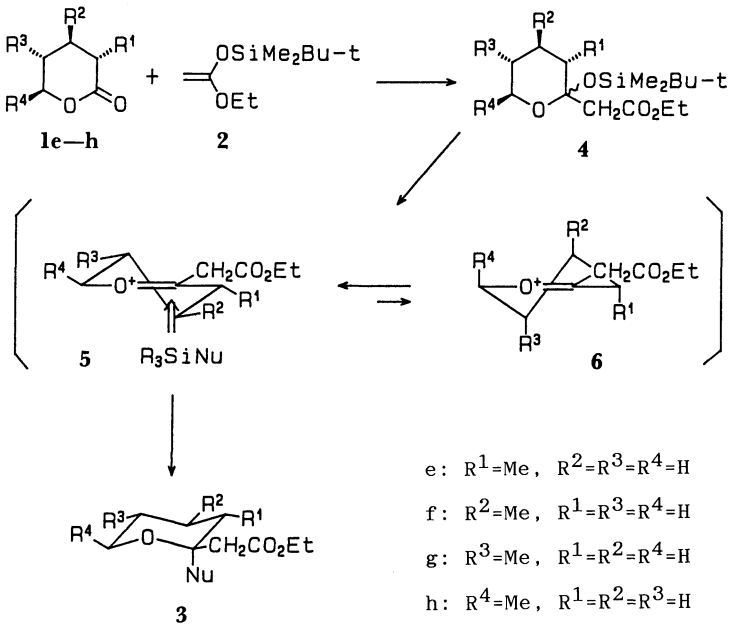
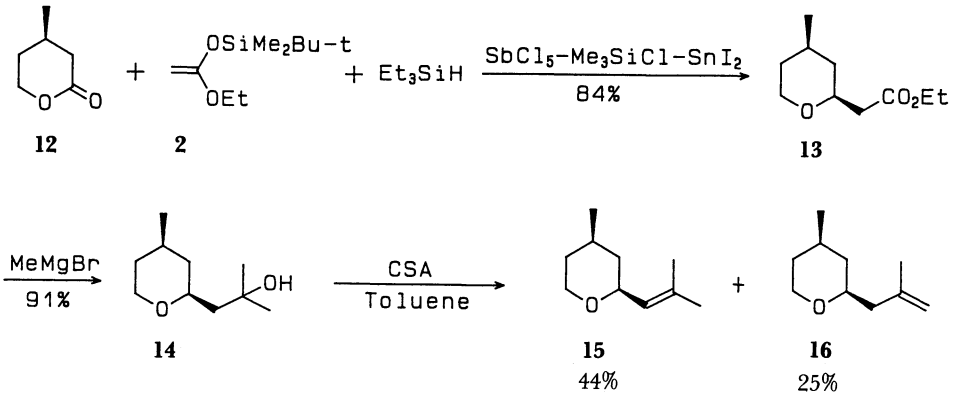


Fig. 3. Stereoview of **11**.



Scheme 3.

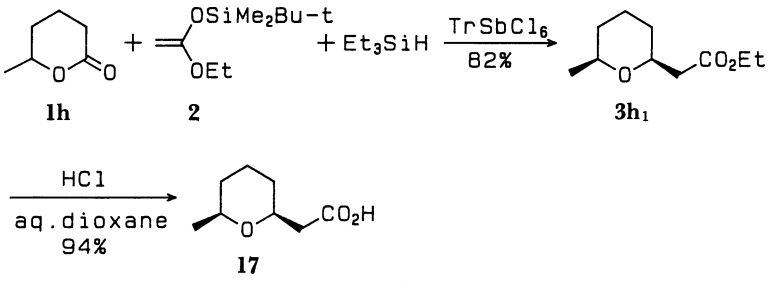


Scheme 4.

Synthesis of (−)-*cis*-Rose Oxide (15). (*R*)-3-Methyl-δ-valerolactone (98%ee) (**12**), prepared according to the method of R. Rossi et al.,[16] reacted with **2** and Et_3SiH in the presence of a catalyst system of $SbCl_5$, Me_3SiCl, and SnI_2 to afford ethyl (2*S*,4*R*)-(4-methyltetrahydro-2-pyranyl)acetate (cis/trans>99:1) (**13**) in 84% yield. The reaction of the ester (**13**) with methylmagnesium bromide afforded the tertiary alcohol (cis/trans>99:1) (**14**) in 91% yield, which in turn underwent acid-catalyzed dehydration (*dl*-10-camphorsulfonic acid (CSA)/toluene, reflux) to afford (−)-*cis*-rose oxide (cis/trans=93:7) (**15**), $[\alpha]_D^{20}$ −68.3° (*c* 3.0, $CHCl_3$) (lit,[17] $[\alpha]_D$ −58.1°), in 44% yield, along with (2*S*,4*R*)-4-methyl-2-(2-methylallyl)-tetrahydropyran (cis/trans >99:1) (**16**), $[\alpha]_D^{20}$ −7.9° (*c*, 3.0, $CHCl_3$), in 25% yield (Scheme 4).

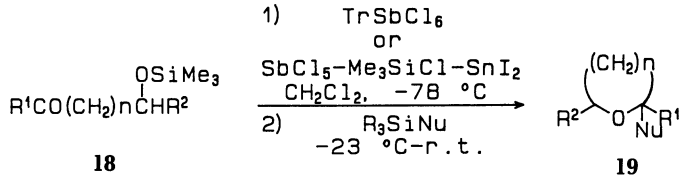
Synthesis of (*cis*-6-Methyltetrahydro-2-pyranyl)acetic Acid (17). Ethyl (*cis*-6-methyltetrahydro-2-pyranyl)-acetate (**3h**$_1$), prepared in 82% yield by the reaction of 5-methyl-δ-valerolactone (**1h**) with **2** and Et_3SiH in the presence of a catalytic amount of $TrSbCl_6$, was hydrolyzed under acidic conditions to give (*cis*-6-methyltetrahydro-2-pyranyl)acetic acid (**17**), mp 51—53 °C (lit.[18] 52—53 °C), in 94% yield (Scheme 5).

Preparation of Cyclic Ethers from Siloxy Carbonyl Compounds. In the presence of a catalytic amount of $TrSbCl_6$ or a catalyst system of $SbCl_5$, Me_3SiCl, and SnI_2, five—seven membered cyclic ethers were prepared according to the following two step procedure, that is, cyclization of γ-, δ-, and ε-siloxy carbonyl compounds, followed by the nucleophilic substitution of initially formed silylated cyclic hemiacetals with silyl nucleophiles (Table 3).[19] The results show that the combined use of $SbCl_5$, Me_3SiCl, and SnI_2 is superior to that of $TrSbCl_6$ in terms of yield in every case, and that in the case of preparation of tetrahydropyrans, an



1h 2 3h1 17

Scheme 5.



18 19

Scheme 6.

Table 3. Preparation of Cyclic Ethers from Siloxy Carbonyl Compound

Entry	18	n	R^1	R^2	R_3SiNu	Yield/%	
						Method A[a]	Method B[b]
1	**18a**	2	Ph	H	Et_3SiH	89	91
2	**18b**	3	Ph	H	Et_3SiH	90	95
3	**18c**	3	Ph	Me	Et_3SiH	92 (cis)[c]	96 (cis)[c]
4	**18d**	3	H	Ph	Et_3SiH	76	90
5	**18d**	3	H	Ph	CH_2=$CHCH_2SiMe_3$	75 (trans)[c]	83 (trans)[c]
6	**18d**	3	H	Ph	Me_3SiCN	19 (trans)	53 (trans)
						11 (cis)	28 (cis)
7	**18e**	4	Ph	H	Et_3SiH	68	77
8	**18f**	4	$PhCH_2$	H	Et_3SiH	80	95

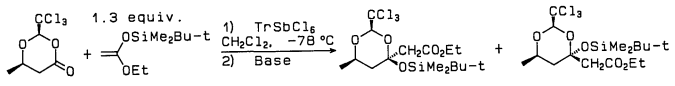
a) $TrSbCl_6$ (10 mol%) was used as a catalyst. b) $SbCl_5$ (10 mol%) combined with Me_3SiCl (10 mol%) and SnI_2 (10 mol%) was used as a catalyst. c) No stereoisomer was detected by either ^1H or ^{13}C NMR.

axial attack of nucleophiles to the oxonium intermediate is preferred to an equatorial attack (Entries 3, 5, and 6) due to torsional strain. It is worthwhile to note that there is a marked tendency toward an axial attack when Et_3SiH or allyltrimethylsilane was used as a silyl nucleophile (Entries 3 and 5).

The configuration of *cis*-2-methyl-6-phenyltetrahydropyran (**19c**) and *trans*-2-allyl-6-phenyltetrahydropyran (**19d$_2$**) were assigned by the NOE analysis (400-MHz NMR spectrum) for the ring methine protons. The stereochemistry for *trans*- and *cis*-2-cyano-6-phenyltetrahydropyran (**19d$_{3a}$** and **19d$_{3b}$**) was determined by the spin–spin coupling constants for the ring methine protons in the 400-MHz ^1H NMR spectrum.

Preparation of *syn*-1,3-Diols. In the presence of a catalytic amount of $TrSbCl_6$, 6-*cis*-substituted 2-trichloromethyl-1,3-dioxan-4-ones (**20**), easily prepared from β-hydroxy carboxylic acids,[4] are stereoselectively attacked by **2** to afford 1,3-dioxane-4-acetic acid derivatives (**21** and **22**). First, we examined the effect of the amount of $TrSbCl_6$ and the kind of bases used for quenching (Table 4). It was found there that the amount of catalyst employed had a significant effect on the stereochemical outcome of the reaction. When 5 mol% of $TrSbCl_6$ was employed, the 2,4-*cis* isomer (**21a**) was obtained exclusively. The 2,4-*cis* isomer (**21a**)/2,4-*trans* isomer (**22a**) ratio decreases with an increase in the amount of $TrSbCl_6$, and **22a** became predominant with 20 mol% of $TrSbCl_6$. The base used for quenching had only a marginal effect on the diastereomer ratio. Pyridine and cesium fluoride gave the highest stereoselectivity when 5 mol% of $TrSbCl_6$ is used as the catalyst.

Next, the stereoselectivity of the addition of **2** to several 2-trichloromethyl-1,3-dioxan-4-ones (**20a—e**) was examined (Table 5). 2,4-*cis* Isomers (**21c—e**) are preferentially produced in the cases of 5,5-disubstituted 1,3-dioxan-4-ones (**20c—e**) irrespective of the amount of $TrSbCl_6$ (Entries 5—10). While, in the cases of 5-unsubstituted 1,3-dioxan-4-ones (**20a** and **20b**), the stereoselectivity is dependent on the amount of $TrSbCl_6$: 2,4-*trans* isomer (**22a** and **22b**) are mainly



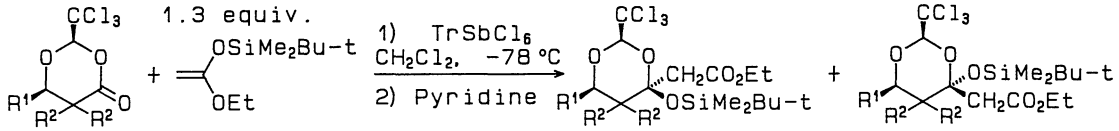
20a **2** **21a** **22a**

Scheme 7.

Table 4. The Effect of the Amount of $TrSbCl_6$ and the Bases for Quenching

Entry	$TrSbCl_6$ mol%	Base	Yield/% 21a	22a
1	20	Pyridine	7.1	80
2	10	Pyridine	19	71
3	5	Pyridine	93	—
4	5	CsF	92	—
5	5	Aqueous $NaHCO_3$	88	4.7
6	5	Phosphate buffer (pH=7.0)	84	5.1

produced in the presence of 20 mol% of $TrSbCl_6$ (Entries 1 and 3) and 2,4-*cis* isomers (**21a** and **21b**) are exclusively produced by using 5 mol% of $TrSbCl_6$ (Entries 2 and 4). When *c*-6-*t*-butyl-6-methyl-*r*-2-trichloromethyl-1,3-dioxan-4-one (**20f**) is used, the addition of **2** does not proceed under the same conditions (Scheme 9). Therefore, we assumed that the nucleophile (**2**) attacks from the axial side due to torsional strain to afford the adduct anion (**23**) (Scheme 10). When 5 mol% of $TrSbCl_6$ is used, **23** is trapped very rapidly with *t*-butyldimethylsilyl cation. On the other hand, when more than 10 mol% of $TrSbCl_6$ is used, the oxo anion of **23** is blocked by triphenylmethyl cations, and thereby under these reaction conditions, the adduct anions (**23** and **25**) are in equilibrium via keto anion (**24**) similar to the tautomeric equilibrium between lactol and hydroxy ketone.[20] As the adduct anion (**25**) may be thermodynamically more stable than the other anion (**23**) in the cases of 5-unsubstituted 1,3-dioxan-4-ones, 2,4-*trans* isomers are mainly produced. On the other hand, in the cases of 5,5-disubstituted 1,3-dioxan-4-ones, **23** is more stable than **25** probably due to steric repulsion between the geminal methyl groups at 5-position and the acetate group at 4-position leading to the preferential formation of the 2,4-*cis* isomers. The thermodynamical stability was suggested by heats of formation of ethyl 4-hydroxy-6-methyl-2-trichloromethyl-1,3-dioxane-4-acetates, which were determined by molecular mechanics calculations.

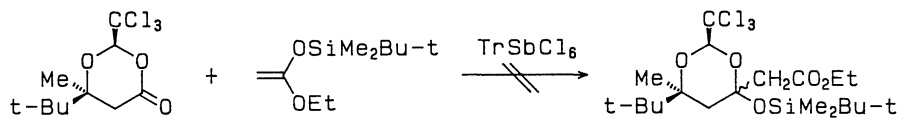


20 **2** **21** **22**

Scheme 8.

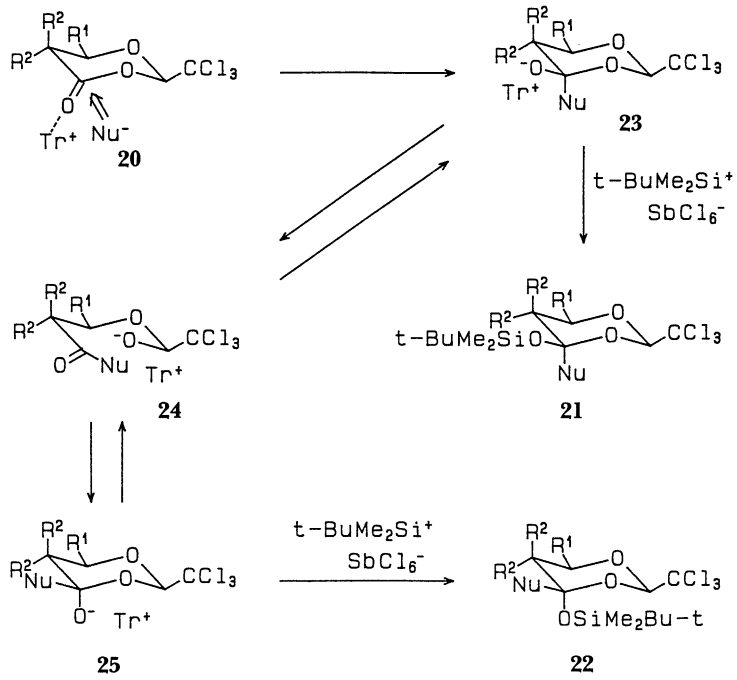
Table 5. The Reaction of 2-Trichloromethyl-1,3-dioxan-4-ones and 1-(*t*-Butyldimethylsiloxy)-1-ethoxyethene

Entry	20	R^1	R^2	$TrSbCl_6$ mol %	Yield/% 21	22
1	**20a**	Me	H	20	7.1	80
2	**20a**	Me	H	5	93	—
3	**20b**	Ph	H	20	6.6	77
4	**20b**	Ph	H	5	91	—
5	**20c**	*n*-C_7H_{15}	Me	20	98	—
6	**20c**	*n*-C_7H_{15}	Me	5	100	—
7	**20d**	Ph	Me	20	92	0.8
8	**20d**	Ph	Me	5	96	—
9	**20e**	$PhCH_2CH_2$	Me	20	93	—
10	**20e**	$PhCH_2CH_2$	Me	5	99	—

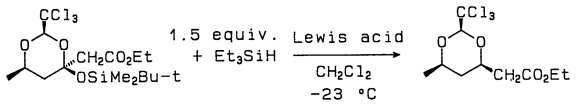


20f **2** **21f** and/or **22f**

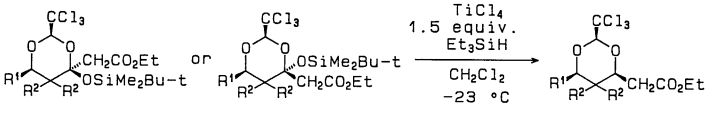
Scheme 9.



Scheme 10.



Scheme 11.



Scheme 12.

Table 6. Effect of Lewis Acids

Entry	Lewis acid (equiv)	Yield/% (2,4-cis/trans)[a]
1	$TiCl_4$ (1.1)	62 (98:2)
2	$TiCl_4$ (3.0)	91 (98:2)
3	$SnCl_4$ (3.0)	54 (97:3)
4	$AlCl_3$ (3.0)	16 (96:4)
5	$SbCl_5$ (3.0)	4 (97:3)
6	$BF_3 \cdot Et_2O$ (3.0)	1 (91:9)

a) The selectivity was determined by 400-MHz ^1H NMR.

Table 7. Reduction of Siloxy Group

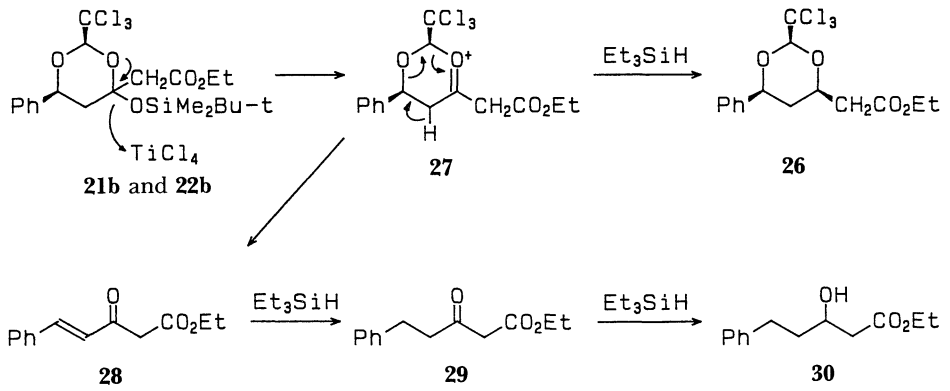
Entry	21 or 22	R^1	R^2	Yield/% (2,4-cis/trans)[a]
1	**22a**	Me	H	92 (>99:1)
2	**21a**	Me	H	91 (98:2)
3	**22b**	Ph	H	67 (97:3)
4	**21b**	Ph	H	65 (98:2)
5	**21c**	n-C_7H_{15}	Me	94 (>99:1)
6	**21d**	Ph	Me	97 (>99:1)
7	**21e**	$PhCH_2CH_2$	Me	98 (>99:1)

a) The selectivity was determined by 400-MHz ^1H NMR.

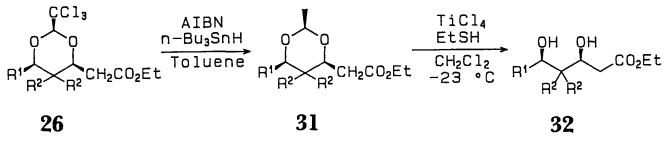
Several Lewis acids were screened for the reduction of the siloxyl group of **21a**, because a catalytic amount of $TrSbCl_6$ does not promote the reduction (Table 6.). The results show that $TiCl_4$ was superior to the other Lewis acids in terms of yield and selectivity. Adducts **21** and **22** were reduced with Et_3SiH by use of $TiCl_4$ as a promoter to afford *c*-6-substituted *r*-2-trichloromethyl-1,3-dioxane-*c*-4-acetates (**26**) stereoselectively (Table 7). The selectivity follows a similar tendency to that of cyclic ethers derived from lactones or siloxy carbonyl compounds, suggesting that the reaction proceeds via oxonium intermediates. When **21b** was reduced using 5 equivalents of Et_3SiH, ethyl *c*-6-phenyl-*r*-2-trichloromethyl-1,3-dioxane-*c*-4-acetate (**26b**) was obtained in 71% yield along with ethyl 3-hydroxy-5-phenylvalerate (**30**) in 23% yield. Therefore, in the cases of **21b** and **22b**, the competitive pathway, the elimination of chloral from **27** to form conjugated olefin (**28**) was accelated by phenyl group at 6-position due to stabilizing **28** (Scheme 13).

Trichloromethyl group of **26** was reduced in good yields according to the method of B. Giese et al.[21] (Table 8).

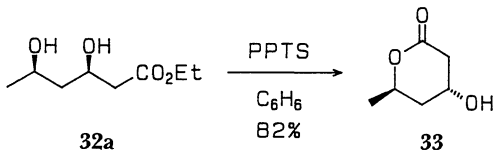
Conventional methods for cleavage of the acetaldehyde acetals (**31**) by acid-catalyzed hydrolysis (e.g., 50% H_2SO_4,[21] HCl-aq EtOH,[22] 80% AcOH[23] did not



Scheme 13.



Scheme 14.



Scheme 15.

Table 8. Preparation of *syn*-1,3-Diols

Entry	26	R^1	R^2	Yield/%[a]	
				31	32
1	**26a**	Me	H	70	87
2	**26b**[b]	Ph	H	79[c]	95
3	**26c**	n-C_7H_{15}	Me	94	90
4	**26d**	Ph	Me	95	97
5	**26e**	$PhCH_2CH_2$	Me	95	90

a) No stereoisomer was detected by ^1H NMR in all cases.
b) The ratio of 2,4-*cis* isomer/2,4-*trans* isomer is 97:3.
c) The other isomer could not be purified.

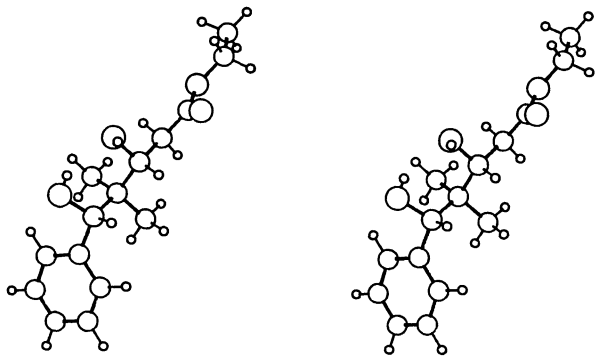


Fig. 4. Stereoview of **32d**

give successful results, due to the unstability of 1,3-diols (**32**) under the reaction conditions. The cleavage of **31** with Me_2BBr was also unsuccessful.[24] Desired 1,3-diols (**32**) were obtained in satisfactory yields by treatment of **31** with $AlCl_3$–EtSH system,[25] and then the yields were further improved by substituting $TiCl_4$ for $AlCl_3$ (Table 8).

It was verified by the following two experiments that no epimerization occurred under these reaction conditions. (1) The ^1H NMR spectra of 3-hydroxy-5-methyl-δ-valerolactone (**33**) which was derived from ethyl *syn*-3,5-dihydroxyhexanoate (**32a**) by use of pyridinium *p*-toluenesulfonate showed 3,5-*trans* relationship, that is, the coupling constants between axial proton at 4-position and vicinal protons showed axial–axial (11.3 Hz) and axial–equatorial (3.2 Hz) relationship (Scheme 15). (2) The X-ray crystallographic analysis of ethyl 3,5-dihydroxy-4,4-dimethyl-5-phenylvalerate (**32d**) showed 3,5-*syn* relationship (Fig. 4).

Thus, it is concluded that, in the presence of a catalytic amount of $TrSbCl_6$ or a catalyst system of $SbCl_5$, Me_3SiCl, and SnI_2, α-substituted cyclic ethers are stereoselectively prepared in good yields by the following two procedures: (1) The addition of **2** to lactones, followed by nucleophilic substitution of initially formed silylated cyclic hemiacetals with silyl nucleophiles by one-pot procedure. (2) The cyclization of γ-, δ- and ε-trimethylsiloxy carbonyl compounds, followed by nucleophilic substitution of initially formed silylated cyclic hemiacetals with silyl nucleophiles by one-pot procedure. Furthermore, a convenient method for the preparation of *syn*-1,3-diols from lactone analogue, 6-*cis*-substituted 2-trichloromethyl-1,3-dioxan-4-ones, was established.

Experimental

General Procedures. All the melting points were uncorrected. Infrared spectra were taken with a Hitachi IR-215

or an Analect FX-6200 FT-IR spectrophotometer. NMR spectra were recorded with a Hitachi R-90H, a JEOL JNM-FX-200 or a JEOL JNM-GSX-400 spectrometer. Chemical sifts are given as δ values from tetramethylsilane as an internal standard. The following abbreviations are used; s=singlet, bs=broad singlet, d=doublet, t=triplet, q=quartet, quint=quintet, dd=double doublet, dt=double triplet, dq=double quartet, dh=double heptet, tt=triple triplet, ddd=double double doublet, ddt=double double triplet, ddq=double double quartet, dddd=double double double doublet, dddt=double double double triplet, and dddq=double double double quartet. Mass spectra (EI) were recorded with a Finnigan Mat INCOS 50 or a JEOL JMS-HX 100 mass spectrometer. Microanalyses were performed on a Perkin-Elmer 2400 C, H, N, analyzer, a Yokogawa IC-100 ion chromatographic analyzer and a Hitachi Z-8000 atomic absorption spectrophotometer. Optical rotations were measured on a Union PM-201 polarimeter. Preparative thin layer chromatography was carried out on Kieselgel 60 F_{254} (Merck). Silica Gel 60 K-230 (230—400 mesh) (Katayama) were used for flash column chromatography.

Materials. $TrSbCl_6$,[26] $TrSbF_6$,[27] $TrClO_4$[28] and 1-(*t*-butyldimethylsiloxy)-1-ethoxyethene (**2**)[29] were prepared by the previously reported method. γ-Butyrolactone (**1a**), γ-valerolactone (**1c**), δ-valerolactone (**1d**) and ε-caprolactone (**1i**) were commercially available and were purified by distillation. 2-Methyl-γ-butyrolactone (**1b**),[30] 2-methyl-δ-valerolactone (**1e**),[30] (*R*)-3-methyl-δ-valerolactone ($[\alpha]_D^{27}$ +26.93° (*c* 5.7 $CHCl_3$); 98% ee.) (**12**),[16] 4-methyl-δ-valerolactone (**1g**),[31] 5-methyl-δ-valerolactone (**1h**),[31] and 2-methyl-ε-caprolactone (**1j**)[30] were synthesized by the previously reported method. 3-Methyl-δ-valerolactone (**1f**) was prepared by oxidative lactonization of 3-methylpentane-1,5-diol with $NaBrO_2$.[32] 6-Methyl-ε-caprolactone (**1k**) was prepared by the Baeyer-Villiger oxidation of 2-methylcyclohexanone with *m*-chloroperbenzoic acid. 4-Trimethylsiloxybutyrophenone (**18a**) was prepared from 4-oxo-4-phenylbutyric acid by (i) reduction with $LiAlH_4$, (ii) oxidation with MnO_2, and (iii) trimethylsilylation with hexamethyldisilazane. 5-Trimethylsiloxyvalerophenone (**18b**) was also prepared from 5-oxo-5-phenylvaleric acid by the above method. 5-Trimethylsiloxyhexanophenone (**18c**) was prepared by Grignard reaction of 5-trimethylsiloxyhexanenitrile with phenylmagnesium bromide. 5-Trimethylsiloxy-5-phenylpentanal (**18d**) was prepared by reduction of methyl 5-trimethylsiloxy-5-phenylvalerate with diisobutylaluminum hydride. 6-Trimethylsiloxyhexanophenone (**18e**) was prepared from 2-phenyl-1,3-dithiane by (i) alkylation with 5-(tetrahydro-2-pyranyloxy)pentyl bromide, (ii) deprotection of 1,3-dithiane and tetrahydropyranyl moieties, and (iii) trimethylsilylation. 1-Phenyl-7-trimethylsiloxy-2-heptanone (**18f**) was prepared from 1,3-dithiane by the similar manner. 3-Hydroxybutyric acid was commercial available and was used without further purification. Other β-hydroxy carboxylic acids were prepared by (i) the aldol condensation of carbonyl compounds with silyl ketene acetal using $TrSbCl_6$ as a catalyst and (ii) hydrolysis.

Preparation of Cyclic Ethers from Lactones (Method A). A typical procedure is described for ethyl (2-allyltetrahydro-2-pyranyl)acetate (**3d$_2$**) from δ-valerolactone (**1d**) using $TrSbCl_6$ as a catalyst: Under an argon atmosphere, $TrSbCl_6$ (28 mg, 0.05 mmol) was added to a solution of δ-valerolactone (101 mg, 1.0 mmol), 1-(*t*-butyldimethylsiloxy)-1-ethoxyethene (226 mg, 1.1 mmol) and allyltrimethylsilane (169 mg, 1.5 mmol) in CH_2Cl_2 (4.5 ml) at −78 °C, and then the reaction mixture was stirred for 30 min at the same temperature and for 4.5 h at −23 °C. After being warmed gradually to room temperature, the reaction was quenched with aqueous saturated $NaHCO_3$. The organic materials were washed with brine, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by preparative thin layer chromatography on silica gel (8:1 hexane–ethyl acetate as a developing solvent) to give **3d$_2$** (186 mg, 87%). IR (neat) 1735(C=O) and 1640 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=1.26 (3H, t, *J*=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 1.4—1.75 (6H, m), 2.39 (1H, ddt, *J*=14, 7 and 1 Hz, $C\underline{H}_2CH{=}CH_2$), 2.51 (1H, d, *J*=13.7 Hz, $C\underline{H}_2CO_2Et$), 2.57 (1H, dd, *J*=14 and 7 Hz, $C\underline{H}_2CH{=}CH_2$), 2.63 (1H, d, *J*=13.7 Hz, $C\underline{H}_2CO_2Et$), 3.71 (2H, t, *J*=5 Hz, 6-H), 4.14 (2H, q, *J*=7.1 Hz, $CO_2C\underline{H}_2CH_3$), 5.05—5.2 (2H, m, $C\underline{H}_2{=}CHCH_2$), and 5.7—5.95 (1H, m, $CH_2{=}C\underline{H}CH_2$); MS, *m/z* (rel intensity) 171(M^+–C_3H_5; base peak), 125 (66), 97 (83), 83 (17), 69 (32), 55 (44), and 41 (71).

Preparation of Cyclic Ethers from Lactones (Method B). A typical procedure is described for ethyl (tetrahydro-2-pyranyl)acetate (**3d$_1$**) from δ-valerolactone (**1d**) using a catalyst system of $SbCl_5$, Me_3SiCl, and SnI_2: Under an argon atmosphere, a 0.2 molar solution of Me_3SiCl in CH_2Cl_2 (0.5 ml, 0.1 mmol) and SnI_2 (38 mg, 0.1 mmol) were added to a solution of δ-valerolactone (100 mg, 1.0 mmol), 1-(*t*-butyldimethylsiloxy)-1-ethyoxyethene (222 mg, 1.1 mmol) and Et_3SiH (174 mg, 1.5 mmol) in CH_2Cl_2 (4.5 ml) at −78 °C. To the reaction mixture was added dropwise a 0.5 molar solution of $SbCl_5$ in CH_2Cl_2 (0.1 ml, 0.05 mmol) at the same temeprature. After stirring for 30 min at −78 °C and for 4 h at −23 °C, the reaction mixture was gradually warmed to room temperature. The reaction was quenched with aqueous saturated $NaHCO_3$. The organic materials were washed with brine, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by preparative thin layer chromatography on silica gel (8:1 hexane–ethyl acetate as a developing solvent) to give **3d$_1$** (164 mg, 95%). IR (neat) 1740 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=1.26 (3H, t, *J*=7.3 Hz, $CO_2CH_2C\underline{H}_3$), 1.3—1.9 (6H, m), 2.37 (1H, dd, *J*=14.8 and 5.4 Hz, $C\underline{H}_2CO_2Et$), 2.50 (1H, dd, *J*=14.8 and 7.6 Hz, $C\underline{H}_2CO_2Et$), 3.39—3.52 (1H, m), 3.68—3.81 (1H, m), 3.9—4.0 (1H, m), and 4.15 (2H, q, *J*=7.3 Hz, $CO_2C\underline{H}_2CH_3$); MS, *m/z* (rel intensity) 173 (M^++H; 1.8), 172 (M^+; 1.5), 143 (35), 130 (78), 97 (42), 85 (base peak), 55 (50), and 41 (86).

Physical properties of other products are presented:

Ethyl (tetrahydro-2-furyl)acetate (**3a**). IR (neat) 1735 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=1.27 (3H, t, *J*=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 1.47—1.61 (1H, m), 1.83—2.17 (3H, m), 2.46 (1H, dd, *J*=15.1 and 6.3 Hz, $C\underline{H}_2CO_2Et$), 2.58 (1H, dd, *J*=15.1 and 7.3 Hz, $C\underline{H}_2CO_2Et$), 3.69—3.94 (2H, m), 4.09—4.32 (1H, m), and 4.16 (2H, t, *J*=7.1 Hz, $CO_2C\underline{H}_2CH_3$); MS, *m/z* (rel intensity) 159 (M^++H; 1.0), 158 (M^+; 0.6), 130 (33), 115 (13), 87 (16), 84 (22), 71 (base peak), 55 (21), and 43 (84).

Ethyl (3-methyltetrahydro-2-furyl)acetate (**3b**). IR (neat) 1735 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) (the cis isomer) δ=0.93 (3H, d, *J*=7.1 Hz, 3-Me), 1.27 (3H, t, *J*=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 1.5—1.65 (1H, m), 2.05—2.15 (1H, m), 2.3—2.4 (1H, m), 2.41 (1H, dd, *J*=15.2 and 5.5 Hz, $C\underline{H}_2CO_2Et$), 2.48 (1H, dd, *J*=15.2 and 8.5 Hz, $C\underline{H}_2CO_2Et$), 3.74 (1H, dt, *J*=6.5 and 8 Hz, 5-H), 3.93 (1H, dt, *J*=5.9 and 8 Hz, 5-H), 4.26 (1H, dt, *J*=8.5 and

5.5 Hz, 2-H), and 4.17 (2H, q, J=7.1 Hz, $CO_2C\underline{H}_2CH_3$) (NOE was observed between methylene of acetate group at 2-position and 3-Me but no NOE was detected between 2-H and 3-Me), (the trans isomer) δ=1.06 (3H, d, J=6.6 Hz, 3-Me), 1.27 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 1.5—1.65 (1H, m, 4-H), 1.85—1.95 (1H, m, 3-H), 2.05—2.15 (1H, m, 4-H), 2.47 (1H, dd, J=15 and 7.9 Hz, $C\underline{H}_2CO_2Et$), 2.53 (1H, dd, J=15 and 4.6 Hz, $C\underline{H}_2CO_2Et$), 3.78 (1H, dt, J=4.6 and 7.9 Hz, 2-H), 3.85 (2H, dd, J=7.9 and 6 Hz, 5-H), and 4.17 (2H, q, J=7.1 Hz, $CO_2C\underline{H}_2CH_3$) (NOE was observed between one proton of methylene of acetate group at 2-position and 3-Me and between 2-H and 3-Me); MS, m/z (rel intensity) 171 (M^+—H; 0.5), 144 (62), 129 (18), 98 (23), 85 (base peak), 71 (18), and 56(44).

Ethyl (5-methyltetrahydro-2-furyl)acetate (**3c**). IR (neat) 1740 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) (the cis isomer) δ=1.23 (3H, d, J=6 Hz, 5-Me), 1.26 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 1.43—1.52 (1H, m), 1.59—1.68 (1H, m), 1.95—2.1 (2H, m), 2.46 (1H, dd, J=15.2 and 6.7 Hz, $C\underline{H}_2CO_2Et$), 2.63 (1H, dd, J=15.2 and 6.7 Hz, $C\underline{H}_2CO_2Et$), 3.95—4.03 (1H, m, 5-H), 4.15 (2H, q, J=7.1 Hz, $CO_2C\underline{H}_2CH_3$), and 4.23 (1H, quint., J=6.7 Hz, 2-H) (NOE was observed between 2-H cand 5-H), (the trans isomer) δ=1.21 (3H, d, J=6.2 Hz, 5-Me), 1.26 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$) 1.45—1.54 (1H, m), 1.57—1.65 (1H, m), 2.0—2.1 (1H, m), 2.1—2.2 (1H, m), 2.42(1H, dd, J=15 and 6.8 Hz, $C\underline{H}_2CO_2Et$), 2.60 (1H, dd, J=15 and 6.8 Hz, $C\underline{H}_2CO_2Et$), 4.08—4.19 (1H, m, 5-H), 4.15 (2H, q, J=7.1 Hz, $CO_2C\underline{H}_2CH_3$), and 4.41 (1H, quint., J=6.8 Hz, 2-H) (no NOE between 2-H and 5-H was detected); MS, m/z (rel intensity) 171 (M^+—H; 1.0), 157 (5.3), 130 (63) and 85 (base peak).

Ethyl (2-cyanotetrahydro-2-pyranyl)acetate (**3d$_3$**). IR (neat) 1740 cm^{-1} (C=O); ^{13}C NMR ($CDCl_3$) δ=14.1 (q), 19.9 (t), 24.4 (t), 34.5 (t), 45.0 (t), 61.1 (t), 65.7 (t), 72.1 (s), 117.8 (s), and 167.5 (s); ^1H NMR ($CDCl_3$) δ=1.29 (3H, t, J=7 Hz, $CO_2CH_2C\underline{H}_3$), 1.5—1.95 (5H, m, 3-H_{ax}, 4-H and 5-H), 2.08 (1H, dt, J=13.2 and 2.5 Hz, 3-H_{eq}), 2.76 (1H, d, J=15.4 Hz, $C\underline{H}_2CO_2Et$), 2.82 (1H, d, J=15.4 Hz, $C\underline{H}_2CO_2Et$), 3.75—4.05 (2H, m, 6-H), and 4.21 (2H, q, J=7 Hz, $CO_2C\underline{H}_2CH_3$); MS, m/z (rel intensity) 197 (M^+; 3.5), 168 (24), 152 (29), 124 (26), 110 (82), 82 (36), 55 (66), and 41 (base peak).

Ethyl (2-benzylthiotetrayhydro-2-pyranyl)acetate (**3d$_4$**). IR (neat) 1730 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=1.28 (3H, t, J=7 Hz, $CO_2CH_2C\underline{H}_3$), 1.5—1.7 (3H, m),1.7—2.1 (3H, m), 2.84 (1H, d, J=13.7 Hz, $C\underline{H}_2CO_2Et$), 2.89 (1H, d, J=13.7 Hz, $C\underline{H}_2CO_2Et$), 3.62 (1H, d, J=12.3 Hz, $PhC\underline{H}_2S$), 3.6—3.8 (1H, m, 6-H), 3.81 (1H, d, J=12.3 Hz, $PhC\underline{H}_2S$), 3.9—4.1 (1H, m, 6-H), 4.17 (2H, q, J=7 Hz, $CO_2C\underline{H}_2CH_3$), and 7.1—7.35 (5H, m, Ph); MS, m/z (rel intensity) 296 (M^++H_2; 0.5), 294 (M^+; 0.3), 249 (3.7), 171 (75), 124 (46), 97 (45), 91 (base peak), and 55 (57).

Ethyl (3-methyltetrahydro-2-pyranyl)acetate (**3e$_1$**). IR (neat) 1735 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) (the trans isomer) δ=0.84 (3H, d, J=6.8 Hz, 2-Me), 1.18—1.28 (1H, m), 1.27 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 1.43 (1H, dddq, J=11.7, 9.7, 3.7 and 6.8 Hz, 3-H_{ax}), 1.49—1.56 (1H, m), 1.6—1.7 (1H, m), 1.75—1.83 (1H, m), 2.36(1H, dd, J=14.9 and 9.3 Hz, $C\underline{H}_2CO_2Et$), 2.62 (1H, dd, J=14.9 and 3.3 Hz, $C\underline{H}_2CO_2Et$), 3.35—3.42 (2H, m), 3.93—3.97 (1H, m), 4.15 (1H, dq, J=10.6 and 7.1 Hz, $CO_2C\underline{H}_2CH_3$), and 4.17 (1H, dq, J=10.6 and 7.1 Hz, $CO_2C\underline{H}_2CH_3$), (the cis isomer) δ=0.99 (3H, d, J=6.7 Hz, $CO_2CH_2C\underline{H}_3$), 2.29 (1H, dd, J=15 and 4.7 Hz, $C\underline{H}_2CO_2Et$), and 2.52 (1H, dd, J=15.9 and 9 Hz, $C\underline{H}_2CO_2Et$); MS, m/z (rel intensity) 186 (M^+; 1.2), 156 (14), 144 (35), 130 (41), 111 (25), 99 (base peak), 71 (38), and 55 (53).

Ethyl (2-allyl-3-methyltetrahydro-2-pyranyl)acetate (**3e$_2$**). IR (neat) 1730 (C=O) and 1635 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) (the trans isomer) δ=0.91 (3H, d, J=7 Hz, 3-Me), 1.26 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 1.3—1.5 (1H, m), 1.54—1.67 (3H, m), 1.99 (1H, dd, J=14.8 and 8.4 Hz, $C\underline{H}_2CH{=}CH_2$), 2.0—2.1 (1H, m), 2.47 (1H, d, J=13.6 Hz, $C\underline{H}_2CO_2Et$), 2.60 (1H, d, J=13.6 Hz, $C\underline{H}_2CO_2Et$), 2.78 (1H, ddt, J=14.8, 5.8 and 1 Hz, $C\underline{H}_2CH{=}CH_2$), 3.5—3.6 (1H, m, 6-$H_{ax}$), 3.65—3.75 (1H, m, 6-$H_{eq}$), 4.13 (1H, dq, J=10.9 and 7.1 Hz, $CO_2C\underline{H}_2CH_3$), 4.16 (1H, dq, J=10.9 and 7.1 Hz, $CO_2C\underline{H}_2CH_3$), 5.1—5.2 (2H, m, $C\underline{H}_2{=}CH$), and 5.81—5.91 (1H, m, $CH_2{=}C\underline{H}$) (upon irradiation of 6-H_{ax}, 4.0% NOE was observed on one proton of methylene of allyl group, whereas upon irradiation of 3-Me, 7.2% and 4.5% NOE were observed on the other of methylene of allyl group and one proton of methylene of acetate group respectively), (the cis isomer) δ=0.80 (3H, d, J=6.9 Hz, 3-Me), 1.26 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 2.19 (1H, d, J=13.6 Hz, $C\underline{H}_2CO_2Et$), 2.41 (1H, dd, J=14.8 and 8.7 Hz, $C\underline{H}_2CH{=}CH_2$), 2.71 (1H, ddt, J=14.8, 5.5 and 1 Hz, $C\underline{H}_2CH{=}CH_2$), and 2.92 (1H, d, J=13.6 Hz, $C\underline{H}_2CO_2Et$); MS, m/z (rel intensity) 226 (M^+; 0.1), 185 (63), 139 (30), 111 (base peak), 97 (24), 69 (40), 55 (22), and 41 (42).

Ethyl (*cis*-4-methyltetrahydro-2-pyranyl)acetate (**3f**). IR (neat) 1735 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.9—1.0 (1H, m, 3-H_{ax}), 0.94 (3H, d, J=6.3 Hz, 4-Me), 1.14—1.28 (1H, m, 5-H_{ax}), 1.26 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 1.49—1.55 (1H, m, 5-H_{eq}), 1.57—1.7 (1H, m, 4-H_{ax}), 1.62—1.7 (1H, m, 3-H_{eq}), 2.38 (1H, dd, J=15 and 5.3 Hz, $C\underline{H}_2CO_2Et$), 2.51 (1H, dd, J=15 and 7.8 Hz, $C\underline{H}_2CO_2Et$), 3.44 (1H, ddd, J=12.5, 11.4, and 2.3 Hz, 6-H_{ax}), 3.73 (1H, dddd, J=11.3, 7.8, 5.3, and 1.9 Hz, 2-H_{ax}), 3.97 (1H, ddd, J=11.4, 4.6, and 1.5 Hz, 6-H_{eq}) and 4.15 (2H, q, J=7.1 Hz, $CO_2C\underline{H}_2CH_3$) (upon irradiation of 6-H_{ax}, 6.1% and 4.5% NOE were observed on 2-H_{ax} and 4-H_{ax} respectively); MS, m/z (rel intensity) 187 (M^++H; 0.7), 185 (M^+—H; 0.7), 171 (0.9), 157 (27), 143 (13), 130 (77), 111 (40), 99 (base peak) 69 (38), and 55 (52).

Ethyl (*trans*-5-methyltetrahydro-2-pyranyl)acetate (**3g**). IR (neat) 1735 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.78 (3H, d, J=6.7 Hz, 5-Me), 1.1—1.2 (1H, m), 1.26 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 1.3—1.4 (1H, m), 1.6—1.7 (2H, m), 1.8—1.9 (1H, m), 2.39 (1H, dd, J=15.1 and 5.3 Hz, $C\underline{H}_2CO_2Et$), 2.51 (1H, dd, J=15.1 and 7.8 Hz, $C\underline{H}_2CO_2Et$), 3.02 (1H, t, J=11.2 Hz, 6-H_{ax}), 3.67 (1H, dddd, J=11, 7.8, 5.3, and 2.2 Hz, 2-H), 3.85 (1H, ddd, J=11.2, 4.4, and 2.3 Hz, 6-H_{eq}) and 4.15 (2H, q, J=7.1 Hz, $CO_2C\underline{H}_2CH_3$) (upon irradiation of 6-H_{ax}, 7.2% and 3.3% NOE were observed on 2-H_{ax} and 5-Me_{eq} respectively); MS, m/z (rel intensity) 186 (M^+; 0.4) 157 (16), 143 (28), 130 (80), 112 (31), 99 (base peak), 81 (61), 55 (64), and 43 (45).

Ethyl (*cis*-6-methyltetrahydro-2-pyranyl)acetate (**3h$_1$**). IR (neat) 1730 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=1.12—1.27 (2H, m), 1.15 (3H, d, J=6.2 Hz, 6-Me), 1.26 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 1.47—1.66 (3H, m), 1.78—1.85 (1H, m), 2.37 (1H, dd, J=14.9 and 6 Hz, $C\underline{H}_2CO_2Et$), 2.54 (1H, dd, J=14.9 and 7.4 Hz, $C\underline{H}_2CO_2Et$), 3.47 (1H, ddq, J=11, 2, and 6.2 Hz, 6-H), 3.77 (1H, dddd, J=11.1, 7.4, 6, and 2 Hz, 2-H), and 4.15 (2H, q, J=7.1 Hz, $CO_2C\underline{H}_2CH_3$) (upon irradiation of 6-H_{ax}, 8.5% NOE was observed on 2-H_{ax}); MS, m/z (rel intensity) 186(M^+; 2.4), 171 (2.1), 157 (4.8), 143 (44), 130 (base peak), 99 (92), 81 (51), 71 (45), 55 (75), and 42 (83).

Ethyl (2-allyl-*c*-6-methyltetrahydro-*r*-2-pyranyl)acetate (**3h$_2$**). IR (neat) 1725 cm^{-1} (C=O) and 1635 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ=1.09 (3H, d, J=6.2 Hz, 6-Me), 1.1—1.2 (1H, m), 1.25 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 1.52—1.7 (5H, m), 2.33(1H, dd, J=14.5 and 8.3 Hz, $C\underline{H}_2CH=CH_2$), 2.40 (1H, dd, J=13.8 and 1 Hz, $C\underline{H}_2CO_2Et$), 2.51 (1H, d, J=13.8 Hz, $C\underline{H}_2CO_2Et$), 2.75 (1H, ddq, J=14.5, 5.3, and 1 Hz, $C\underline{H}_2CH=CH_2$), 3.67—3.72 (1H, m, 6-H), 4.12 (2H, q, J=7.1 Hz, $CO_2C\underline{H}_2CH_3$), 5.1—5.14 (2H, m, $C\underline{H}_2=CH$), and 5.74—5.85 (1H, m, $CH_2=C\underline{H}$) (upon irradiation of one proton of methylene of allkyl group, 7.2% NOE was observed on 6-H_{ax}); MS, *m/z* (rel intensity) 227 (M^++H; 0.2), 185 (91), 143 (18), 139 (54), 115 (36), 111 (22), 97 (base peak), 69 (86), 55 (47), and 41 (55).

Ethyl (2-oxepanyl)acetate (**3i$_1$**). IR (neat) 1740 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.26 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 1.4—1.9 (8H, m, 3-, 4-, 5-, and 6-H), 2.36 (1H, dd, J=15 and 5.1 Hz, $C\underline{H}_2CO_2Et$), 2.51 (1H, dd, J=15 and 8.8 Hz, $C\underline{H}_2CO_2Et$), 3.5—3.63 (1H, m), 3.77—4.03 (2H, m), and 4.15 (2H, q, J=7.1 Hz, $CO_2C\underline{H}_2CH_3$); MS, *m/z* (rel intensity) 187 (M^++H; 0.6), 143 (58), 130 (52), 99 (79), 81 (48), 71 (49), 55 (base peak), and 42 (95).

Ethyl (2-allyl-2-oxepanyl)acetate (**3i$_2$**). IR (neat) 1735 (C=O) and 1640 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ=1.26 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 1.4—1.9 (8H, m, 3-, 4-, 5-, and 6-H), 2.34 (1H, dd, J=13.8 and 8 Hz, $C\underline{H}_2CH=CH_2$), 2.44 (1H, d, J=14.2 Hz, $C\underline{H}_2CO_2Et$), 2.45 (1H, dd, J=13.8 and 6.8 Hz, $C\underline{H}_2CH=CH_2$), 2.49 (1H, d, J=14.2 Hz, $C\underline{H}_2CO_2Et$), 3.57—3.62 (2H, m, 7-H), 4.12 (2H, q, J=7.1 Hz, $CO_2C\underline{H}_2CH_3$), 5.0—5.16 (2H, m, $C\underline{H}_2=CH$), and 5.77—5.98 (1H, m, $CH_2=C\underline{H}$); MS, *m/z* (rel intensity) 185 (M^+–C_3H_5; base peak), 139 (46), 115 (28), 111 (32), 97 (61), 69 (79), 55 (46), and 41 (76).

Ethyl (2-cyano-2-oxepanyl)acetate (**3i$_3$**). IR (neat) 1735 cm^{-1} (C=O); ^{13}C NMR ($CDCl_3$) δ=14.1(q) 22.5 (t), 28.0 (t), 30.2 (t), 38.8 (t), 44.0 (t), 61.0 (t), 66.7 (t), 74.4 (s), 120.1 (s), and 167.8 (s); ^{1}H NMR ($CDCl_3$) δ=1.30 (3H, t, J=7 Hz, $CO_2CH_2C\underline{H}_3$), 1.4—1.85 (6H, m), 2.1—2.2 (2H, m), 2.71 (1H, d, J=15 Hz, $C\underline{H}_2CO_2Et$), 2.81 (1H, d, J=15 Hz, $C\underline{H}_2CO_2Et$), 3.7—3.9 (2H, m, 7-H) and 4.21 (2H, q, J=7 Hz, $CO_2C\underline{H}_2CH_3$); MS, *m/z* (rel intensity) 211 (M^+; 0.4), 182 (12), 166 (13), 138 (15), 124 (56), 115 (44), 96 (22), 69 (31), 55 (96), and 42 (base peak).

Ethyl (*cis*-3-methyl-2-oxepanyl)acetate (**3j**). IR (neat) 1735 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=0.90 (3H, d, J=7 Hz, 3-Me), 1.27 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 1.4—1.63 (2H, m), 1.63—1.75 (4H, m), 1.8—1.88 (1H, m), 2.29 (1H, dd, J=15.4 and 3.8 Hz, $C\underline{H}_2CO_2Et$), 2.55 (1H, dd, J=15.4 and 9.9 Hz, $C\underline{H}_2CO_2Et$), 3.58—3.64 (1H, m, 7-H), 3.78—3.84 (1H, m, 7-H), 4.03 (1H, ddd, J=9.9, 3.8, and 2.8 Hz, 2-H), 4.15 (1H, dq, J=10.8 and 7.1 Hz, $CO_2C\underline{H}_2CH_3$) and 4.16 (1H, dq, J=10.8 and 7.1 Hz, $CO_2C\underline{H}_2CH_3$); MS, *m/z* (rel intensity) 200 (M^+; 2.2), 157 (37), 144 (31), 130 (27), 117 (43), 113 (72), 89 (54), 82 (38), 71 (84), 55 (base peak), and 41 (86).

Ethyl (7-methyl-2-oxepanyl)acetate (**3k**). IR (neat) 1735 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.12 (3H, d, J=6.3 Hz, 7-Me), 1.27 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 1.45—1.82 (8H, m), 2.37 (1H, dd, J=15.1 and 4.6 Hz, $C\underline{H}_2CO_2Et$), 2.50 (1H, dd, J=15.1 and 9.1 Hz, $C\underline{H}_2CO_2Et$), 3.65—3.74 (1H, m, 7-H), 3.93—4.0 (1H, m, 2-H), 4.14 (1H, dq, J=10.8 and 7.1 Hz, $CO_2C\underline{H}_2CH_3$), and 4.15 (1H, dq, J=10.8 and 7.1 Hz, $CO_2C\underline{H}_2CH_3$) (upon irradiation of 2-H, 14.8% NOE was observed on 7-H); MS, *m/z* (rel intensity) 200(M^+; 2.6), 143 (41), 130 (67), 117 (34), 113 (79), 95 (48), 88 (52), 69 (51), 55 (base peak), and 41 (74).

Preparation of *cis*-2-(2-Hydroxyethyl)-3-methyloxepane (10). $LiAlH_4$ (51 mg, 1.3 mmol) was added to a solution of **3j** (325 mg, 1.9 mmol) in THF (5 ml) at room temperature, and then the reaction mixture was refluxed for 40 min. After cooling to room temperature, the reaction was quenched with aqueous saturated Rochelle salt. The separated precipitate was filtered off. The filtrate was evaporated in vacuo. The residue dissolved in ethyl acetate was washed with brine, dried over Na_2SO_4 and evaporated in vacuo to give **10** (275 mg, 92%). IR (neat) 3360 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$) δ=0.91 (3H, d, J=7.3 Hz, 3-Me), 1.4—1.94 (9H, m), 2.73 (1H, t, J=4.9 Hz, OH), and 3.55—3.94 (5H, m); MS, *m/z* (rel intensity) 158 (M^+; 4.3), 113 (65), 82 (56), 75 (85), 69 (45), 56 (94), and 41 (base peak).

Preparation of 2-(*cis*-3-Methyl-2-oxepanyl)ethyl *N*-(1-Naphthyl)carbamate (11). A solution of **10** (115 mg, 0.73 mmol) and 1-naphtyl isocyanate (132 mg, 0.78 mmol) in benzene (1 ml) was allowed to stand for 2 d, and then evaporated in vacuo. The residue was purified by preparative thin layer chromatography on silica gel (5:1 hexane–ethyl acetate as a developing solvent) to give **11** (221 mg, 93%), mp 88.5—90 °C (diisopropyl ether). IR (Nujol) 3280 (NH) and 1725 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=0.91 (3H, d, J=7 Hz, Me), 1.4—1.95 (9H, m), 3.4—3.6 (2H, m), 3.8—3.95 (1H, m), 4.33 (2H, dd, J=7.1 and 5.2 Hz, 7-H), 6.93 (1H, bs, NH), 7.42—7.56 (3H, m), 7.67 (1H, d, J=8.2 Hz), and 7.75—7.9 (3H, m); MS, *m/z* (rel intensity) 327 (M^+; 1.8), 169 (base peak), 140 (21), and 115 (14). Found: C, 73.40; H, 7.87; N, 4.23%. Calcd for $C_{20}H_{25}NO_3$: C, 73.37; H, 7.70; N, 4.28%.

Preparation of Ethyl [(2*S*,4*R*)-4-Methyltetrahydro-2-pyranyl]acetate (13). Under an argon atmosphere, a 0.2 molar solution of Me_3SiCl in CH_2Cl_2 (2.8 ml, 0.56 mmol) and SnI_2 (203 mg, 0.545 mmol) were added to a solution of (*R*)-4-methyl-δ-valerolactone (626 mg, 5.48 mmol), 1-(*t*-butyldimethylsilyl)-1-ethoxyethene (1.23 g, 6.08 mmol) and Et_3SiH (960 mg, 8.27 mmol) in CH_2Cl_2 (25 ml) at −78 °C. To the reaction mixture was added dropwise a 0.5 molar solution of $SbCl_5$ in CH_2Cl_2 (0.55 ml, 0.275 mmol) at the same temperature. After stirring for 30 min at −78 °C and for 4 h at −23 °C, the reaction mixture was gradually warmed to room temperature. The reaction was quenched with aqueous saturated $NaHCO_3$. The organic materials were washed with brine, dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by flash column chromatography on silica gel (15:1 hexane–ethyl acetate as an eluent) to give **13** (859 mg, 84%). IR, ^{1}H NMR and MS spectra were identical with those of **3f**.

Preparation of (2*S*,4*R*)-2-(2-Hydroxy-2-methylpropyl)-4-methyltetrahydropyran (14). Under an argon atmoshpere, a 2.01 molar solution of MeMgBr in THF (5.4 ml, 10.9 mmol) was added dropwise to a solution of **13** (779 mg, 4.2 mmol) in ether (15 ml) at 0 °C, and then the reaction mixture was stirred for 30 min at the same temperature and for 1 h at room temperature. After cooling to 0 °C, the reaction was quenched with aqueous saturated NH_4Cl. The organic materials were washed with brine, dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by flash column chromatography on silica gel (15:1 hexane–ethyl acetate as an eluent) to give **14** (655 mg, 91%). IR (neat) 3500 and 3430 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$) δ=0.93 (3H, d, J=6.4 Hz, 4-Me), 0.99 (1H, dt, J=12.2 and 10.9 Hz, 3-H_{ax}), 1.16—1.29 (1H, m), 1.20 (3H, s, Me of side chain), 1.26 (3H, s,

Me of side chain), 1.44—1.7 (4H, m), 1.73 (1H, dd, J=14.5 and 10.9 Hz, one proton of methylene of side chain), 3.42 (1H, dt, J=2.2 and 11.3 Hz, 6-H_{ax}), 3.65 (1H, tt, J=10.9 and 2.1 Hz, 2-H), 4.00 (1H, s, OH), and 4.00 (1H, ddd, J=11.3, 4.6, and 1.3 Hz, 6-H_{eq}); MS, m/z (rel intensity) 172 (M^+; 0.2), 157 (14), 154 (7.5), 139 (58), 99 (base peak), 81 (58), 59 (79), 55 (40), and 43 (90).

Dehydration of (2*S*,4*R*)-2-(2-Hydroxy-2-methylpropyl)-4-methyltetrahydropyran (14). *dl*-10-Camphorsulfonic acid (28 mg, 0.12 mmol) was added to a solution of **14** (292 mg, 1.7 mmol) in toluene (10 ml). The reaction mixture was refluxed for 30 h using a Dean–Stark distillation head. After cooling to room temperature, the reaction mixture was purified by flash column chromatography on silica gel (30:1 pentane–ether as an eluent) to give (−)-*cis*-rose oxide (**15**) (115 mg, 44%, cis/trans=93:7) and (2*S*,4*R*)-4-methyl-2-(2-methylallyl)tetrahydropyran (**16**) (64.7 mg, 25%, cis/trans >99:1).

Physical properties of **15**: $[\alpha]_D^{20}$ −68.3° (c 3.0, $CHCl_3$); IR (neat) 1675 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) (the cis isomer) δ=0.93 (3H, d, 6.4 Hz, 4-Me), 1.02 (1H, dt, J=13 and 11.4 Hz, 3-H_{ax}), 1.15—1.26 (1H, m), 1.48—1.75 (3H, m), 1.68 (3H, d, J=1.3 Hz, CH=C$\underline{Me}_2$), 1.72 (3H, d, J=1.3 Hz, CH=C$\underline{Me}_2$), 3.46 (1H, ddd, J=12.4, 11.4, and 2.2 Hz, 6-H_{ax}), 3.95—4.01 (2H, m, 2-H and 6-H_{eq}), and 5.16 (1H, dh, J=8.2 and 1.3 Hz, C$\underline{H}$=CMe), (the trans isomer) δ=1.07 (3H, d, J=7 Hz, 4-Me), 3.65—3.78 (2H, m, 6-H), 4.36 (1H, dt, J=3.5 and 8.2 Hz, 2-H), and 5.28 (1H, dh, J=8.2 and 1.4 Hz, C$\underline{H}$=C$\underline{Me}_2$); MS, m/z (rel intensity) 154 (M^+; 26), 139 (base peak), 83 (53), 69 (78), 55 (47), and 41 (78).

Physical properties of **16**: $[\alpha]_D^{20}$ −7.9° (c 3.0, $CHCl_3$); IR (neat) 1640 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=0.84—0.9 (1H, m, 3-H_{ax}), 0.93 (3H, d, J=6.3 Hz, 4-Me), 1.15—1.25 (1H, m), 1.5—1.64 (3H, m), 1.75 (3H, s, Me of side chain), 2.09 (1H, dd, J=13.8 and 5.6 Hz, C$\underline{H}_2$C(CH_3)=CH_2), 2.27 (1H, dd, J=13.8 and 7.1 Hz, C$\underline{H}_2$C(CH_3)=CH_2), 3.37—3.45 (2H, m, 2-H and 6-H_{ax}), 4.00 (1H, ddd, J=11.4, 4.6, and 1.6 Hz, 6-H_{eq}), 4.73—4.75 (1H, m, C$\underline{H}_2$=C), and 4.78—4.80 (1H, m, C$\underline{H}_2$=C); ^1H NMR (C_6D_6) δ=0.76—0.85 (1H, m, 3-H_{ax}), 0.78 (3H, d, J=6.5 Hz, 4-Me), 1.0—1.1 (1H, m, 5-H_{ax}), 1.15—1.20 (1H, m), 1.20—1.31 (1H, m, 4-H), 1.37—1.42 (1H, m), 1.75 (3H, s, Me of side chain), 2.12 (1H, dd, J=13.8 and 5.7 Hz, C$\underline{H}_2$C(CH_3)=CH_2), 2.38 (1H, dd, J=13.8 and 7.1 Hz, C$\underline{H}_2$C(CH_3)=CH_2), 3.18 (1H, dt, J=2.2 and 11.4 Hz, 6-H_{ax}), 3.26—3.32 (1H, m, 2-H), 3.90 (1H, ddd, J=11.4, 4.6, and 1.6 Hz, 6-H_{eq}), and 4.87—4.88 (2H, m, C$\underline{H}_2$=C) (upon irradiation of 2-H_{ax}, 5.0% NOE was observed on 4-H); MS, m/z (rel intensity) 154 (M^+; 1.8), 99 (base peak), 81 (49), 69 (37), 55 (53), and 43 (98).

Preparation of (*cis*-6-Methyltetrahydro-2-pyranyl)acetic Acid (17). A mixture of ethyl (*cis*-6-methyltetrahydro-2-pyranyl)acetate (**3h$_1$**) (92.4 mg, 0.5 mmol), 6 M HCl (1 ml) and dioxane (1 ml) was refluxed for 40 min (1 M=1 mol dm^{-3}). After cooling to room temperature, the reaction mixture was diluted with water and then extracted with ethyl acetate. The extract was washed with brine, dried over Na_2SO_4 and evaporated in vacuo. The residue was recrystallized from pentane to give **17** (74.0 mg, 94%), mp 51—53 °C (lit.[18] 52—53 °C). IR, ^1H NMR, ^{13}C NMR and MS spectra were identical with those of the authentic sample prepared by B. Maurer.[18]

Preparation of Cyclic Ethers from Siloxy Carbonyl Compounds (Method A). A typical procedure is described for *trans*-2-allyl-6-phenyltetrahydropyran (**19d$_2$**) from 5-phenyl-5-trimethylsiloxypentanal (**18d**) using $TrSbCl_6$ as a catalyst: Under an argon atmosphere, $TrSbCl_6$ (58 mg, 0.1 mmol) was added to a solution of **18d** (250 mg, 1.0 mmol) in CH_2Cl_2 (3 ml) at −78 °C. After stirring for 5 min, to the mixture was added dropwise a solution of allyltrimethylsilane (172 mg, 1.5 mmol) in CH_2Cl_2 (1.5 ml) at the same temperature. The reaction temperature was raised to −23 °C, and then the reaction mixture was stirred for 2 h. After being warmed gradually to room temperature, the reaction was quenched with aqueous saturated $NaHCO_3$. The organic materials were washed with brine, dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by preparative thin layer chromatography on silica gel (20:1 hexane–ethyl acetate as a developing solvent) to give **19d$_2$** (152 mg, 75%). IR (neat) 1640 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=1.43—1.51 (1H, m), 1.63—1.8 (3H, m), 1.9—2.0 (2H, m), 2.28 (1H, dddt, J=14, 1.5, 1, and 7 Hz, C$\underline{H}_2$CH=CH_2), 2.51 (1H, dddt, J=14, 1.5, 1, and 7 Hz, C$\underline{H}_2$CH=CH_2), 3.81 (1H, dq, J=3.8 and 7 Hz, 2-H), 4.85 (1H, t, J=5.3 Hz, 6-H), 5.04 (1H, ddt, J=10, 2, and 1 Hz, C$\underline{H}_2$=CH), 5.09 (1H, ddt, J=17, 2, and 1.5 Hz, C$\underline{H}_2$=CH), 5.85 (1H, ddt, J=17, 10, and 7 Hz, CH_2=C$\underline{H}$), 7.22—7.26 (1H, m), and 7.32—7.40 (4H, m) (upon irradiation of one proton of methylene of allyl groups, 3.8% NOE was observed on 6-H_{ax}); ^{13}C NMR ($CDCl_3$) δ=18.9 (t), 29.3 (t), 29.9 (t), 38.0 (t), 71.4 (d), 72.3 (d), 116.4 (t), 126.3 (d), 126.8 (d), 128.2 (d), 135.2 (d), and 142.0 (s); MS, m/z (rel intensity) 202 (M^+; 3.8), 161 (base peak), 117 (98), and 91 (97).

A Preparation of Cyclic Ethers form Siloxy Carbonyl Compounds (Method B). A typical procedure is described for 2-phenyltetrahydrofuran (**19a**) from 4-trimethylsiloxybutyrophenone (**18a**) using a catalyst system of $SbCl_5$, Me_3SiCl, and SnI_2: Under an argon atmosphere, a 0.5 molar solution of $SbCl_5$ in CH_2Cl_2 (0.2 ml), a 0.2 molar solution of Me_3SiCl in CH_2Cl_2 (0.5 ml) and SnI_2 (38 mg, 0.1 mmol) were added to a solution of **18a** (238 mg, 1.0 mmol) in CH_2Cl_2 (3 ml) at −78 °C. After stirring for 5 min, to the mixture was added dropwise a solution of Et_3SiH (172 mg, 1.5 mmol) in CH_2Cl_2 (1.5 ml) at the same temperature. The reaction temperature was raised to −23 °C, and then the reaction mixture was stirred for 2.5 h. After being warmed gradually to room temperature, the reaction was quenched with aqueous saturated $NaHCO_3$. The organic materials were washed with brine, dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by preparative thin layer chromatography on silica gel (12:1 hexane–ethyl acetate as a developing solvent) to give **19a** (136 mg, 91%). IR (neat), no characteristic peak is detected; ^1H NMR ($CDCl_3$) δ=1.72—1.91 (1H, m), 1.94—2.07 (2H, m), 2.25—2.4 (1H, m), 3.93 (1H, dt, J=8.3 and 6.8 Hz, 5-H), 4.09 (1H, dt, J=8.3 and 6.8 Hz, 5-H), 4.89 (1H, t, J=7.1 Hz, 2-H), and 7.15—7.4 (5H, m); MS, m/z (rel intensity) 148 (M^+; 85), 147 (M^+−H; base peak), 117 (20), 105 (92), 91 (26), 77 (45), 51 (20), and 42 (24).

Physical properties of other products are presented:

2-Phenyltetrahydropyran (**19b**). IR (neat), no characteristic peak is detected; ^1H NMR ($CDCl_3$) δ=1.45—2.0 (6H, m, 3-, 4-, and 5-H), 3.55—3.68 (1H, m, 6-H_{ax}), 4.14 (1H, dt, J=15.1 and 3 Hz, 6-H_{eq}), 4.32 (1H, dd, J=10.3 and 2 Hz, 2-H), and 7.15—7.4 (5H, m); MS, m/z (rel intensity) 162 (M^+; 97), 105 (base peak), 91 (26), 77 (30), and 41 (20).

cis-2-Methyl-6-phenyltetrahydropyran (**19c**). IR (neat),

no characteristic peak is detected; ^{1}H NMR ($CDCl_3$) δ=1.25 (3H, d, J=6.2 Hz, 2-Me), 1.28—1.35 (1H, m), 1.49 (1H, ddt, J=11.2, 3.9, and 12.9 Hz), 1.61—1.73 (2H, m), 1.76—1.82 (1H, m), 1.89—1.94 (1H, m), 3.63 (1H, ddq, J=11, 2, and 6.2 Hz, 2-H), 4.36 (1H, dd, J=11.2 and 2.2 Hz, 6-H) (upon irradiation of 2-H_{ax}, 12.6% NOE was observed on 6-H_{ax}); MS, m/z(rel intensity) 176 (M^+; 40), 107 (base peak), 105 (86), 104 (90), 91 (22), 79 (33), 77(35), 55(20), and 42(31).

trans-2-Cyano-6-phenyltetrahydropyran (**19d$_{3a}$**). IR (neat), no characteristic peak is detected; ^{13}C NMR ($CDCl_3$) δ=20.0 (t), 28.3 (t), 32.6 (t), 65.2 (d), 76.5 (d), 117.6 (s), 125.8 (d), 127.8 (d), 128.5 (d), and 141.0 (s); ^{1}H NMR ($CDCl_3$) δ=1.6—1.7 (1H, m), 1.85—2.1 (5H, m), 4.81 (1H, dd, J=11.4 and 2.2 Hz, 6-H), 5.01 (1H, dd, J=3 and 2 Hz, 2-H), and 7.25—7.4 (5H, m); MS, m/z (rel intensity) 187 (M^+; 31), 158 (31), 133 (23), 105 (base peak), 91 (24), and 77 (46).

cis-2-Cyano-6-phenyltetrahydropyran (**19d$_{3b}$**). IR (neat), no characteristic peak is detected; ^{13}C NMR ($CDCl_3$) δ=23.1 (t), 29.8 (t), 32.4 (t), 66.4 (d), 80.7 (d), 118.0 (s), 125.6 (d), 127.8 (d), 128.3 (d), and 140.9 (s); ^{1}H NMR ($CDCl_3$) δ=1.55—1.8 (2H, m), 1.8—2.1 (4H, m), 4.38 (1H, dd, J=11.2 and 2.1 Hz, 2-H or 6-H), 4.42 (1H, dd, J=11.5 and 3 Hz, 2-H or 6-H), and 7.25—7.4 (5H, m); MS, m/z (rel intensity) 187 (M^+; 27), 158 (28), 133 (23), 105 (base peak), 91 (23), and 77 (44).

2-Phenyloxepane (**19e**). IR (neat), no characteristic peak is detected; ^{1}H NMR ($CDCl_3$) δ=1.4—2.25 (8H, m, 3-, 4-, 5- and 6-H), 3.55—4.1 (2H, m, 7-H), 4.56 (1H, dd, J=8 and 4 Hz, 2-H), and 7.1—7.3 (5H, m); MS, m/z (rel intensity) 176 (M^+; 53), 147 (20), 133 (26), 117 (24), 106 (base peak), 91 (50), 79 (77), 55 (39), 51 (33), and 42 (45).

2-Benzyloxepane (**19f**). IR (neat), no characteristic peak is detected; ^{1}H NMR ($CDCl_3$) δ=1.35—1.85 (8H, m, 3-, 4-, 5- and 6-H), 2.64 (1H, dd, J=13.7 and 5.9 Hz, C$\underline{H}_2$Ph), 2.85 (1H, dd, J=13.7 and 7.3 Hz, C$\underline{H}_2$Ph), 3.4—3.55 (1H, m), 3.6—3.9 (2H, m), and 7.1—7.3 (5H, m, Ph); MS, m/z (rel intensity) 190 (M^+; 0.5), 99 (base peak), 91 (40), 81 (65), 55 (38), and 43 (26).

Preparation of 2-Trichloromethyl-1,3-dioxan-4-ones (20). A typical procedure is described for *cis*-5,5-dimethyl-6-phenyl-2-trichloromethyl-1,3-dioxan-4-one (**20d**) from 2,2-dimethyl-3-hydroxy-3-phenylpropionic acid: A suspension of 2,2-dimethyl-3-hydroxy-3-phenylpropionic acid (2.96 g, 15.2 mmol), chloral (11.3 g, 76.7 mmol) and pyridinium *p*-toluenesulfonate (338 mg, 1.54 mmol) in benzene (100 ml) was refluxed for 2 d using a Dean–Stark distillation head. After cooling to room temperature, the reaction mixture was washed with water, dried over Na_2SO_4 and evaporated in vacuo. The residue was recrystallized from ethyl acetate–hexane to give **20d** (4.51 g, 91%), mp 159—161 °C. IR (Nujol) 1760 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.19 (3H, s, 5-Me), 1.31 (3H, s, 5-Me), 4.92 (1H, s, 6-H), 5.75 (1H, s, 2-H), and 7.25—7.4 (5H, m) (upon irradiation of 6-H_{ax}, 29.8% NOE was observed on 2-H_{ax}); MS, m/z (rel intensity) 322 and 324 (M^+; 0.02 and 0.04), 205 (0.3), 117 (35), 91 (24), and 70 (base peak). Found: C, 48.47; H, 4.02; Cl, 32.65%. Calcd for $C_{13}H_{13}Cl_3O_3$: C, 48.25; H, 4.05; Cl, 32.87%.

Physical properties of other products are presented:

cis-6-Methyl-2-trichloromethyl-1,3-dioxan-4-one (**20a**). Yield: 42%. mp 80—81 °C (ether–hexane). Found: C, 31.04; H, 2.88; Cl, 45.30%. Calcd for $C_6H_7Cl_3O_3$: C, 30.87; H, 3.02; Cl, 45.55%. IR, ^{1}H NMR, and MS spectra were identical with those of (2*R*,6*R*)-6-methyl-2-trichloromethyl-1,3-dioxan-4-one prepared by D. Seebach et al.[4]

cis-6-Phenyl-2-trichloromethyl-1,3-dioxan-4-one (**20b**). Yield: 58%. mp 98—99.5 °C (diisopropyl ether–hexane). IR (Nujol) 1770 and 1755 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=2.91 (1H, dd, J=17.8 and 11.2 Hz, 5-H), 3.06 (1H, dd, J=17.8 and 4 Hz, 5-H), 5.15 (1H, dd, J=11.2 and 4 Hz, 6-H), 5.77 (1H, s, 2-H), and 7.2—7.5 (5H, m, Ph) (upon irradiation of 6-H_{ax}, 27.5% NOE was observed on 2-H_{ax}); MS, m/z (rel intensity) 294, 296 and 298 (M^+; 0.26, 0.23, and 0.05), 177 (8.7), 131 (base peak), 104 (32), and 77 (43). Found: C, 44.78; H, 2.83; Cl, 36.20%. Calcd for $C_{11}H_9Cl_3O_3$: C, 44.70; H, 3.07; Cl, 35.99%.

cis-5,5-Dimethyl-6-heptyl-2-trichloromethyl-1,3-dioxan-4-one (**20c**). Yield: 62%. mp 63—64.5 °C (hexane). IR (Nujol) 1755 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=0.89 (3H, t, J=7 Hz, Me of side chain), 1.25—1.4 (9H, m), 1.28 (3H, s, 5-Me), 1.33 (3H, s, 5-Me), 1.45—1.55 (1H, m), 1.6—1.7 (2H, m), 3.72 (1H, dd, J=10.1 and 1.9 Hz, 6-H), and 5.56 (1H, s, 2-H), (upon irradiation of 6-H_{ax}, 28.5% NOE was observed on 2-H_{ax}); MS, m/z (rel intensity) 345 and 347 (M^++H; 0.05 and 0.05), 315 and 317 (0.05 and 0.05), 154 (19), and 70 (base peak). Found: C, 48.72; H, 6.67; Cl, 30.92%. Calcd for $C_{14}H_{23}Cl_3O_3$: C, 48.64; H, 6.71: Cl, 30.77%.

cis-5,5-Dimethyl-6-phenethyl-2-trichloromethyl-1,3-dioxan-4-one (**20e**). Yield: 85%. mp 90.5—92 °C (hexane). IR (Nujol) 1755 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.20 (3H, s, 5-Me), 1.34 (3H, s, 5-Me), 1.80 (1H, ddt, J=14.3, 1.9, and 8.5 Hz, PhCH$_2$C$\underline{H}_2$), 2.01 (1H, dddd, J=14.3, 10.8, 8.5, and 4.4 Hz, PhCH$_2$C$\underline{H}_2$), 2.73 (1H, dt, J=13.5 and 8.5 Hz, PhC$\underline{H}_2$), 2.98 (1H, ddd, J=13.5, 8.5, and 4.4 Hz, PhC$\underline{H}_2$), 3.66 (1H, dd, J=10.8 and 1.9 Hz, 6-H), and 5.49 (1H, s, 2-H), (upon irradiation of 6-H_{ax}, 27.3% NOE was observed on 2-H_{ax}); MS, m/z (rel intensity) 350, 352, and 354 (M^+; 1.2, 1.1 and 0.5), 233 (5.4), 159 (45), 136 (43), 117 (37), 91 (base peak), and 41 (38). Found: C, 51.16; H, 4.57; Cl, 30.47%. Calcd for $C_{15}H_{17}Cl_3O_3$: C, 51.23; H, 4.87; Cl, 30.25%.

c-6-*t*-Butyl-6-methyl-*r*-2-trichloromethyl-1,3-dioxan-4-one (**20f**). Yield: 40%. mp 61.5—63 °C (hexane). IR (Nujol) 1780 and 1760 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.01 (9H, s, *t*-Bu), 1.42 (3H, s, 6-Me), 2.44 (1H, d, J=17.1 Hz, 5-H), 2.95 (1H, d, J=17.1 Hz, 5-H), and 5.58 (1H, s, 2-H) (upon irradiation of 6-Me$_{ax}$, 21.1% NOE was observed on 2-H_{ax}); MS, m/z (rel intensity) 287 and 289 (M^+–H; 0.1 and 0.1), 273 and 275 (M^+–CH_3; 0.2 and 0.2), 231, 233, 235, and 237 (M^+–C_4H_9; 4.9, 5.5, 2.2, and 0.4), 85 (base peak), 57 (90), and 43 (61). Found: C, 41.70; H, 5.21; Cl, 36.57%. Calcd for $C_{10}H_{15}Cl_3O_3$: C, 41.48; H, 5.22; Cl, 36.73%.

Addition of 1-(*t*-Butyldimethylsiloxy)-1-ethoxyethene (2) to 2-Trichloromethyl-1,3-dioxan-4-ones (20). A typical procedure is described for preparation of ethyl 4-*t*-butyldimethylsiloxy-*c*-6-methyl-*r*-2-trichloromethyl-1,3-dioxane-*t*-4-acetate (**21a**): Under an argon atmosphere, $TrSbCl_6$ (14.6 mg, 0.025 mmol) was added to a solution of *cis*-6-methyl-2-trichloromethyl-1,3-dioxan-4-one (**20a**) (117 mg, 0.5 mmol) and 1-(*t*-butyldimethylsiloxy)-1-ethoxyethene (133 mg, 0.66 mmol) in CH_2Cl_2 (2.5 ml) at −78 °C, and then the reaction mixture was stirred for 2 h at the same temperature. The reaction was quenched with a solution of pyridine (21.1 mg, 0.27 mmol) in CH_2Cl_2 (1 ml). The reaction mixture was washed with brine, dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by flash column chromatography on silica gel (30:1 hexane–ethyl acetate as an eluent) to give **21a** (202 mg, 93%), mp 75—76 °C (petroleum ether). IR (Nujol)

1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.19 (3H, s, MeSi), 0.21 (3H, s, MeSi), 0.87 (9H, s, *t*-BuSi), 1.27 (3H, t, J=7.2 Hz, $CO_2CH_2C\underline{H}_3$), 1.35 (3H, d, J=6.1 Hz, 6-Me), 1.57 (1H, ddd, J=13.6, 12, and 1.4 Hz, 5-H_{ax}), 2.29 (1H, dd, J=13.6 and 2.3 Hz, 5-H_{eq}), 2.74 (1H, dd, J=13 and 1.4 Hz, $C\underline{H}_2CO_2Et$), 2.93 (1H, d, J=13 Hz, $C\underline{H}_2CO_2Et$), 4.01 (1H, ddq, J=12, 2.3, and 6.1 Hz, 6-H), 4.09 (1H, dq, J=10.9 and 7.2 Hz, $CO_2C\underline{H}_2CH_3$), 4.17 (1H, dq, J=10.9 and 7.2 Hz, $CO_2C\underline{H}_2CH_3$), and 4.95 (1H, s, 2-H) (upon irradiation of one proton of methylene of acetate group, 18.6% and 10.1% NOE were observed on 2-H_{ax} and 6-H_{ax}); MS, *m/z* (rel intensity) 419, 421, 423, and 425 (M^+–CH_3; 0.14, 0.14, 0.05, and 0.01), 377, 379, 381, and 383 (M^+–C_4H_9; 4.7, 4.4, 1.6, and 0.21), 231 (41), 187 (base peak), 159 (67), 145 (48), 115 (73), 103 (61), and 75 (90). Found: C, 44.40; H, 6.74; Cl, 24.34; Si, 6.21%. Calcd for $C_{16}H_{29}Cl_3O_5Si$: C, 44.09; H, 6.71; Cl, 24.40; Si, 6.44%.

Physical properties of other products are presented:

4-*t*-butyldimethylsiloxy-*c*-6-methyl-*r*-2-trichloromethyl-1,3-dioxane-*c*-4-acetate (**22a**). IR (neat) 1735 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.20 (3H, s, MeSi), 0.26 (3H, s, MeSi), 0.92 (9H, s, *t*-BuSi), 1.27 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 1.31 (3H, d, J=6.5 Hz, 6-Me), 1.90 (1H, dd, J=13.2 and 2.4 Hz, 5-H_{eq}), 2.00 (1H, dd, J=13.2 an 11.1 Hz, 5-H_{ax}), 2.73 (1H, d, J=14.4 Hz, $C\underline{H}_2CO_2Et$), 2.86 (1H, d, J=14.4 Hz, $C\underline{H}_2CO_2Et$), 4.12 (1H, dq, J=10.9 and 7.1 Hz, $CO_2C\underline{H}_2CH_3$), 4.13 (1H, dq, J=10.9 and 7.1 Hz, $CO_2C\underline{H}_2CH_3$), 4.22 (1H, ddq, J=11.1, 2.4, and 6.5 Hz, 6-H), and 5.23 (1H, s, 2-H) (no NOE was detected between methylene of acetate group and 2-H_{ax}, or between the former and 6-H_{ax}); MS, *m/z* (rel intensity) 433 and 435 (M^+–H; 0.04 and 0.04), 419, 421, 423, and 425 (M^+–CH_3; 0.32, 0.28, 0.09, and 0.01), 377, 379, 381, and 383 (M^+–C_4H_9; 13, 12, 3.8, and 0.57), 271 (21), 247 (27), 231 (22), 187 (base peak), 159 (45), 145 (43), 115 (47), 103 (47), and 75 (96).

t-Butyldimethylsiloxy-*c*-6-phenyl-*r*-2-trichloromethyl-1,3-dioxane-*t*-4-acetate (**21b**): mp 115—116 °C (petroleum ether). IR (Nujol) 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.22 (3H, s, MeSi), 0.23 (3H, s, MeSi), 0.86 (9H, s, *t*-BuSi), 1.29 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 1.85 (1H, ddd, J=13.8, 12, and 1.4 Hz, 5-H_{ax}), 2.55 (1H, dd, J=13.8 and 2.4 Hz, 5-H_{eq}), 2.86 (1H, dd, J=12.9 and 1.4 Hz, $C\underline{H}_2CO_2Et$), 3.09 (1H, d, J=12.9 Hz, $C\underline{H}_2CO_2Et$), 4.12 (1H, dq, J=10.9 and 7.1 Hz, $CO_2C\underline{H}_2CH_3$), 4.20 (1H, dq, J=10.9 and 7.1 Hz, $CO_2C\underline{H}_2CH_3$), 4.95 (1H, dd, J=12 and 2.4 Hz, 6-H), 5.16 (1H, s, 2-H), and 7.3—7.4 (5H, m, Ph), (upon irradiation of one proton of methylene of acetate group, 16.0% and 9.2% NOE were observed on 2-H_{ax} and 6-H_{ax} respectively); MS, *m/z* (rel intensity) 439, 441, and 443 (M^+–C_4H_9; 0.92, 0.96, and 0.35), 187 (base peak), 159 (25), 103 (21), and 75 (73). Found: C, 50.83; H, 6.14; Cl, 21.09; Si, 5.85%. Calcd for $C_{21}H_{31}Cl_3O_5Si$: C, 50.66, H, 6,28; Cl, 21.36; Si, 5.64%.

4-*t*-Butyldimethylsiloxy-*c*-6-phenyl-*r*-2-trichloromethyl-1,3-dioxane-*c*-4-acetate (**22b**). IR (neat) 1735 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.25 (3H, s, MeSi), 0.31 (3H, s, MeSi), 0.98 (9H, s, *t*-BuSi), 1.26 (3H, t, J=7.2 Hz, $CO_2CH_2C\underline{H}_3$), 2.18 (1H, dd, J=13.4 and 2.6 Hz, 5-H_{eq}), 2.30 (1H, dd, J=13.4 and 11.6 Hz, 5-H_{ax}), 2.77 (1H, d, J=14.6 Hz, $C\underline{H}_2CO_2Et$), 2.91 (1H, d, J=14.6 Hz, $C\underline{H}_2CO_2Et$), 4.12 (1H, dq, J=10.9 and 7.2 Hz, $CO_2C\underline{H}_2CH_3$), 4.13 (1H, dq, J=10.9 and 7.2 Hz, $CO_2C\underline{H}_2CH_3$), 5.17 (1H, dd, J=11.6 and 2.6 Hz, 6-H), 5.43 (1H, s, 2-H), and 7.2—7.45 (5H, m, Ph) (upon irradiation of 2-H_{ax}, 4.9% and 2.4% NOE were observed on the two methyl groups at siloxyl group, whereas upon irradiation of 6-H_{ax}, 19.3% NOE was observed on 2-H_{ax}); MS, *m/z* (rel intensity) 481 and 483 (M^+–CH_3; 0.04 and 0.04), 439 and 441 (M^+–C_4H_9; 2.6 and 2.6), 187 (27), 131 (27), 103 (48), and 75 (base peak).

4-*t*-Butyldimethylsiloxy-5,5-dimethyl-*c*-6-heptyl-*r*-2-trichloromethyl-1,3-dioxane-*t*-4-acetate (**21c**). IR (neat) 1735 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.10 (3H, s, MeSi), 0.18 (3H, s, MeSi), 0.83 (3H, s, 5-Me), 0.88 (3H, t, J=6.9 Hz, Me of side chain), 0.93 (9H, s, *t*-BuSi), 1.04 (3H, s, 5-Me), 1.25—1.35 (9H, m), 1.27 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 1.35—1.65 (3H, m), 2.72 (1H, d, J=13 Hz, $C\underline{H}_2CO_2Et$), 3.11 (1H, d, J=13 Hz, $C\underline{H}_2CO_2Et$), 3.66 (1H, dd, J=9.6 and 0.5 Hz, 6-H), 4.06 (1H, dq, J=10.9 and 7.1 Hz, $CO_2C\underline{H}_2CH_3$), 4.19 (1H, dq, J=10.9 and 7.1 Hz, $CO_2C\underline{H}_2CH_3$), and 5.32 (1H, s, 2-H), (upon irradiation of one proton methylene of acetate group, 14.5% and 12.9% NOE were observed on 2-H_{ax} and 6-H_{ax} respectively); MS, *m/z* (rel intensity) 489 and 491 (M^+–C_4H_9; 0.04 and 0.03), 247 (19), 215 (57), 115 (29), 75 (base peak), 57 (35), and 41 (48).

4-*t*-Butyldimethylsiloxy-5,5-dimethyl-*c*-6-phenyl-*r*-2-trichloromethyl-1,3-dioxane-*t*-4-acetate (**21d**): mp 132.5—134 °C (hexane). IR (Nujol) 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.14 (3H, s, MeSi), 0.22 (3H, s, MeSi), 0.82 (3H, s, 5-Me), 0.92 (9H, s, *t*-BuSi), 0.93 (3H, s, 5-Me), 1.30 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 2.89 (1H, d, J=12.9 Hz, $C\underline{H}_2CO_2Et$), 3.30 (1H, d, J=12.9 Hz, $C\underline{H}_2CO_2Et$), 4.11 (1H, dq, J=10.9 and 7.1 Hz, $CO_2C\underline{H}_2CH_3$), 4.23 (1H, dq, J=10.9 and 7.1 Hz, $CO_2C\underline{H}_2CH_3$), 4.91 (1H, s, 6-H), 5.55 (1H, s, 2-H), and 7.25—7.35 (5H, m, Ph) (upon irradiation of one proton methylene of acetate, 18.2% and 19.5% NOE were observed on 2-H_{ax} and 6-H_{ax}); MS, *m/z* (rel intensity) 523 and 525 (M^+–H; 0.02 and 0.02), 467 and 469 (M^+–C_4H_9; 0.26 and 0.30), 215 (69), 132 (base peak), and 75 (36). Found: C, 52.50; H, 6.69; Cl, 20.37; Si, 5.36%. Calcd for $C_{23}H_{35}Cl_3O_5Si$: C, 52.52; H, 6.71; Cl, 20.22; Si, 5.34%.

4-*t*-Butyldimethylsiloxy-5,5-dimethyl-*c*-6-phenyl-*r*-2-trichloromethyl-1,3-dioxane-*c*-4-acetate (**22d**): IR ($CHCl_3$) 1735 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.36 (3H, s, MeSi), 0.38 (3H, s, MeSi), 0.85 (3H, s, 5-Me), 1.04 (9H, s, *t*-BuSi), 1.08 (3H, s, 5-Me), 1.27 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 2.82 (1H, d, J=13.8 Hz, $C\underline{H}_2CO_2Et$), 3.00 (1H, d, J=13.8 Hz, $C\underline{H}_2CO_2Et$), 4.13 (2H, q, J=7.1 Hz, $CO_2C\underline{H}_2CH_3$), 5.26 (1H, s, 6-H), 5.46 (1H, s, 2-H), and 7.25—7.35 (5H, m, Ph) (upon irradiation of 2-H_{ax}, 5.3% and 4.6% NOE were observed on one of methyl and *t*-butyl group at siloxy group respectively and upon irradiation of 6-H_{ax}, 11.2% NOE was observed on 2-H_{ax}); MS, *m/z* (rel intensity) 467 and 469 (M^+–C_4H_9; 0.9 and 0.8), 215 (17), 132 (62), 75 (base peak), and 57 (70).

4-*t*-Butyldimethylsiloxy-5,5-dimethyl-*c*-6-phenethyl-*r*-2-trichloromethyl-1,3-dioxane-*t*-4-acetate (**21e**): IR (neat) 1735 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.10 (3H, s, MeSi), 0.19 (3H, s, MeSi), 0.77 (3H, s, 5-Me), 0.92 (9H, s, *t*-BuSi), 1.06 (3H, s, 5-Me), 1.26 (3H, t, J=7.2 Hz, $CO_2CH_2C\underline{H}_3$), 1.71—1.77 (1H, m, $PhCH_2C\underline{H}_2$), 1.87—1.92 (1H, m, $PhCH_2C\underline{H}_2$), 2.65 (1H, d, J=13 Hz, $C\underline{H}_2CO_2Et$), 2.66 (1H, dt, J=13.8 and 8.3 Hz, $PhC\underline{H}_2$), 2.94 (1H, dt, J=13.8 and 4.6 Hz, $PhC\underline{H}_2$), 2.98 (1H, d, J=13 Hz, $C\underline{H}_2CO_2Et$), 3.65 (1H, dd, J=10.3 and 1.8 Hz, 6-H), 4.06 (1H, dq, J=10.9 and 7.2 Hz, $CO_2C\underline{H}_2CH_3$), 4.16 (1H, dq, J=10.9 and 7.2 Hz, $CO_2C\underline{H}_2CH_3$), 5.32 (1H, s, 2-H), and 7.18—7.32 (5H, m, Ph) (upon irradiation of 6-H_{ax}, 16.3% and 11.0% NOE were observed on 2-H_{ax} and one proton of methylene of acetate group, respectively); MS, *m/z* (rel intensity) 495, 497, 499, and 501

($M^+-C_4H_9$; 0.73, 0.67, 0.25, and 0.02), 247 (35), 215 (base peak), 91 (50), and 75 (59).

Preparation of *c*-6-Substituted Ethyl *r*-2-Trichloromethyl-1,3-dioxane-*c*-4-acetate (26). A typical procedure is descried for ethyl 5,5-dimethyl-*c*-6-phenyl-*r*-2-trichloromethyl-1,3-dioxane-*c*-4-acetate (**26d**): Under an argon atmosphere, a solution of **21d** (2.63 g, 5.0 mmol) and Et_3SiH (871 mg, 7.5 mmol) in CH_2Cl_2 (30 ml) was added dropwise to a 1.0 molar solution of $TiCl_4$ in CH_2Cl_2 (15 ml, 15 mmol) at −23 °C. After stirring for 30 min, the reaction was quenched with aqueous saturated $NaHCO_3$. The organic materials were washed with brine, dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by flash column chromatography on silica gel (10:1 hexane–ethyl acetate as an eluent) to give **26d** (1.92 g, 97%).mp 113.5—114.5 °C (ethyl acetate–hexane). IR (Nujol) 1730 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.80 (3H, s, 5-Me),0.87 (3H, s, 5-Me), 1.28 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 2.59 (1H, d, J=6.5 Hz, $C\underline{H}_2CO_2Et$), 4.19 (2H, q, J=7.1 Hz, $CO_2C\underline{H}_2CH_3$), 4,26 (1H, t, J=6.5 Hz, 4-H), 4,62 (1H, s, 6-H), 5.10 (1H, s, 2-H), and 7.31—7.37 (5H, m, Ph) (upon irradiation of 4-H_{ax}, 17.1% and 10.3% NOE were observed on 2-H_{ax} and 6-H_{ax} respectively); MS, *m/z* (rel intensity) 393, 395, and 397 (M^+–H; 0.01, 0.02, and 0.01), 142 (base peak), 96 (31), and 69 (43). Found: C, 51.54; H, 5.11; Cl, 26.67%. Calcd for $C_{17}H_{21}Cl_3O_4$: C, 51.60; H, 5.35; Cl, 26.88%.

Physical properties of other products are presented:

Ethyl *c*-6-methyl-*r*-2-trichloromethyl-1,3-dioxane-*c*-4-acetate (**26a**). IR (neat) 1735 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=1.27 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 1.34 (3H, d, J=6.2 Hz, 6-Me), 1.44 (1H, dt, J=13.2 and 11.3 Hz, 5-H_{ax}), 1.72 (1H, dt, J=13.2 and 2.4 Hz, 5-H_{eq}), 2.52 (1H, dd, J=15.7 and 6.2 Hz, $C\underline{H}_2CO_2Et$), 2.73 (1H, dd, J=15.7 and 7 Hz, $C\underline{H}_2CO_2Et$), 3.98 (1H, ddq, J=11.3, 2.4, and 6.2 Hz, 6-H), 4.16 (2H, q, J=7.1 Hz, $CO_2C\underline{H}_2CH_3$), 4.27 (1H, dddd, J=11.3, 7, 6.2, and 2.4 Hz, 4-H), and 4.86 (1H, s, 2-H) (upon irradiation of 2-H_{ax}, 14.5% and 9.8% NOE were observed on 4-H_{ax} and 6-H_{ax} respectively); MS, *m/z* (rel intensity), 303, 305, 307, and 309 (M^+–H and M^++H; 0.1, 0.2, 0.2, and 0.07), 259, 261, and 263 (0.6, 0.4, and 0,2), 217, 219, 221, and 223 ($M^+-C_4H_7O_2$; 1.9, 1.8, 0.6, and 0.1), 157 (25), 141 (68), 115 (32), 99 (37), 71 (79), 55 (36), and 43 (base peak).

Ethyl *c*-6-phenyl-*r*-2-trichloromethyl-1,3-dioxane-*c*-4-acetate (**26b**). IR (neat) 1725 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=1.27 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 1.73 (1H, dt, J=13.3 and 11.3 Hz, 5-H_{ax}), 2.00 (1H, dt, J=13.3 and 2.4 Hz, 5-H_{eq}), 2.56 (1H, dd, J=15.9 and 6.2 Hz, $C\underline{H}_2CO_2Et$), 2.79 (1H, dd, J=15.9 and 7 Hz, $C\underline{H}_2CO_2Et$), 4.17 (2H, q, J=7.1 Hz, $CO_2C\underline{H}_2CH_3$), 4.45 (1H, dddd, J=11.3, 7, 6.2, and 2.4 Hz, 4-H), 4.92 (1H, dd, J=11.3 and 2.4 Hz, 6-H), 5.07 (1H, s, 2-H), and 7.25—7.4 (5H, m, Ph) (upon irradiation of 4-H_{ax}, 18.3% and 6.0% NOE were observed on 2-H_{ax} and 6-H_{ax} respectively); MS, *m/z* (rel intensity), 366, 368, and 370 (M^+; 0.43, 0.52, and 0.17), 203 (26), 157 (54), 129 (base peak), 105 (52), and 77 (40).

Ethyl 5,5-dimethyl-*c*-6-heptyl-*r*-2-trichloromethyl-1,3-dioxane-*c*-4-acetate (**26c**). IR (neat) 1735 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.79 (3H, s, 5-Me), 0.88 (3H, t, J=6.8 Hz, Me of side chain), 0.95 (3H, s, 5-Me), 1.2—1.4 (9H, m), 1.26 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 1.45—1.65 (3H, m), 2.51 (1H, dd, J=15.6 and 4.7 Hz, $C\underline{H}_2CO_2Et$), 2.53 (1H, dd, J=15.6 and 7.7 Hz, $C\underline{H}_2CO_2Et$), 3.40—3.43 (1H, m, 6-H), 4.01 (1H, dd, J=7.7 and 4.7 Hz, 4-H), 4.16 (2H, q, J=7.1 Hz, $CO_2C\underline{H}_2CH_3$), and 4.89 (1H, s, 2-H) (upon irradiation of 6-H_{ax}, 18.1% and 13.6% NOE were observed on 2-H_{ax} and 4-H_{ax} respectively); MS, *m/z* (rel intensity), 415, 417, and 419 (M^+–H; 0.01, 0.02, and 0.01), 142 (base peak), 96 (36), 69 (76), and 41 (56).

Ethyl 5,5-dimethyl-*c*-6-phenethyl-*r*-2-trichloromethyl-1,3-dioxane-*c*-4-acetate (**26e**). IR (neat) 1735 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.71 (3H, s, 5-Me), 0.97 (3H, s, 5-Me), 1.25 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 1.76—1.93 (2H, m, $PhCH_2C\underline{H}_2$), 2.48 (1H, dd, J=15.7 and 3.8 Hz, $C\underline{H}_2CO_2Et$), 2.51 (1H, dd, J=15.7 and 8.6 Hz, $C\underline{H}_2CO_2Et$), 2.67 (1H, dt, J=13.8 and 8.3 Hz, $PhC\underline{H}_2$), 2.92 (1H, ddd, J=13.8, 8.3, and 4.8 Hz, $PhC\underline{H}_2$), 3.37 (1H, dd, J=10.3 and 2 Hz, 6-H), 3.95 (1H, dd, J=8.6 and 3.8 Hz, 4-H), 4.15 (2H, q, J=7.1 Hz, $CO_2C\underline{H}_2CH_3$), 4.88 (1H, s, 2-H), and 7.18—7.31 (5H, m), (upon irradiation of 4-H_{ax}, 19.9% and 11.7% NOE were observed on 2-H_{ax} and 6-H_{ax} respectively); MS, *m/z* (rel intensity) 422, 424, 426, and 428 (M^+; 0.8, 0.7, 0.2, and 0.05), 142 (86), 91 (67), 69 (base peak), and 41 (38).

Reduction of Trichloromethyl Group of *c*-6-Substituted Ethyl *r*-2-Trichloromethyl-1,3-dioxane-*c*-4-acetates (26). A typical procedure is described for preparation of ethyl *c*-6-phenethyl-*r*-2,5,5,-trimethyl-1,3-dixona-*c*-4-acetate (**31e**): Under an argon atmosphere, 2.2′-azobisisobutyronitrile (82.8 mg, 0.5 mmol) was added to a solution of **26e** (424 mg, 1.0 mmol) and *n*-Bu_3SnH (1.20 g, 4.0 mmol) in toluene (4 ml). The reaction mixture was refluxed for 5 h, and then evaporated in vacuo. The residue was passed through a column of silica gel (15:1 hexane–ethyl acetate as an eluent) to remove a large portion of organotin compounds. After the collected effluent was evaporated in vacuo, the residue was purified by preparative thin layer chromatography on silica gel (6:1 hexane–ethyl acetate as a developing solvent) to give **31e** (304 mg, 95%). IR (neat) 1735 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.69 (3H, s, 5-Me), 0.89 (3H, s, 5-H), 1.25 (3H, t, J=7.2 Hz, $CO_2CH_2C\underline{H}_3$), 1.34 (3H, d, J=5.1 Hz, 2-Me), 1.7—1.76 (2H, m, $PhCH_2C\underline{H}_2$), 2.39 (1H, dd, J=15.5 and 8.6 Hz, $C\underline{H}_2CO_2Et$), 2.43 (1H, dd, J=15.5 and 3.6 Hz, $C\underline{H}_2CO_2Et$), 2.67 (1H, dt, J=13.7 and 8.3 Hz, $PhC\underline{H}_2$), 2.89 (1H, dt, J=13.7 and 7.1 Hz $PhC\underline{H}_2$), 3.23 (1H, t, J=6.1 Hz, 6-H), 3.78 (1H, dd, J=8.6 and 3.6 Hz, 4-H), 4.14 (1H, dq, J=10.9 and 7.2 Hz, $CO_2C\underline{H}_2CH_3$), 4.16 (1H, dq, J=10.9, and 7.2 Hz, $CO_2C\underline{H}_2CH_3$), 4.75 (1H, q, J=5.1 Hz, 2-H), 7.17—7.2 (3H, m), and 7.26—7.3 (2H, m) (upon irradiation of 4-H_{ax}, 14.1% and 11.3% NOE were observed on 2-H_{ax} and 6-H_{ax} respectively); MS, *m/z* (rel intensity) 319 (M^+–H; 0.4), 276 (1.2), 142 (40), 91 (99), 69 (base peak), and 41 (55).

Physical properties of other products are presented:

Ethyl *r*-2,*c*-6-dimethyl-1,3-dioxane-*c*-4-acetate (**31a**). IR (neat) 1735 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=1.2—1.35 (1H, m, 5-H_{ax}), 1.23 (3H, d, J=6.3 Hz, 6-Me), 1.26 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 1.32 (3H, d, J=5.1 Hz, 2-Me), 1.61 (1H, dt, J=12.9 and 2.4 Hz, 5-H_{eq}), 2.42 (1H, dd, J=15.5 and 6.2 Hz, $C\underline{H}_2CO_2Et$), 2.61 (1H, dd, J=15.5 and 7.1 Hz, $C\underline{H}_2CO_2Et$), 3.77 (1H, ddq, J=10.7, 2.4, and 6.3 Hz, 6-H), 4.04—4.11 (1H, m, 4-H), 4.16 (2H, q, J=7.1 Hz, $CO_2C\underline{H}_2CH_3$), and 4.74 (1H, q, J=5.1 Hz, 2-H) (upon irradiation of 2-H_{ax}, 11.6% and 8.8% NOE were observed on 4-H_{ax} and 6-H_{ax} respectively); MS, *m/z* (rel intensity) 201 (M^+–H; 4.1), 187 (22), 158 (15), 141 (68), 113 (41), 99 (59), 71 (69), and 45 (base peak).

Ethyl *r*-2-methyl-*c*-6-phenyl-1,3-dioxane-*c*-4-acetate (**31b**). IR (neat) 1730 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=1.26 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 1.41 (3H, d, J=5.1 Hz, 2-Me), 1.62 (1H, dt, J=13.1 and 11.3 Hz, 5-H_{ax}), 1.86 (1H, dt, J=13.1 and

2.5 Hz, 5-H_{eq}), 2.46 (1H, dd, J=15.6 and 6.2 Hz, $C\underline{H}_2CO_2Et$), 2.67 (1H, dd, J=15.6 and 7 Hz, $C\underline{H}_2CO_2Et$), 4.16 (2H, q, J=7.1 Hz, $CO_2C\underline{H}_2CH_3$), 4.25 (1H, dddd, J=11.3, 7.1, 6.2, and 2.5 Hz, 4-H), 4.70 (1H, dd, J=11.3 and 2.5 Hz, 6-H), 4.94 (1H, q, J=5.1 Hz, 2-H), 7.26—7.3 (1H, m), and 7.32—7.38 (4H, m) (upon irradiation of 4-H_{ax}, 16.0% and 6.7% NOE were observed on 2-H_{ax} and 6-H_{ax} respectively); MS, *m/z* (rel intensity) 264 (M^+; 0.7), 220 (9.4), 203 (5.2), 175 (19), 158 (29), 129 (31), 114 (81), 105 (77), and 77 (base peak).

Ethyl *c*-6-heptyl-*r*-2,5,5-trimethyl-1,3-dioxane-*c*-4-acetate (**31c**). IR (neat) 1735 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.74 (3H, s, 5-Me), 0.88 (3H, s, 5-Me), 0.88 (3H, t, J=6.9 Hz, Me of side chain), 1.2—1.6 (12H, m), 1.26 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 1.30 (3H, d, J=5.1 Hz, 2-Me), 2.40 (1H, dd, J=15.6 and 9.1 Hz, $C\underline{H}_2CO_2Et$), 2.45 (1H, dd, J=15.6 and 3.3 Hz, $C\underline{H}_2CO_2Et$), 3.21 (1H, dd, J=9.5 and 2 Hz, 6-H), 3.81 (1H, dd, J=9.1 and 3.3 Hz, 4-H), 4.15 (1H, dq, J=10.8 and 7.1 Hz, $CO_2C\underline{H}_2CH_3$), 4.16 (1H, dq, J=10.8 and 7.1 Hz, $CO_2C\underline{H}_2CH_3$) and 4.75 (1H, q, J=5.1 Hz, 2-H) (upon irradiation of 6-H_{ax}, 14.0% and 14.1% NOE were observed on 2-H_{ax} and 4-H_{ax} respectively); MS, *m/z* (rel intensity) 313 (M^+–H; 0.3), 142 (base peak), 96 (23), and 69 (54).

Ethyl *c*-6-phenyl-*r*-2,5,5-trimethyl-1,3-dioxane-*c*-4-acetate (**31d**). IR (neat) 1735 cm^{-1} (C–O); ^1H NMR ($CDCl_3$) δ=0.73 (3H, s, 5-Me), 0.82 (3H, s, 5-Me), 1.28 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_2$), 1.39 (3H, d, J=5.1 Hz, 2-Me), 2.45 (1H, dd, J=15.5 and 9.2 Hz, $C\underline{H}_2CO_2Et$), 2.51 (1H, dd, J=15.5 and 3.2 Hz, $C\underline{H}_2CO_2Et$), 4.05 (1H, dd, J=9.2 and 3.2 Hz, 4-H), 4.18 (1H, dq, J=10.8 and 7.1 Hz, $CO_2C\underline{H}_2CH_3$), 4.19 (1H, dq, J=10.8 and 7.1 Hz, $CO_2C\underline{H}_2CH_3$), 4.42 (1H, s, 6-H), 4.97 (1H, q, J=5.1 Hz, 2-H), and 7.26—7.34 (5H, m, Ph), (upon irradiation of 6-H_{ax}, 14.1% and 12.0% NOE were observed on 2-H_{ax} and 4-H_{ax} respectively); MS, *m/z* (rel intensity) 291 (M^+–H; 0.34), 203 (4.4), 142 (base peak), 96 (50), and 69 (60).

Preparation of *syn*-1,3-Diols (32). A typical procedure is described for ethyl *syn*-3,5-dihydroxy-5-phenylvalerate (**32b**): Under an argon atmosphere, a 1.0 molar solution of $TiCl_4$ in CH_2Cl_2 (2.5 ml, 2.5 mmol) was added dropwise to a mixture of **31b** (133 mg, 0.5 mmol) and EtSH (2.0 ml, 27 mmol) at −23 °C. After stirring for 30 min, the reaction was quenched with aqueous saturated $NaHCO_3$. The organic materials were washed with brine, dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by flash column chromatography on silica gel (3:1 hexane–ethyl acetate as an eluent) to give **32b** (114 mg, 95%). IR (neat) 3400 (OH), 1725, and 1715 (shoulder) cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=1.27 (3H, t, J=7.2 Hz, $CO_2CH_2C\underline{H}_3$), 1.77 (1H, dt, J=14.4 and 3 Hz, 4-H), 1.93 (1H, dt, J=14.4 and 9.7 Hz, 4-H), 2.47 (1H, dd, J=16.5 and 5.1 Hz, 2-H), 2.50 (1H, dd, J=16.5 and 7.1 Hz, 2-H), 3.60 (1H, s, 5-OH), 3.85 (1H, d, J=2.2 Hz, 3-OH), 4.17 (2H, q, J=7.2 Hz, $CO_2C\underline{H}_2CH_3$), 4.25—4.45 (1H, m, 3-H), 4.97 (1H, dd, J=9.4 and 3.5 Hz, 5-H), and 7.25—7.45 (5H, m, Ph); MS, *m/z* (rel intensity) 220 (M^+–H_2O; 3.5), 192 (0.6), 174 (13), 146 (20), 105 (53), 77 (base peak), 51 (42), and 43 (82).

Physical properties of other products are presented:

Ethyl *syn*-3,5-dihydroxyhexanoate (**32a**). IR (neat) 3370 (OH), 1725, and 1715 (shoulder) cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=1.20 (3H, d, J=6.3 Hz, 6-H), 1.28 (3H, t, J=7.2 Hz, $CO_2CH_2C\underline{H}_3$), 1.56 (1H, dt, J=14.2, and 3.4 Hz, 4-H), 1.60 (1H, dt, J=14.2, and 9.4 Hz, 4-H), 2.47 (1H, dd, J=16.6 and 5.6 Hz, 2-H), 2.48 (1H, dd, J=16.6 and 7 Hz, 2-H), 3.35 (1H, bs, OH), 3.80 (1H, bs, OH), 4.05—4.15 (1H, m), 4.18 (2H, q, J=7.2 Hz, $CO_2C\underline{H}_2CH_3$), and 4.2—4.3 (1H, m); MS, *m/z* (rel intensity) 158 (M^+–H_2O; 1.2), 117 (17), 114 (18), 89 (25), 71 (43), and 43 (base peak).

Ethyl *syn*-3,5-dihydroxy-4,4-dimethyldodecanoate (**32c**). IR (neat) 3440 (OH), 1740 (shoulder), and 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.76 (3H, s, 4-Me), 0.88 (3H, t, J=6.8 Hz, 12-H), 0.91 (3H, s, 4-Me), 1.2—1.65 (12H, m), 1.28 (3H, t, J=7.3 Hz, $CO_2CH_2C\underline{H}_3$), 2.44 (1H, dd, J=16.1 and 9.8 Hz, 2-H), 2.57 (1H, dd, J=16.1 and 2.9 Hz, 2-H), 3.16 (1H, bs, OH), 3.55 (1H, bd, J=8.3 Hz, 5-H), 3.82 (1H, bs, OH), 4.01 (1H, dd, J=9.8 and 2.9 Hz, 3-H), and 4.18 (2H, q, J=7.3 Hz, $CO_2C\underline{H}_2CH_3$); MS, *m/z* (rel intensity) 225 (M^+–$C_2H_7O_2$; 0.26), 200 (4.8), 142 (32), 96 (23), and 72 (base peak).

Ethyl *syn*-3,5-dihydroxy-4,4-dimethyl-5-phenylvalerate (**32d**). mp 74.5—76 °C (ether–hexane). IR (Nujol) 3520 and 3440 (OH), and 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.63 (3H, s, 4-Me), 0.96 (3H, s, 4-Me), 1.28 (3H, t, J=7.1 Hz, $CO_2CH_2C\underline{H}_3$), 2.49 (1H, dd, J=16.4 and 9 Hz, 2-H), 2.56 (1H, dd, J=16.4 and 3.9 Hz, 2-H), 3.74 (1H, bs, OH), 4.04 (1H, bs, OH), 4.05—4.12 (1H, m, 3-H), 4.19 (2H, q, J=7.1 Hz, $CO_2C\underline{H}_2CH_3$), 4.75 (1H, s, 5-H) and 7.25—7.4 (5H, m, Ph); MS, *m/z* (rel intensity) 220 (M^+–C_2H_6O; 1.3), 142 (62), 132 (22), 117 (27), 107 (39), 77 (base peak), 72 (47), 70 (47), 57 (42), and 43 (72). Found: C, 67.54; H, 8.61%. Calcd for $C_{15}H_{22}O_4$: C, 67.65; H, 8.33%.

Ethyl *syn*-3,5-dihydroxy-4,4-dimethyl-7-phenylheptanoate (**32e**). IR (neat) 3420 (OH), 1735 (shoulder), and 1715 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.74 (3H, s, 4-Me), 0.92 (3H, s, 4-Me), 1.28 (3H, t, J=7.3 Hz, $CO_2CH_2C\underline{H}_3$), 1.6—1.9 (2H, m, 6-H), 2.43 (1H, dd, J=16.6 and 9.8 Hz, 2-H), 2.55 (1H, dd, J=16.6 and 2.9 Hz, 2-H), 2.62 (1H, ddd, J=13.7, 9.3, and 6.4 Hz, 7-H), 2.93 (1H, ddd, J=13.7, 9.8, and 5.4 Hz, 7-H), 3.49 (1H, bs, OH), 3.60 (1H, dd, J=10.2 and 2.4 Hz, 5-H), 3.81 (1H, bs, OH), 3.98 (1H, dd, J=9.8 and 2.9 Hz, 3-H), 4.18 (2H, q, J=7.3 Hz, $CO_2C\underline{H}_2CH_3$), and 7.15—7.35 (5H, m, Ph); MS, *m/z* (rel intensity) 248 (M^+–C_2H_6O; 3.7), 230 (7.0), 117 (18), 104 (48), 91 (base peak), 72 (48), 57 (30), and 43 (53).

Preparation of *trans*-3-Hydroxy-5-methyl-δ-valerolactone (33): Pyridinium *p*-toluenesulfonate (15.9 mg, 0.063 mmol) was added to a solution of ethyl *syn*-3,5-dihydroxyhexanoate (**32a**) (47.7 mg, 0.27 mmol) in benzene (5 ml), and then the reaction mixture was refluxed for 30 min. After the mixture were evaporated in vacuo, the residue was purified by flash column chromatography on silica gel (1:1 hexane–ethyl acetate as an eluent) to give **33** (29.0 mg, 82%). IR (Nujol) 3405 (OH) and 1695 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=1.40 (3H, d, J=6.5 Hz, 5-Me), 1.72 (1H, ddd, J=14.5, 11.3, and 3.2 Hz, 4-H_{ax}), 1.99 (1H, dddd, J=14.5, 3.8, 3.1, and 1.7 Hz, 4-H_{eq}), 2.62 (1H, ddd, J=17.7, 3.6, and 1.7 Hz, 2-H_{eq}), 2.70 (1H, dd, J=17.7 and 4.8 Hz, 2-H_{ax}), 2.75 (1H, bs, OH), 4.34—4.38 (1H, m, 3-H), and 4.82—4.9 (1H, m, 5-H); MS, *m/z* (rel intensity) 130 (M^+; 0.78) and 43 (base peak).

X-Ray Crystal Structure Analysis of 2-(*cis*-3-Methyl-2-oxepanyl)ethyl *N*-(1-Naphthyl)carbamate (11) and Ethyl *syn*-3,5-Dihydroxy-4,4-dimethyl-5-phenylvalerate (32d). The X-ray diffraction data were collected by RIGAKU AFC/5, with monochromated Cu Kα radiation (λ=1.5418 Å). Both structures were solved by direct method (MULTAN 80'),[33] and the refinements of atomic parameters were carried out using block-diagonal least-squares method, with anisotropic temperature factors for non hydrogen atoms, and with isotropic temperature factors for hydrogen atoms, of which

located on the difference Fourier maps. The positions of the other hydrogen atoms were assumed geometrically, and fixed. Throughout the refinement, the function $\sum(|F_o|-|F_c|)^2$ was minimized. The weight of $\sqrt{W}=1/\sigma(F_o)$ was used during the final refinement stage for each compounds. The atomic scattering factors were taken from "International Tables for Crystallography".[34] **11**: $C_{20}H_{25}NO_3$= 327.42. A colorless transparent prism, which was recrystallized from methyl acetate–hexane, was used for date collection and accurate cell determination, with the dimension of 0.50×0.50× 0.45 mm³. Crystal data are as follows: a=16.916(1), b=15.260(2), c=7.090(1) Å, β=98.33(1)°, V=1810.8(3) Å³, monoclinic, $P2_1/a$, Z=4, D_c=1.201 g cm^{-3}, $F(000)$=704, μ (Cu Kα)=6.505 cm^{-1}. 3086 unique reflections ($2\theta\leqq130°$) were measured, of which 2767 with $|F_o|\geqq2.67\sigma(F_o)$ were considered as observed. No absorption correction was applied. The final R value is 0.061 (R_w=0.079). **32d**: $C_{15}H_{22}O_4$=266.34. A colorless transparent prism, which was recrystallized from diisopropyl ether–pentate by vapor diffusion method, was used for data collection and accurate cell determination, with dimension of 0.50×0.40×0.35 mm³. Crystal data are as follows: a=7.354(1), b=9.765(1), c=20.425(4) Å, V=1466.6(5) Å³, orthorhombic, $Pca2_1$, Z=4, D_c=1.206 g cm^{-3}, $F(000)$=576, μ (Cu Kα)=7.131 cm^{-1}. 1123 unique reflections ($2\theta\leqq120°$) were measured, of which 1066 with $|F_o|\geqq2.67\sigma(F_o)$ were considered as observed. No absorption correction were applied. The final R value is 0.043 (R_w=0.052). The computation for structure determinations were carried out by Apollo DN/460. The complete F_o-F_c tables, atomic coordinates with equivalent isotropic or isotropic thermal parameters, bond lengths, bond angles and anisotropic thermal parameters for non H atoms were deposited as Document No. 8925 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Molecular Mechanics Calculations. The structural modelling and all calculations were performed on an IRIS 4D/80GT 3d-graphics workstation (Silicon Graphics) using the molecular modelling program SYBYL (Tripos Associates) and MOL-GRAPH (Daikin Industries). In the case of cycloheptene, chair, twisted boat and boat form models were built with MOL-GRAPH, and then each of them was minimized with MM2 (Allinger's MM2 1977-force field). Models of the other compounds were built with SYBYL or MOL-GRAPH. The energetically possible conformations were searched by use of the SEARCH command in SYBYL with Tripos force field. Each of them was minimized with MM2, thus the local minimal energy conformations were determined.

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