Trityl Antimonate-Catalyzed Sequential Reactions of Epoxides with Silylated Nucleophiles. Rearrangement of Epoxides and C–C or C–O Bond Forming Nucleophilic Reaction onto the Intermediate Carbonyl Compounds

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In the presence of a catalytic amount of trityl hexafluoroantimonate, sequential reactions of epoxides with silylated nucleophiles, rearrangement of epoxides and C–C or C–O bond forming nucleophilic reaction onto the intermediate carbonyl compounds, proceed smoothly to afford the corresponding products in fairly good yields by one-pot procedure. Trityl hexafluoroantimonate (5 mol %) efficiently promotes the above plural sequential reactions.

β-Hydroxy ester units constitute important building blocks of numerous natural products,[1] and these compounds have generally been synthesized starting from carbonyl or related compounds. On the other hands, the preparation of ethers is conventionally accomplished by coupling reactions of alkyl halides and sodium alkoxides,[2] however, formation of olefins from the halides sometimes takes place under these basic conditions. Recently, there have been reported several methods for the preparation of ethers by reductive condensation reaction from carbonyl or related compounds using trialkylsilane and some Lewis acids, for example, iodotrimethylsilane, TMSOTf, $TrClO_4$, and ZnI_2.[3] Here we would like to report a one-pot catalytic synthesis of the above-mentioned two types of compounds, β-hydroxy ester derivatives and several ethers, by way of the $TrSbF_6$-catalyzed sequential reactions of epoxides, rearrangement of epoxides followed by the respective nucleophilic reactions onto the initially formed carbonyl compounds with several silylated nucleophiles.

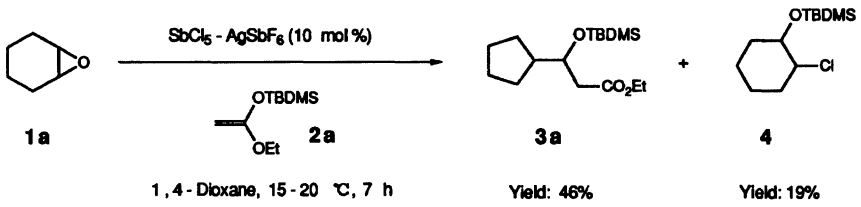
In the previous communications,[4] we have reported that, in the presence of catalytic amounts of metal halides and silver salts, fundamental synthetic reactions such as esterification, glycosylation, the Friedel–Crafts acylation, the Beckmann rearrangement, and pinacol rearrangement proceed smoothly to give the corresponding products in good yields. In order to expand the synthetic utility of these catalyst systems, new sequential reactions using epoxides and silylated nucleophiles were studied. Then, it was found that the sequential reactions, rearrangement and reductive condensation of epoxides proceeded in the presence of a catalytic amount of $SbCl_5$–$AgSbF_6$ or $TrSbF_6$, as it has been briefly reported in preliminary communication.[5] We also found that the sequential reactions, rearrangement of epoxides and addition reaction of ketene silyl acetals onto the intermediate carbonyl compounds proceeded smoothly under the similar reaction conditions to give β-hydroxy ester derivatives.

We now describe in full the results of our investigation on the above-mentioned several types of sequential reactions promoted by a catalytic amount of antimony(V) salt, and further application to the possible use of the other silylated nucleophiles as allyltrimethylsilane, cyanotrimethylsilane, and alkoxytrimethylsilane including allyltributyltin.

Results and Discussion

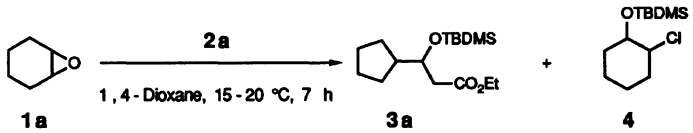
One-Pot Reactions of Epoxides and Ketene Silyl Acetals. First, the one-pot reaction of 7-oxabicyclo[4.1.0]heptane (**1a**) with 1-(*t*-butyldimethylsiloxy)-1-ethoxyethene (**2a**) was tried in several solvents using an antimony(V) salt. This salt is easily prepared in situ from $SbCl_5$ and $AgSbF_6$ and was effective in the catalytic Beckmann rearrangement[4d,4e] and pinacol rearrangement,[4f] as a catalyst. It was found that in the presence of the above catalyst (10 mol%) the sequential reactions proceeded smoothly at 15—20°C in 1, 4-dioxane to afford ethyl 3-(*t*-butyldimethylsiloxy)-3-cyclopentylbutanoate (**3a**) and 1-(*t*-butyldimethylsiloxy)-2-chlorocyclohexane (**4**) in 46 and 19% yields, respectively (Scheme 1). It is noted that only 1,4-dioxane was a suitable solvent whereas the reaction did not proceed in CH_2Cl_2, CH_3CN,[6] toluene, THF, and ether. The pathway of this method is postulated as shown in Scheme 2. The catalyst is considered to promote two sequential reactions; the rearrangement of epoxides and addition reaction of the intermediate cyclopentanecarbaldehyde (**5**) with **2a**.

Next, several Lewis acids and the amount of those Lewis acids were examined by taking the above-mentioned reaction of **1a** with **2a** as a model (Table 1). When the amount of $SbCl_5$–$AgSbF_6$ was decreased from 10 to 2 mol%, the yield of the desired compound **3a** was 56%, though the yield of **4** decreased from 19 to 4% (Entries 1—3). When the combinations of $SnCl_4$ or $TiCl_4$ and $AgSbF_6$ were employed as catalyst systems, **4** was also produced as a by-product. Only **4** was produced and the desired **3a** was not produced at all when $SbCl_5$ was employed alone as a catalyst (Entry 9). $AgSbF_6$ itself exhibited a rather good catalytic activity and **3a** was isolated in 40% yield (Entry 10). Next, triphenylmethylium salts such as $TrSbF_6$, $TrSbCl_6$, and $TrClO_4$ were employed as catalysts in the above reaction and the best result was obtained when **1a** and **2a** were added at once to the solution of a catalytic



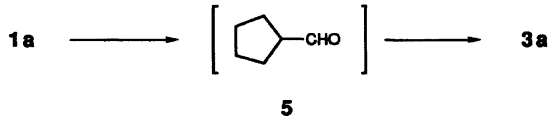
Scheme 1.

Table 1. Effect of Catalyst (Method A)

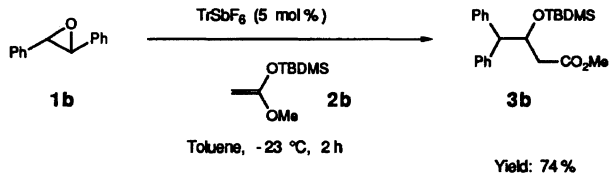


Entry	Catalyst	(mol%)	Yield/%	
			3a	4
1	$SbCl_5$–$AgSbF_6$	(10)	46	19
2	$SbCl_5$–$AgSbF_6$	(5)	52	10
3	$SbCl_5$–$AgSbF_6$	(2)	56	4
4	$SbCl_5$–$AgClO_4$	(2)	—	—[a]
5	$SbCl_5$–$AgBF_4$	(2)	—	—[a]
6	$SbCl_5$–AgOTf	(2)	—	—[a]
7	$TiCl_4$–$AgSbF_6$	(2)	51	—[a]
8	$SnCl_4$–$AgSbF_6$	(2)	50	—[a]
9	$SbCl_5$	(10)	—	23
10	$AgSbF_6$	(2)	40	
11	BF_3·OEt_2	(10)	—	
12	Ph_3CSbF_6	(2)	55	
13	Ph_3CSbF_6	(5)	66	
14	Ph_3CSbF_6	(10)	42	
15	Ph_3CClO_4	(10)	—	
16	Ph_3CSbCl_6	(10)	—	—[a]

a) **4** was not isolated.



Scheme 2.

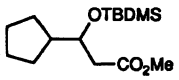
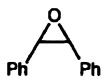
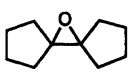
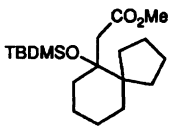
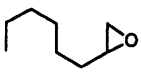
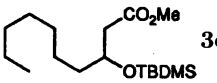
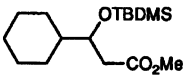


Scheme 3.

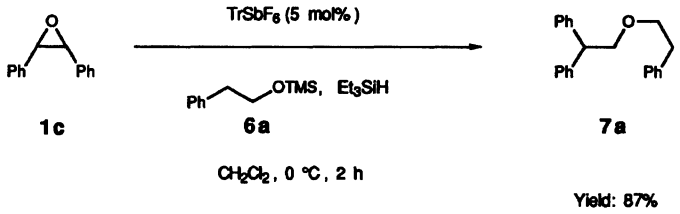
amount of $TrSbF_6$ in 1,4-dioxane at 15—20°C (Method A).[7] It is noted that SbF_6^- played an important role as a counterion of the active catalyst in this reaction (Table 1). Next, Method A was applied to the reaction of *trans*-2,3-diphenyloxirane (**1b**) and 1-(*t*-butyldimethylsiloxy)-1-methoxyethene (**2b**), but the reaction was not effectively promoted. Then, another method was investigated in which **1b** was added to the solution of a catalytic amount of $TrSbF_6$ in toluene at −23°C, and after stirring for 1 h, **2b** was added to the above reaction mixture (Method B). It was found that the one-pot reaction proceeded smoothly to afford methyl 3-(*t*-butyldimethylsiloxy)-4,4-diphenylbutanoate (**3b**) in 74% yield (Scheme 3).

Several examples of the present reaction are demonstrated in Table 2. In all cases, the reaction proceeds smoothly to give the corresponding products in moderate yields. The results show that, in the case of the substrates in which phenyl group or alkyl group migrates, the products were obtained in fairly good yields (Entries 1—4). While, in the case of the substrates in which hydrogen atom migrates, the products were obtained below 50% yield (Entries 6, 7). An interesting and unusual β-hydroxy ester derivative (**3d**) having a spiro unit, was also obtained by choosing a starting epoxide (Entry 5). The facility of rearrangement of phenyl group in the two geometric isomers **1b** or **1c** was not varied, and the same results were obtained starting from **1b** or **1c** (Entry 3, 4). The Method A was successfully applied to electron-rich epoxides with little steric hin-

Table 2. One-Pot Synthesis of β-Hydroxy Ester Derivatives from Eposides

Entry	Substrate	Nucleophile	Product	Method[a)]	Solvent	Temperature/°C	Yield/%
1	**1a**	**2b**	 **3c**	A	1,4-Dioxane	15—20	73
2	**1a**	**2a**	**3a**	A	1,4-Dioxane	15—20	66
3	**1b**	**2b**	**3b**	B	Toluene	−23	74
4	 **1c**	**2b**	**3b**	B	Toluene	−23	74
5	 **1d**	**2b**	 **3d**	B	Toluene	0	50
6	 **1e**	**2b**	 **3e**	A	1,4-Dioxane	15—20	48
7	 **1f**	**2b**	 **3f**	B	Toluene	−23	45

a) Method A: Epoxides and nucleophile were added at once to the solution of the catalyst in 1,4-dioxane at 15—20°C. B: First epoxide was added to the solution of the catalyst in toluene or CH_2Cl_2 at −23°C or 0°C, and after stirring for 1 h, a nucleophile was added to the reaction mixture.



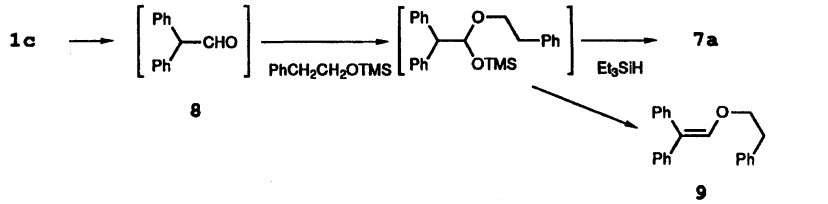
Scheme 4.

drance (Entries 1, 2, 6).

One-Pot Synthesis of Ethers from Epoxides. The above results indicate that a catalytic amount of $TrSbF_6$ would be effective for the sequential reactions of epoxides. This method was applied to a one-pot synthesis of ethers by treating *cis*-2,3-diphenyloxirane (**1c**) with trimethyl(2-phenylethoxy)silane (**6a**). The sequential reactions proceeded smoothly to afford 2, 2-diphenylethyl 2-phenylethyl ether (**7a**) in 87% yield (Scheme 4). The catalyst is considered to promote the two reactions; rearrangement of the epoxide and reductive condensation of diphenylacetaldehyde (**8**) with **6a** and triethylsilane. After screening detailed reaction conditions, it was shown that by-product, 2-2-diphenylethenyl 2-phenylethyl ether (**9**) was produced in 33% yield when $TrClO_4$ was used as a catalyst, while **9** was obtained as a main product when TMSOTf was used as a catalyst. Concerning the effect of solvent, CH_2Cl_2 was found to give the best result. While the rearrangement of the epoxide was not smoothly promoted in CH_3CN or ether. After all, the best promotion of the above sequential reactions was achieved when the reaction was carried out in CH_2Cl_2 in the presence of a catalytic amount of $TrSbF_6$ (Table 3).[8)]

Several examples of the present reaction are demonstrated in Table 4. Regardless of the type of the migrating groups (phenyl group (Entries 1—7, 10, 11), alkyl group (Entries 8, 12), or hydrogen atom (Entries 9, 13)), the reaction proceeds smoothly to give the corresponding products in good yields. Primary, secondary, and tertiary alkoxytrimethylsilanes are successfully employed in the present reaction. Among the reactions using the above silanes, (benzyloxy)trimethylsilane, *t*-butoxytrimethylsilane, or (allyloxy)trimethylsilane provides a convenient method for the preparation of alcohols having synthetically useful protecting groups (Entries 3, 5, 6). When alkoxysilane was not added to the reaction mixture, a symmetrical ether (**7b**) was produced in good yield (Entry 1, 7). Since epoxides are starting materials of this new sequential procedure, the preparations of ethers are successfully performed even when the corresponding carbonyl compounds are un-

Table 3. Effect of Catalyst and Solvent[a)]



Entry	Catalyst (5 mol%)	Solvent	Yield/%	
			7a	9
1	$SbCl_5$–$AgSbF_6$	CH_2Cl_2	60	—[b)]
2	$SbCl_5$–$AgClO_4$	CH_2Cl_2	39	—[b)]
3	Ph_3CSbF_6	CH_2Cl_2	87	2
4	Ph_3CClO_4	CH_2Cl_2	47	33
5	TMSOTf	CH_2Cl_2	Trace	43
6	BF_3·OEt_2	CH_2Cl_2	—	—[b)]
7	Ph_3CSbF_6	Toluene	65	—[b)]
8	Ph_3CSbF_6	CH_3CN	—	—
9	Ph_3CSbF_6	Ether	—	—

a) Reactions were carried out at 0°C for 2 h. b) **9** was not isolated.

stable.

One-Pot Reaction of 2,3-Diphenyloxiranes with Various Nucleophiles. In order to expand the scope of effectiveness of the above-mentioned new sequential reactions, one-pot reactions of 2,3-diphenyloxiranes with various nucleophiles were studied. As shown in Scheme 5, three types of routes (A—C) were considered to give the desired products, homoallyl alcohol, α-alkoxy nitrile, and β-hydroxy ketone derivatives, and it was found that the corresponding products were obtained in fairly good yields by choosing the best conditions for each nucleophile. Several examples of the reactions are demonstrated in Table 5. Route A[9)] is successfully applied to the reactions using allyltin or silyl enol ethers as a nucleophile (Entries 3, 4, 10, 11, 12). Route B[10)] is the best route for the one-pot synthesis of ethers using epoxides, alkoxysilanes, and triethylsilane (Entries 1, 2). Route C[11)] is successfully applied to the reactions using allylsilane or TMSCN as a nucleophile (Entries 6, 8). Acetal (**10e**) is also obtained in 74% yield by this one-pot procedure using 2,2 times molar quantity of TMSOMe to the epoxide (Entry 9).[12)] It is noted that in the case of the reactions using allylsilane or TMSCN as a nucleophile, $TrSbF_6$ (5 mol%) efficiently promotes the three sequential reactions; that is (1) rearrangement of an epoxide, (2) acetalization of the initially formed **8**, and (3) cyanation or allylation of the formed acetal (**10e**).

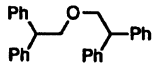
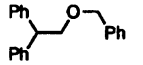
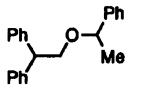
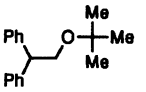
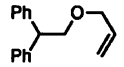
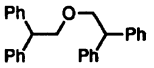
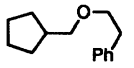
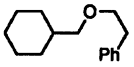
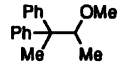
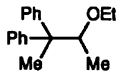
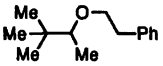
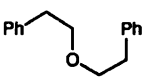
It is concluded that in the presence of a catalytic amount of $TrSbF_6$, two types of sequential reactions; (1) the reaction of epoxides with ketene silyl acetals, (2) the reaction of epoxides with alkoxysilanes and triethylsilane, are promoted smoothly by one-pot procedure. Furthermore, sequential reactions of epoxides, rearrangement of epoxides followed by acetalization onto the initially formed carbonyl compound, or followed by C–C bond forming reactions onto the initially formed carbonyl or related compounds by way of allylation, cyanation, or aldol reaction, have been achieved according to the present one-pot procedure.

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, d=doublet, t=triplet, q=quartet, dt=doublet triplet, dq=double quartet, ddt=double double triplet, ddd=double double doublet, dddd=double double double doublet, ddddd=double double double double doublet. Mass spectra (EI) or (CI) 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. 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. $TrSbF_6$,[13)] $TrSbCl_6$,[14)] and $TrClO_4$[15)] were prepared by the previously reported methods. *trans*-2,3-diphenyloxirane (**1b**), 7-oxabicyclo[4.1.0]heptane (**1a**), 2-phenyloxirane (**1i**), 2-hexyloxirane (**1e**), methoxytrimethylsilane, ethoxytrimethylsilane, (allyloxy)trimethylsilane were commercially available and were purified by distillation or recrystallization. *cis*-2,3-Diphenyloxirane (**1c**) and 2,2,3,3-tetramethyloxirane (**1h**) were prepared by oxidation reaction of the corresponding olefins with *m*-chloroperbenzoic acid. 1-Oxaspiro[2.5]octane (**1f**) was prepared by the previously reported method.[16)] 11-Oxadispiro[4.0.4.1]undecane

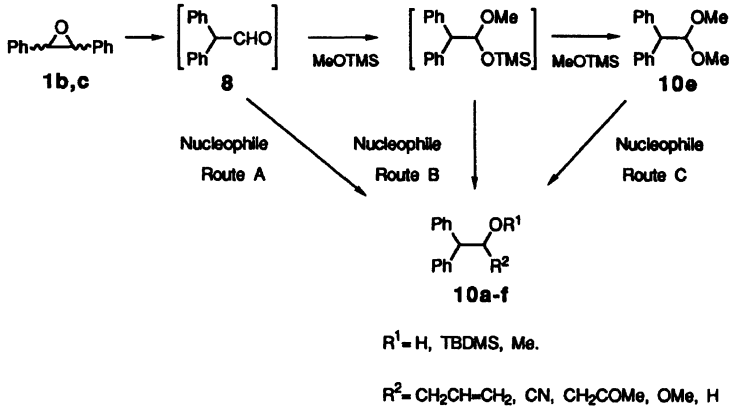
Table 4. One-Pot Synthesis of Ethers from Epoxides[a)]

Entry	Substrate	R (ROTMS)	Product		Temperature/°C	Time/h	Yield/%
1	**1c**	—		**7b**	0	2	85
2	**1c**		**7a**		0	2	87
3	**1c**			**7c**	0	2	83
4	**1c**			**7d**	0	3	65
5	**1c**			**7e**	0	3	65
6	**1c**			**7f**	0	2	89
7	**1b**	—		**7b**	0	2	84
8[b)]	**1a**			**7g**	15—20	2	73
9		**1f** 		**7h**	0	2	85
10[c)]		**1g**	Me		**7i**	15—20	Overnight	88
11[c)]	**1g**		Et		**7j**	R.T.	48	49
12		**1h** 		**7k**	0	2	74
13		**1i** 		**7l**	0	2	31

a) Catalyst: Ph_3CSbF_6 (5 mol%). Solvent: CH_2Cl_2. b) The reaction was carried out in 1,4-dioxane. After addition of epoxide and **6a** to a solution of the catalyst, Et_3SiH was added. c) MeOTMS was used 3 times molar quantity to the epoxide.

(**1d**) and *cis*-2,3-diphenyl-2,3-dimethyloxirane (**1g**) were prepared by reductive coupling reaction[17)] of the corresponding ketones, followed by oxidation reaction of the produced olefins with *m*-chloroperbenzoic acid. Silyl enol ethers or ketene silyl acetals were prepared by silylation of the corresponding enolates of ketones or esters, and purified by distillation. Alkoxysilanes except for *t*-butoxytrimethylsilane were prepared by treatment of the corresponding alcohols with chlorotrimethylsilane and triethylamine, and purified by distillation. *t*-Butoxytrimethylsilane was prepared by treatment of *t*-butyl alcohol with chlorotrimethylsilane and imidazole in DMF, and purified by distillation.

Preparation of β-Hydroxy Ester Derivatives from Epoxides. $SbCl_5$–$AgSbF_6$ as a Catalyst: A CH_2Cl_2 solution of 1.0 M (1 M=1 mol dm^{-3}) antimony(V) chloride (0.05 ml, 0.05 mmol) was added to a solution of $AgSbF_6$ (17.2 mg, 0.0501 mmol) in 1,4-dioxane (3.0 ml) under ice cooling with the protection from the light. After stirring for



Scheme 5.

1 h, a 1,4-dioxane (1.5 ml) solution of 7-oxabicyclo[4.1.0]-heptane (**1a**) (49.1 mg, 0.500 mmol) and 1-(*t*-butyldimethylsiloxy)-1-ethoxyethene (**2a**) (151.8 mg, 0.7500 mmol) was added. After stirring for 7 h at 15—20°C, the mixture was quenched with aqueous saturated $NaHCO_3$. The organic materials were extracted with CH_2Cl_2, and combined extract was dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by flash column chromatography on silica gel (70 : 1 hexane–ethyl acetate as an eluent) to give **3a** (68.5 mg, 46%) and 1-(*t*-butyldimethylsiloxy)-2-chlorocyclohexane (**4**) (23.6 mg, 19%). IR, ^{1}H NMR, and MS spectra of **3a** were identical with those of the authentic sample prepared by Method A in Table 2.

1-(*t*-Butyldimethylsiloxy)-2-chlorocyclohexane (4). IR (neat) 1010, 840, and 780 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ= 0.08 (3H, s), 0.11 (3H, s), 0.90 (9H, s), 1.2—1.4 (3H, m), 1.6—1.8 (3H, m), 1.9—2.0 (1H, m), 2.1—2.3 (1H, m), 3.59 (1H, dt, J=3.9 and 7.8 Hz), 3.72 (1H, ddd, J=3.9, 7.8, and 8.8 Hz); MS m/z (rel intensity) 249 (M^++1; 0.014), 247 (M^+−1; 0.042), 235 (0.2), 233 (0.6), 193 (8), 191 (23), 125 (11), 123 (39), 93 (34), 91 (base peak), and 75 (23). Found: C, 57.77; H, 10.28; Cl, 13.94%. Calcd for $C_{12}H_{25}OClSi$: C, 57.92; H, 10.13; Cl, 14.25%.

TrSbF$_6$ as a Catalyst (Method A): A typical procedure is described for methyl 3-(*t*-butyldimethylsiloxy)-3-cyclopentylpropanoate (**3c**) from 7-oxabicyclo[4.1.0]heptane (**1a**) using $TrSbF_6$ as a catalyst: Under an argon atmosphere, a solution of 7-oxabicyclo[4.1.0]heptane (**1a**) (49.1 mg, 0.500 mmol) and 1-(*t*-butyldimethylsiloxy)-1-methoxyethene (**2b**) (113 mg, 0.600 mmol) in 1,4-dioxane (1.5 ml) was added to a solution of $TrSbF_6$ (12 mg, 0.025 mmol) in 1, 4-dioxane (3.0 ml) at 15—20°C. After stirring for 7 h, the reaction was quenched with phosphate buffer (pH 7). The organic materials were extracted with CH_2Cl_2, and combined extract was separated and dried over Na_2SO_4. The evaporation of the solvent gave a crude product which was purified by flash column chromatography on silica gel (70 : 1 hexane–ethyl acetate as an eluent) to give **3c** (104.1 mg, 73%). IR (neat) 1740 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=0.02 (3H, s), 0.06 (3H, s), 0.87 (9H, s), 1.2—1.8 (8H, m), 1.9—2.1 (1H, m), 2.46 (2H, d, J=6.4 Hz, $CH_2CO_2CH_3$), 3.66 (3H, s, CO_2CH_3), 4.05 (1H, m); MS m/z (rel intensity) 285 (M^+−1; 0.1), 271 (1.7), 255 (1.6), 229 (78), 197 (16), 89 (base peak), 73 (51), 59 (25), and 41 (14). Found: C, 62.72; H, 10.55%. Calcd for $C_{15}H_{30}O_3Si$: C, 62.89; H, 10.55%.

Physical properties of other products are presented:

Ethyl 3-(*t*-Butyldimethylsiloxy)-3-cyclopentylpropanoate (3a). IR (neat) 1740 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=0.03 (3H, s), 0.06 (3H, s), 0.87 (9H, s), 1.26 (3H, t, J=7.3 Hz, CH_2CH_3), 1.3—1.8 (8H, m), 1.9—2.1 (1H, m), 2.44 (2H, d, J=5.7 Hz, CH_2CO_2Et), 4.0—4.15 (3H, m); MS m/z (rel intensity) 299 (M^+−1; 0.04), 285 (0.7), 255 (2.4), 243 (48), 215 (21), 173 (21), 103 (31), 81 (36), 75 (base peak), 59 (24), and 41 (23). Found: C, 64.01; H, 10.72%. Calcd for $C_{16}H_{32}O_3Si$: C, 63.95; H, 10.73%.

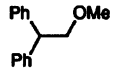
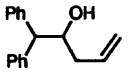
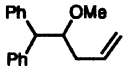
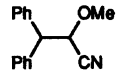
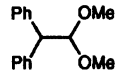
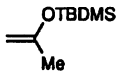
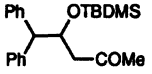
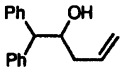
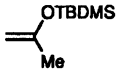
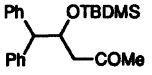
Methyl 3-(*t*-Butyldimethylsiloxy)decanoate (3e). IR (neat) 1740 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=0.03 (3H, s), 0.06 (3H, s), 0.86 (9H, s), 0.88 (3H, t, J=6.4 Hz), 1.2—1.5 (12H, m), 2.43 (2H, d, J=6.4 Hz, CH_2CO_2Me), 3.66 (3H, s, CO_2CH_3), 4.0—4.1 (1H, m); MS m/z (rel intensity) 315 (M^+−1; 0.1), 301 (1.3), 285 (0.8), 259 (63), 217 (12), 159 (12), 131 (14), 89 (base peak), 73 (35), 59 (16), and 41 (9). Found: C, 64.68; H, 11.70%. Calcd for $C_{17}H_{36}O_3Si$: C, 64.50; H, 11.46%.

TrSbF$_6$ as a Catalyst (Method B): A typical procedure is described for methyl 3-(*t*-butyldimethylsiloxy)-4,4-diphenylbutanoate (**3b**) from *trans*-2,3-diphenyloxirane (**1b**) using $TrSbF_6$ as a catalyst: Under an argon atmosphere, a solution of *trans*-2,3-diphenyloxirane (**1b**) (98.1 mg, 0.500 mmol) in toluene (1.5 ml) was added to a solution of $TrSbF_6$ (12 mg, 0.025 mmol) in toluene (2.0 ml) at −23°C. After stirring for 1 h, a solution of 1-(*t*-butyldimethylsiloxy)-1-methoxyethene (**2b**) (113 mg, 0.600 mmol) in toluene (0.5 ml) was added to the reaction mixture. After stirring for 1 h, the reaction was quenched with phosphate buffer (pH 7). The organic layer was separated and dried over Na_2SO_4. The evaporation of the solvent gave a crude product which was purified by preparative thin-layer chromatography on silica gel (10 : 1 hexane–ethyl acetate as a developing solvent) to give **3b** (142.3 mg, 74%). IR (neat) 1740 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=−0.49 (3H, s), −0.07 (3H, s), 0.72 (9H, s), 2.44 (1H, dd, J=5.3 and 15.6 Hz, CH_2CO_2Me), 2.54 (1H, dd, J=5.3 and 15.6 Hz, CH_2CO_2Me), 3.61 (3H, s, CO_2CH_3), 4.10 (1H, d, J=7.3 Hz, Ph_2CH), 4.7—4.9 (1H, m), 7.1—7.4 (10H, m); MS m/z (rel intensity) 383 (M^+−1; 0.1), 369 (0.9), 327 (46), 253 (11), 217 (42), 165 (12), 115 (30), 89 (91), 73 (base peak), 59 (37), and 41 (6). Found: C, 71.74; H, 8.41%. Calcd for $C_{23}H_{32}O_3Si$: C, 71.83; H, 8.39%.

Physical properties of other products are presented:

Methyl 6-(*t*-Butyldimethylsiloxy)spiro[4.5]decane-

Table 5. One-Pot Reactions of 2,3-Diphenyloxirane and Various Nucleophiles[a)]

Entry	Substrate	Equiv (MeOTMS)	Nucleophile	Product	Route	Yield/%
1	 **1c**	1.2	Et_3SiH	 **10a**	B	84
2	**1c**	2.2	Et_3SiH	**10a**	C	67
3	**1c**	—	CH_2=$CHCH_2SnBu_3$	 **10b**	A	87
4	**1c**	1.2	CH_2=$CHCH_2SnBu_3$	 **10c**	B	—
5	**1c**	1.2	CH_2=$CHCH_2SiMe_3$	**10c**	B	39
6	**1c**	2.2	CH_2=$CHCH_2SiMe_3$	**10c**	C	74
7	**1c**	1.2	TMSCN	 **10d**	B	51
8	**1c**	2.2	TMSCN	**10d**	C	72
9	**1c**	1.2	TMSOMe	 **10e**		74
10	**1c**	—		 **10f**	A	70
11	 **1b**	—	CH_2=$CHCH_2SnBu_3$	 **10b**	A	79
12	**1b**	—		 **10f**	A	66

a) Reactions were carried out by Method B in Table 2.

6-acetate (3d). IR (neat) 1740 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.03 (3H, s), 0.11 (3H, s), 0.87 (9H, s), 1.0—2.2 (16H, m), 2.54 (1H, d, J=13.7 Hz, CH_2CO_2Me), 2.78 (1H, d, J=13.7 Hz, CH_2CO_2Me), 3.64 (3H, s, CO_2CH_3); MS m/z (rel intensity) 325 (M^+-15; 0.9), 283 (base peak), 131 (39), 89 (57), 73 (37), 59 (14), and 41 (8). Found: C, 67.01; H, 10.82%. Calcd for $C_{19}H_{36}O_3Si$: C, 67.01; H, 10.65%.

Methyl 3-(*t*-Butyldimethylsiloxy)-3-cyclohexylpropanoate (3f). IR (neat) 1740 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.01 (3H, s), 0.05 (3H, s), 0.87 (9H, s), 0.9—1.8 (11H, m), 2.41 (2H, d, J=6.4 Hz, CH_2CO_2Me), 3.66 (3H, s, CO_2CH_3), 3.9—4.0 (1H, m); MS m/z (rel intensity) 299 (M^+-1; 0.1), 285 (1.8), 243 (base peak), 211 (14), 159 (14), 131 (21), 95 (39), 89 (88), 73 (56), 59 (37), and 41 (25). Found: C, 63.98; H, 10.94%. Calcd for $C_{16}H_{32}O_3Si$: C, 63.95; H, 10.73%.

Preparation of Ethers from Epoxides. $TrClO_4$ as a Catalyst: TrCl (7.0 mg, 0.025 mmol) was added to a CH_2Cl_2 (2.0 ml) solution of $AgClO_4$ (5.2 mg, 0.025 mmol) under ice cooling with the protection from the light. After stirring for 1 h, a CH_2Cl_2 (1.5 ml) solution of *cis*-2,3-diphenyloxirane (**1c**) (98.1 mg, 0.50 mmol) was added. The reaction mixture was stirred for 1 h. A CH_2Cl_2 (0.5 ml) solution of trimethyl(2-phenylethoxy)silane (**6a**) (117 mg, 0.602 mmol) was added to the mixture, followed by addtion of a CH_2Cl_2 solution of triethylsilane (64 mg, 0.55 mmol). After stirring for 1 h, the reaction was quenched with phosphate buffer (pH 7). The organic layer was separated and dryed over Na_2SO_4. The evaporation of the solvent gave a crude product which was purified by preparative thin-layer chromatography on silica gel (toluene as a developing solvent) to afford **7a** (76 mg, 50%) and 2,2-diphenylethenyl 2-phenylethyl ether (**9**) (49 mg, 33%). IR, ^1H NMR, MS spectra of **7a** were identical with those of the authentic sample

prepared by the method in Table 4.

2,2-Diphenylethenyl 2-Phenylethyl Ether (9). IR (neat) 1200, 1120, and 1020 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.00 (2H, t, J=7.1 Hz), 4.13 (2H, t, J=7.1 Hz), 6.47 (1H, s), 7.1—7.4 (15H, m); MS m/z (rel intensity) 300 (M^+; 4), 195 (2), 105 (base peak), 91 (3), and 77 (9). Found: C, 87.75; H, 6.76%. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71%.

$TrSbF_6$ as a Catalyst: A typical procedure is described for 2-2-diphenylethyl 2-phenylethyl ether (**7a**) from *cis*-2,3-diphenyloxirane (**1c**) using $TrSbF_6$ as a catalyst: Under an argon atmosphere, a solution of *cis*-2,3-diphenyloxirane (**1c**) (98.1 mg, 0.50 mmol) in CH_2Cl_2 (1.5 ml) was added to a solution of $TrSbF_6$ (12 mg, 0.025 mmol) in CH_2Cl_2 (2.0 ml) at 0°C. After stirring for 1 h, a solution of trimethyl(2-phenylethoxy)silane (**6a**) (117 mg, 0.602 mmol) in CH_2Cl_2 (0.5 ml) was added, followed by addition of a solution of triethylsilane (64 mg, 0.55 mmol) in CH_2Cl_2 (0.5 ml). After stirring for 1 h, the reaction was quenched with phosphate buffer (pH 7). The organic layer was separated and dried over Na_2SO_4. The evaporation of the solvent gave a crude product which was purified by preparative thin-layer chromatography (toluene as a developing solvent) to give **7a** (131 mg, 87%). IR (neat) 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.83 (2H, t, J=7.1 Hz), 3.67 (2H, t, J=7.1 Hz), 3.97 (2H, d, J=7.2 Hz, Ph_2CHCH_2), 4.27 (1H, t, J=7.2 Hz, Ph_2CHCH_2), 7.0—7.3 (15H, m); MS m/z (rel intensity) 301 (M^+-1; 17), 197 (4), 181 (75), 167 (19), 105 (base peak), 91 (24), and 77 (12). Found: C, 87.20; H, 7.37%. Calcd for $C_{22}H_{22}O$: C, 87.38; H, 7.33%.

Physical properties of other products are presented:

Bis(2,2-diphenylethyl) Ether (7b). IR (neat) 1120 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.98 (4H, d, J=6.8 Hz, Ph_2CHCH_2), 4.23 (2H, t, J=6.8 Hz, Ph_2CHCH_2), 7.0—7.3 (20H, m); MS m/z (rel intensity) 379 (M^++1; 1.7), 197 (8), 181 (base peak), 167 (21), 154 (46), 137 (37), 119 (45), 103 (28), 91 (32), 77 (23), and 39 (13). Found: C, 88.68; H, 6.90%. Calcd for $C_{28}H_{26}O$: C, 88.85; H, 6.92%.

2,2-Diphenylethyl Phenylmethyl Ether (7c). IR (neat) 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.98 (2H, d, J=7.3 Hz, Ph_2CHCH_2), 4.33 (1H, t, J=7.3 Hz, Ph_2CHCH_2), 4.54 (2H, s, CH_2Ph), 7.1—7.4 (15H, m); MS m/z (rel intensity) 288 (M^+; 0.7), 167 (base peak), 152 (11), 91 (42), 77 (6), 65 (12), 51 (4), and 39 (4). Found: C, 87.23; H, 7.03%. Calcd for $C_{21}H_{20}O$: C, 87.46; H, 6.99%.

2,2-Diphenylethyl 1-Phenylethyl Ether (7d). IR (neat) 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.36 (3H, d, J=6.6 Hz, CH_3), 3.82 (2H, m, Ph_2CHCH_2), 4.26 (1H, t, J=7.1 Hz, Ph_2CHCH_2), 4.39 (1H, q, J=6.6 Hz, $PhCHCH_3$), 7.1—7.4 (15H, m); MS m/z (rel intensity) 302 (M^+; 0.2), 167 (base peak), 105 (65), 91 (6), 77 (20), 65 (3), 51 (6), and 39 (4). Found: C, 87.37; H, 7.40%. Calcd for $C_{22}H_{22}O$: C, 87.38; H, 7.33%.

***t*-Butyl 2,2-Diphenylethyl Ether (7e).** IR (neat) 1080 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.14 (9H, s), 3.87 (2H, d, J=6.8 Hz, Ph_2CHCH_2), 4.17 (1H, t, J=6.8 Hz, Ph_2CHCH_2), 7.1—7.3 (10H, m); MS m/z (rel intensity) 254 (M^+; 0.8), 196 (2), 181 (10), 167 (base peak), 152 (8), 103 (8), 77 (9), 57 (73), 51 (4), and 41 (17). Found: C, 84.87; H, 8.77%. Calcd dor $C_{18}H_{22}O$: C, 84.99; H, 8.72%.

Allyl 2,2-Diphenylethyl Ether (7f). IR (neat) 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.96 (2H, d, J=7.3 Hz, Ph_2CHCH_2), 4.00 (2H, dt, J=5.4 and 1.5 Hz, $OCH_2CH=CH_2$), 4.29 (1H, t, J=7.3 Hz, Ph_2CHCH_2), 5.14 (1H, dq, J=9.5 and 1.5 Hz, $OCH_2CH=CH_2$), 5.21 (1H, dq, J=15.6 and 1.5 Hz, $OCH_2CH=CH_2$), 5.87 (1H, ddt, J=9.5, 5.4, and 15.6 Hz, $OCH_2CH=CH_2$), 7.1—7.4 (10H, m); MS m/z (rel intensity) 239 (M^++1; 5), 197 (6), 181 (base peak), 167 (34), 103 (17), 91 (28), 77 (8), and 41 (22). Found: C, 85.71; H, 7.56%. Calcd for $C_{17}H_{18}O$: C, 85.68; H, 7.61%.

Cyclopentylmethyl 2-Phenylethyl Ether (7g). IR (neat) 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.1—1.3 (2H, m), 1.4—1.6 (4H, m), 1.6—1.8 (2H, m), 2.0—2.2 (1H, m), 2.88 (2H, t, J=7.3 Hz), 3.31 (2H, d, J=7.3 Hz, $C_5H_9CH_2O$), 3.63 (2H, t, J=7.3 Hz), 7.1—7.3 (5H, m); MS m/z (rel intensity) 204 (M^+; 0.7), 135 (0.1), 122 (1), 113 (2), 105 (15), 91 (16), 83 (base peak), 77 (12), 55 (55), and 41 (25). Found: C, 81.92; H, 10.11%. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87%.

Cyclohexylmethyl 2-Phenylethyl Ether (7h). IR (neat) 1120 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.8—1.0 (2H, m), 1.1—1.4 (3H, m), 1.5—1.8 (6H, m), 2.88 (2H, t, J=7.3 Hz), 3.23 (2H, d, J=6.4 Hz, $C_6H_{11}CH_2O$), 3.61 (2H, t, J=7.3 Hz), 7.1—7.3 (5H, m); MS m/z (rel intensity) 218 (M^+; 11), 127 (14), 113 (2), 105 (33), 97 (base peak), 91 (23), 77 (21), 55 (78), and 41 (26). Found: m/z 219.1731. Calcd for $C_{15}H_{22}O$: M+H, 219.1749.

1,2,2-Trimethylpropyl 2-Phenylethyl Ether (7k). IR (neat) 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.84 (9H, s), 1.03 (3H, d, J=6.3 Hz, $CHCH_3$), 2.85 (2H, m), 2.98 (1H, q, J=6.3 Hz, $CHCH_3$), 3.4—3.5 (1H, m), 3.7—3.8 (1H, m), 7.1—7.3 (5H, m); MS m/z (rel intensity) 206 (M^+; 0.7), 191 (0.1), 149 (56), 105 (base peak), 91 (13), 85 (34), 77 (25), 65 (6), 57 (18), 51 (6), and 43 (31). Found: m/z 207.1777. Calcd for $C_{14}H_{22}O$: M+H, 207.1749.

Methyl 1-Methyl-2,2-diphenylpropyl Ether (7i). IR (neat) 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.97 (3H, d, J=6.1 Hz, CH_3OCHCH_3), 1.66 (3H, s, Ph_2CHCH_3), 3.34 (3H, s), 4.05 (1H, q, J=6.1 Hz, CH_3OCHCH_3), 7.0—7.4 (10H, m); MS m/z 181 (M^+-59; 27), 165 (22), 103 (21), 91 (6), 77 (12), and 59 (base peak). Found: C, 84.80; H, 8.46%. Calcd for $C_{17}H_{20}O$: C, 84.96; H, 8.39%.

Ethyl 1-Methyl-2,2-diphenylpropyl Ether (7j). IR (neat) 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.99 (3H, d, J=6.4 Hz, $CH_3CH_2OCHCH_3$), 1.11 (3H, t, J=7.2 Hz, OCH_2CH_3), 1.67 (3H, s, Ph_2CHCH_3), 3.2—3.4 (1H, m, CH_3CH_2O), 3.5—3.7 (1H, m, CH_3CH_2O), 4.10 (1H, q, J=6.4 Hz, $CH_3CH_2OCHCH_3$), 7.0—7.4 (10H, m); MS m/z (rel intensity) 253 (M^+-1; 6), 239 (2), 209 (40), 181 (12), 105 (32), 91 (33), 73 (base peak), and 45 (67). Found: C, 84.80; H, 8.86%. Calcd for $C_{18}H_{22}O$: C, 84.99; H, 8.72%.

Bis(2-phenylethyl) Ether (7l). IR (neat) 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.88 (4H, t, J=7.1 Hz), 3.66 (4H, t, J=7.1 Hz), 7.1—7.4 (10H, m); MS m/z (rel intensity) 226 (M^+; 0.5), 135 (13), 105 (base peak), 91 (20), and 77 (18). Found: m/z 227.1436. Calcd for $C_{16}H_{18}O$: M+H, 227.1394.

Methyl 2,2-Diphenylethyl Ether (10a). IR (neat) 1120 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.36 (3H, s, CH_3), 3.92 (2H, d, J=7.3 Hz, CH_2OCH_3), 4.28 (1H, t, J=7.3 Hz, Ph_2CHCH_2); MS m/z (rel intensity) 213 (M^++1; 38), 181 (base peak), 167 (21), 135 (6), 91 (2), 85 (2), and 73 (4). Found: C, 84.63; H, 7.61%. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60%.

Preparation of Homoallyl Alcohol Derivatives and β-Hydroxy Carbonyl Compound from Epoxides (Route A). A typical procedure is described for 1,1-

diphenyl-4-penten-2-ol (**10b**) from *cis*-2,3-diphenyloxirane (**1c**) using $TrSbF_6$ as a catalyst: Under an argon atmosphere, a solution of *cis*-2,3-diphenyloxirane (**1c**) (98.1 mg, 0.500 mmol) in CH_2Cl_2 (1.5 ml) was added to a solution of $TrSbF_6$ (12 mg, 0.025 mmol) in CH_2Cl_2 (2.0 ml) at 0°C. After stirring for 1 h, a solution of allyltributyltin (173.8 mg, 0.5250 mmol) in CH_2Cl_2 (0.5 ml) was added to the mixture. After stirring for 1 h, the reaction was quenched with phosphate buffer (pH 7). The organic layer was separated and dried over Na_2SO_4. The evaporation of the solvent gave a crude product which was purified by preparative thin-layer chromatography on silica gel (15 : 1 hexane–ethyl acetate as a developing solvent) to give **10b** (100 mg, 84%). IR (neat) 3560, 3450 (OH), 1640, 1600, 1500, 1450, 1060, and 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.74 (1H, d, J=3.5 Hz, OH), 2.13 (1H, ddddd, J=14.2, 8.0, 7.8, 1.5, and 1.2 Hz, CH_2=CHCH_2), 2.32 (1H, ddddd, J=14.2, 6.4, 3.7, 1.5, and 1.2 Hz, CH_2=CHCH_2), 3.92 (1H, d, J=8.5 Hz, Ph_2CH), 4.43 (1H, dddd, J=8.5, 8.0, 3.7, and 3.5 Hz, C*H*OH), 5.07 (1H, dddd, J=17.1, 2.2, 1.5, and 1.2 Hz, CH_2=CHCH_2), 5.12 (1H, dddd, J=10.5, 2.2, 1.5, and 1.2 Hz, CH_2=CHCH_2), 5.90 (1H, dddd, J=17.1, 10.5, 7.8, and 6.4 Hz, CH_2=C*H*CH_2), 7.1—7.2 (10H, m); MS *m/z* (rel intensity) 238 (M^+; 0.1), 220 (0.2), 197 (5), 168 (base peak), 152 (15), 105 (13), 91 (18), and 77 (10). Found: C, 85.39; H, 7.62%. Calcd for $C_{17}H_{18}O$: C, 85.68; H, 7.61%.

Physical properties of other products are presented:

5,5-Diphenyl-4-methoxy-1-pentene (10c). IR (neat) 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.17 (1H, ddddd, J=14.6, 7.1, 5.1, 1.5, and 1.2 Hz, CH_2CH=CH_2), 2.34 (1H, ddddd, J=14.6, 7.0, 5.1, 1.5, and 1.2 Hz, CH_2CH=CH_2), 3.23 (3H, s, CH_3), 3.95 (1H, dt, J=8.3 and 5.1 Hz, C*H*OCH_3), 4.02 (1H, d, J=8.3 Hz, Ph_2CH), 4.99 (1H, dddd, J=17.1, 1.9, 1.5, and 1.2 Hz, CH_2CH=CH_2), 5.07 (1H, dddd, J=10.1, 1.9, 1.5, and 1.2 Hz, CH_2CH=CH_2), 5.87 (1H, dddd, J=17.1, 10.1, 7.1, and 7.0 Hz, CH_2C*H*=CH_2); MS *m/z* (rel intensity) 251 (M^+-1; 0.02), 220 (0.08), 211 (11), 167 (13), 165 (18), 105 (8), 91 (7), 85 (base peak), 77 (6), and 55 (23). Found: C, 85.55; H, 7.99%. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99%.

4-(*t*-Butyldimethylsiloxy)-5,5-diphenyl-2-pentanone (10f). IR (neat) 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=−0.48 (3H, s), −0.11 (3H, s), 0.71 (9H, s), 1.97 (3H, s, COCH_3), 2.62 (2H, d, J=5.9 Hz, CH_2COCH_3), 4.03 (1H, d, J=6.4 Hz, Ph_2CH), 4.8—5.0 (1H, m), 7.1—7.4 (10H, m); MS *m/z* (rel intensity) 353 (M^+-15; 0.1), 311 (6), 253 (12), 201 (22), 165 (17), 129 (17), 115 (base peak), 75 (44), 59 (5), and 43 (12). Found: C, 75.12; H, 8.88%. Calcd for $C_{23}H_{32}O_2Si$: C, 74.95; H, 8.75%.

Preparation of α-Alkoxy Nitriles from Epoxides (Route B). A typical procedure is described for 2-methoxy-3,3-diphenylpropanenitrile (**10d**) from *cis*-2,3-diphenyloxirane (**1c**) using $TrSbF_6$ as a catalyst: Under an argon atmosphere, a solution of *cis*-2,3-diphenyloxirane (**1c**) (98.1 mg, 0.500 mmol) in CH_2Cl_2 (1.5 ml) was added to a solution of $TrSbF_6$ (12 mg, 0.025 mol%) in CH_2Cl_2 (2.0 ml) at 0°C. After stirring for 1 h, methoxytrimethylsilane (0.083 ml, 0.60 mmol) was added, followed by addition of a solution of trimethylsilyl cyanide (59.5 mg, 0.600 mmol) in CH_2Cl_2 (0.5 ml). After stirring for 1 h, the reaction was quenched with phosphate buffer (pH 7). The organic layer was separated and dried over Na_2SO_4. The evaporation of the solvent gave a crude product which was purified by preparative thin-layer chromatography on silica gel (10 : 1 hexane–ethyl acetate as a developing solvent) to afford **10d** (60.1 mg, 51%). IR (neat) 2240 (CN), 1600, 1500, 1450, and 1120 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.51 (3H, s, OCH_3), 4.40 (1H, d, J=7.8 Hz), 4.67 (1H, d, J=7.8 Hz), 7.1—7.4 (10H, m); MS *m/z* (rel intensity) 237 (M^+; 0.06), 167 (base peak), and 152 (16). Found: C, 80.70; H, 6.29; N, 5.53%. Calcd for $C_{16}H_{15}NO$: C, 80.99; H, 6.37; N, 5.90%.

Preparation of Acetals from Epoxides. (2,2-Dimethoxy-1-phenylethyl)benzene (10e). Under an argon atmosphere, a solution of *cis*-2,3-diphenyloxirane (**1c**) (98.1 mg, 0.500 mmol) in CH_2Cl_2 (1.5 ml) was added to a solution of $TrSbF_6$ (12 mg, 0.025 mmol) in CH_2Cl_2 (2.0 ml) at 0°C. After stirring for 1 h, methoxytrimethylsilane (0.15 ml, 1.1 mmol) was added to the mixture. After stirring for 1 h, the reaction was quenched with phosphate buffer (pH 7). The organic layer was separated and dried over a 1 : 1 mixture of Na_2CO_3 and Na_2SO_4. The evaporation of the solvent gave a crude product which was purified by preparative thin-layer chromatography on silica gel (25 : 2 hexane–ethyl acetate as a developing solvent) to afford **10e** (90.1 mg, 74%). IR (neat) 1600, 1500, 1450, 1190, 1080, 1060, and 1120 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.30 (6H, s, OCH_3), 4.23 (1H, d, J=7.8 Hz), 4.99 (1H, d, J=7.8 Hz), 7.1—7.4 (10H, m); MS *m/z* (rel intensity) 211 (M^+-15; 0.1), 165 (16), 152 (6), 75 (base peak), and 47 (22). Found: C, 79.31; H, 7.49%. Calcd for $C_{16}H_{18}O_2$: C, 79.36; 7.46%.

References

1) For examples: T. Mukaiyama, *Angew. Chem., Int. Ed. Engl.*, **16**, 817 (1977).

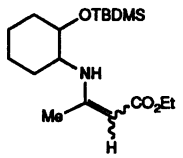
2) For recent examples of the Williamson reaction: H. Taniguchi and E. Nomura, *Chem. Lett.*, **1988**, 1773; J. J. Chapman and J. R. Reid, *J. Org. Chem.*, **54**, 3757 (1989); B. Jursic, *Tetrahedron*, **21**, 6677 (1988).

3) a) J. Kato, N. Iwasawa, and T. Mukaiyama, *Chem. Lett.*, **1985**, 743; b) R. Noyori, S. Murata, and M. Suzuki, *Tetrahedron*, **37**, 3899 (1981); c) M. B. Sassaman, K. D. Kotian, G. K. S. Prakash, and G. A. Olah, *J. Org. Chem.*, **52**, 4314 (1987); d) M. B. Sassaman, G. K. S. Parakash, and G. A. Olah, *Tetrahedron*, **44**, 3771 (1988); e)S. Torii, S. Takagishi, T. Inokuchi, and H. Okumoto, *Bull. Chem. Soc. Jpn.*, **60**, 775 (1987); f) K. C. Nicolaou, C. -K. Hwang, and D. A. Nugiel, *J. Am. Chem. Soc.*, **111**, 4136 (1989); g) R. L. Mulholland, Jr. and A. R. Chamberlin, *J. Org. Chem.*, **53**, 1082 (1988); h) K. Nagakawa, M. Osuka, K. Sasaki, Y. Aso, T. Otubo, and F. Ogura, *Chem. Lett.*, **1987**, 1331.

4) a) T. Mukaiyama, I. Siina, and M. Miyashita, *Chem. Lett.*, **1992**, 625; b) T. Mukaiyama, M. Katsurada, T. Takashima, *Chem. Lett.*, **1991**, 985; c) T. Mukaiyama, K. Suzuki, J. S. Han, and S. Kobayashi, *Chem. Lett.*, **1992**, 435, and references cited therein; d) T. Mukaiyama and T. Harada, *Chem. Lett.*, **1991**, 1653; e) T. Harada, T. Ohno, S. Kobayashi, and T. Mukaiyama, *Synthesis*, **1991**, 1216; f) T. Harada and T. Mukaiyama, *Chem. Lett.*, **1992**, 81.

5) T. Harada and T. Mukaiyama, *Chem. Lett.*, **1992**, 1901.

6) When CH_3CN was used as a solvent, compound **11** was produced in 31% yield. It is assumed that **11** was produced by the Ritter reaction of epoxide and CH_3CN, fol-



11

Scheme 6.

lowed by addition reaction of ketene silyl acetal to the activated nitrile carbone (Scheme 6). [Compound **11**.] IR (neat) 3280 (NH) and 1650 (α,β-unsaturated ester) cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.02 (3H, s), 0.03 (3H, s), 0.85 (9H, s), 1.1—1.5 (7H, m), 1.24 (t, J=7.3 Hz), 1.5—2.0 (7H, m), 1.94 (s), 3.1—3.4 (2H, m), 4.08 (2H, q, J=7.3 Hz), 4.38 (1H, s), 8.58 (1H, bd, NH); MS m/z (rel intensity) 341 (M^+; 4), 326 (4), 296 (8), 284 (base peak), 238 (12), 212 (15), 155 (48), and 75 (53).

7) We had already reported that various trityl salts are quite effective catalysts in synthetic reactions. For example: T. Mukaiyama and S. Kobayashi, *Heterocycles*, **25**, 205 (1987); K. Homma, H. Takenoshita, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **63**, 1898 (1990), and references cited therein.

8) The preparative method of various ethers from carbonyl compounds in the presence of a catalytic amount of trityl perchlorate was already reported from our laboratory.[3a] In the present method, a better result was obtained by using trityl hexafluoroantimonate as a catalyst than trityl perchlorate (Table 3).

9) For examples of addition reaction using carbonyl compounds as a substrate: T. Mukaiyama, S. Kobayashi, M. Tamura, and Y. Sagawa, *Chem. Lett.*, **1987**, 491, and references cited therein; S. Kobayashi, Y. Tsuchiya, and T. Mukaiyama, *Chem. Lett.*, **1991**, 537; T. Mukaiyama and T. Harada, *Chem. Lett.*, **1981**, 1527; A. Hosomi, H. Iguchi, M. Endo, and H. Sakurai, *Chem. Lett.*, **1979**, 977; Y. Yamamoto and K. Saito, *J. Chem. Soc., Chem. Commun.*, **1989**, 1676; A. P. Davis and M. Jaspars, *Angew. Chem., Int. Ed. Engl.*, **31**, 470 (1992), and references cited therein.

10) For example of nucleophilic substitution of hemiacetal intermediates as a substrate: T. Mukaiyama, M. Ohshima, and N. Miyoshi, *Chem. Lett.*, **1987**, 1121; I. E. Marko, A. Mekhalfia, D. J. Bayston, and H. Adams, *J. Org. Chem.*, **57**, 2211 (1992), and Refs. 10 and 3.

11) For example of nucleophilic substitution of acetals: T. Mukaiyama, H. Nagaoka, M. Murakami, and M. Ohshima, *Chem. Lett.*, **1985**, 977; T. Mukaiyama, S. Kobayashi, and M. Murakami, *Chem. Lett.*, **1984**, 1759; S. Murata, M. Suzuki, and R. Noyori, *J. Am. Chem. Soc.*, **102**, 3248 (1980); H. Sakurai, K. Sasaki, J. Hayashi, and A. Hosomi, *J. Org. Chem.*, **49**, 2808 (1984); T. Soga, H. Takenoshita, M. Yamada, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **63**, 3122 (1990).

12) Acetal synthesis from carbonyl compounds as a substrate in the presence of a catalytic amount of TMSOTf has been reported: J. R. Hwu and J. M. Wetzel, *J. Org. Chem.*, **50**, 3948 (1985); T. Tsunoda, M. Suzuki, and R. Noyori, *Tetrahedron Lett.*, **21**, 1357 (1980).

13) R. D. Thummel and P. Chayangkoon, *J. Org. Chem.*, **48**, 596 (1983).

14) J. Holmes and R. Pettit, *J. Org. Chem.*, **28**, 1695 (1963).

15) H. J. Dauben, Jr., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

16) G. B. Payne, *Tetrahedron*, **18**, 763 (1962).

17) T. Mukaiyama, T. Sato, and J. Hanna, *Chem. Lett.*, **1973**, 1041.