Electrogenerated Acid-Catalyzed Reactions of Acetals, Aldehydes, and Ketones with Organosilicon Compounds, Leading to Aldol Reactions, Allylations, Cyanations, and Hydride Additions

Sigeru Torii,* Tsutomu Inokuchi, Sadahito Takagishi, Hirofumi Horike, Hideki Kuroda, and Kenji Uneyama
Department of Industrial Chemistry, School of Engineering, Okayama University, Okayama 700
(Received January 21, 1987)

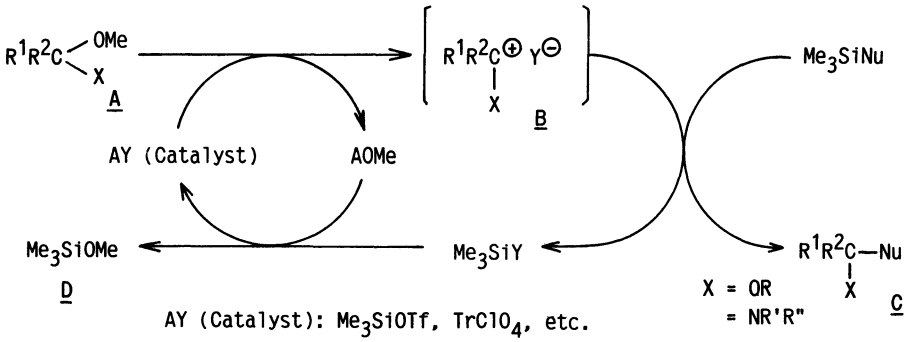
Exquisite use of electrogenerated acid (EG acid) in the silicon-mediated acid-catalyzed reactions; e.g., aldol reactions, allylations, cyanations, and hydride additions is described. The aldol reaction of acetals **1** with enol trimethylsilyl ethers **3** and 1,2-bis(trimethylsiloxy)alkenes **4** gives the corresponding adducts **5** and **6**, respectively. The reaction proceeds smoothly with EG acid derived from perchlorate salts such as $LiClO_4$, n-Bu_4NClO_4, and $Mg(ClO_4)_2$ in dichloromethane using platinum electrodes. The amount of electricity required to complete the reaction implies a cationic process which is mediated by the trimethylsilyl moiety. This aldol reaction is further developed with unprotected carbonyl compounds **2** with **3**, giving the trimethylsilyl ethers of the adducts **7**. Further utility of this EG acid as a catalyst for a chain reaction is exemplified by the successful application in the following conversions: (1) The allylation of acetals **1** with allyltrimethylsilane (**8**) to give **9**, (2) the cyanation of acetals **1** and unmasked **2** with trimethylsilyl cyanide (**10**) to give **11**, **12**, and **13**, and (3) the hydride addition of acetals **1** with triethylsilane (**14**) to give **15**.

The reaction of organosilicon compounds[1] bearing a nucleophilic site with an electron-deficient center has demonstrated one of the most efficiently designed examples of acid-catalyzed reactions, in which the silyl moiety serves as a chain carrier.[2] This reaction can be understood as illustrated in Scheme 1.

Thus, acetals and aldehydes **A** are activated by an acid-catalyst to give cationic intermediates **B**. These carbocations $[R^1R^2C\text{-}X]^+$ (X=OR, NR'R", etc.) may be stabilized by buffering with counter ion such as perchlorate ion or triflate ion present in the media. When nucleophilic silicon compounds are added to this media, cation **B** undergoes nucleophilic attack to produce the substituted product **C** together with a stable methoxysilane **D**. The formation of methoxysilane **D**, therefore, favors the equilibration of this acid-catalyzed reaction to proceed to completion. These silicon-mediated cationic reactions including aldol reaction,[2,3] acetalization,[2,12] allylation,[2] hydride additions,[2] cyanation,[2,4] and others[2,5] have been effected by very oxophilic reagents such as trimethylsilyl triflate (TMSOTf),[2] triphenylmethyl perchlorate ($TrClO_4$),[3,5,6] and other Lewis acids.[4] Unfortunately, these moisture sensitive reagents are cumbersome to use and it is still of considerable interest to develop new effective reagents which can be easily prepared and handled. In the previous paper from our laboratory, we have explored the potential utility of an electrogenerated acid (EG acid)[7] as a catalyst for selective epoxy ring openings,[8] tetrahydropyranylation of alcohols,[9] conversion of nerolidol to bisaborol,[10] biogenetic-type cyclization,[11] and acetalization of carbonyl compounds.[12] These results indicates an oxophilic ability of EG acid to oxygen containing compounds and prompted us to investigate the possibility of EG acid as an alternative to hitherto known catalysts in the above silicon-mediated catalytic reactions. In this paper, we describe an EG acid-assisted activation of acetals as well as unprotected aldehydes and ketones in the presence of organosilicon compounds bearing a nucleophilic site, leading to (1) aldol reactions, (2) allylations, (3) cyanations, and (4) hydride additions.

Results and Discussion

Aldol Reaction of Acetals, Aldehydes, and Ketones with Enol Trimethylsilyl Ethers. The aldol condensation has long been recognized to be one of the most versatile synthetic tools for a carbon-cabon bond formation.[13] The reaction of acetals **1** with enol silyl



Scheme 1.

ethers **3** is an important method of obtaining the corresponding adducts **5**, selectively.[3,14-16] The electrochemical version of this condensation was attempted using benzaldehyde dimethyl acetal (**1a**) and cyclohexanone enol trimethylsilyl ether (**3a**) as a typical substrate. Thus, the electrolysis was carried out by using platinum foil electrodes in dichloromethane (CH_2Cl_2) containing lithium perchlorate ($LiClO_4$) and/or tetrabutylammonium perchlorate (n-Bu_4NClO_4) for both an electrolyte and a source of the electrogenerated acid (EG acid). During the electrolysis a constant current of 2.67 mA cm^{-2} (applied voltage: 8—10 V) was charged until the starting materials **1a** or **3a** disappeared completely on TLC. After the electrolysis (0.07 F mol^{-1} of electricity based on the starting **3a** as one electron process has been passed), the reaction was quenched with a few drops of triethylamine and the concentrated products, without aqueous working up, were purified by column chromatography on silica gel to give *threo*-**5a** and *erythro*-**5a** in 93% yield as an isolable 14:86 mixture. No polycondensation product, self-condensation product, or α,β-unsaturated enone was formed by this reaction. The stereochemistry of the diastereoisomers **5a** was determined based on the ^{1}H NMR signals due to the methine proton on the methoxylated carbon (spectral data are given in the Experimental).[14b] On the other hand, no aldol reaction was observed for the acetal **1a** with cyclohexanone enol acetate, cyclohexanone enol methyl ether, and cyclohexanone morpholine enamine by treatment with the EG acid.

In order to know the applicability of the present procedure to the large-scale operation, we attempted to perform this reaction in the circulating flow-cell system as illustrated in Fig. 1, in which the electrolyte was circulated at a linear rate of about 15 cm min^{-1}. By using this flow-cell system, we were capable of preparing the aldol **5a** in 82—86% yields by the electrolysis of an appreciably concentrated solution of **1a** and **3a** (0.8—1.3 M in $ClCH_2CH_2Cl$) with SUS-27 electrodes.

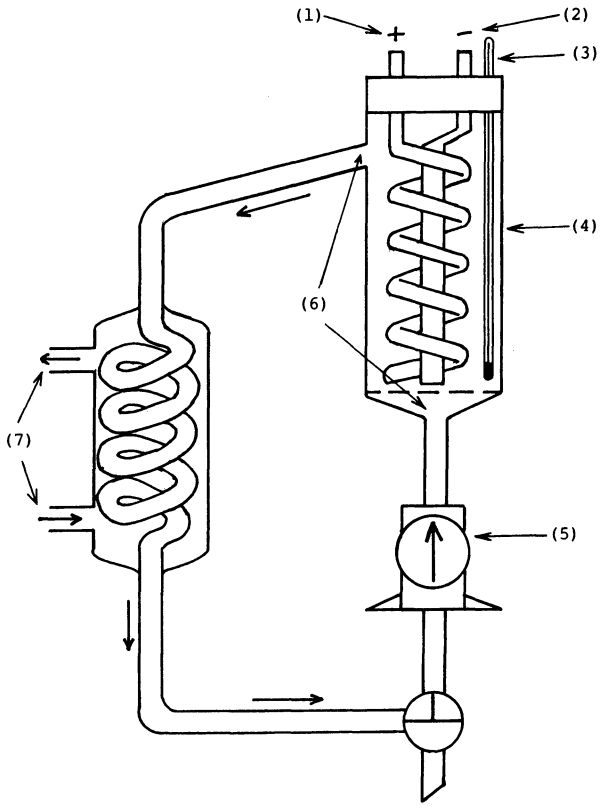


Fig. 1. Schematic drawing of a circulating flow cell for EG acid catalyzed reaction; (1): anode (SUS-27), (2): cathode (SUS-27), (3): thermometer, (4): glass electrolysis cell. (ca. 30 mm diameter and 150 mm height), (5): circulating pump, (6): electrolyte outlet and inlet, (7): heat exchanger by cold ethanol.

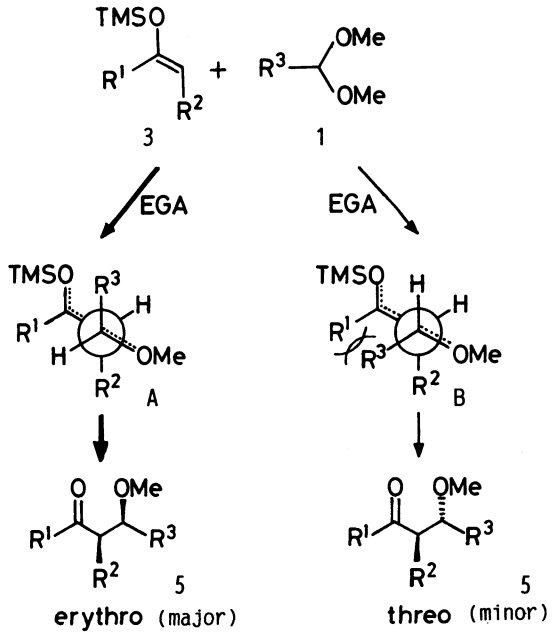
The effect of a supporting electrolyte is remarkable in this aldol reaction. The current efficiencies summarized in Table 1 were determined at the time when the necessary amount of electricity for the complete conversion has been passed based on the starting material **3a**. As shown in Entries 5—7, good to excellent conversion yields were obtained with perchlorate salts

Table 1. Effect of Electrolytes and Temperature in the Aldol Reaction of **1a** and **3a** to **5a**[a]

Entry	Electrolyte[b]	Solvent[c]	Temp °C	F mol^{-1}[d]	Yield of **5a**[e]/% (CE)[f]	(erythro/threo)[g]
1	$LiClO_4$-n-Bu_4NClO_4 (1:1)	CH_2Cl_2	20	0.01	75 (7500)	(79/21)
2	$LiClO_4$-n-Bu_4NClO_4 (1:1)	CH_2Cl_2	0	0.02	78 (3900)	(85/15)
3	$LiClO_4$-n-Bu_4NClO_4 (1:1)	CH_2Cl_2	−30—−40	0.04	86 (2150)	(83/17)
4	$LiClO_4$-n-Bu_4NClO_4 (1:1)	CH_2Cl_2	−78	0.07	93 (1329)	(86/14)
5	n-Bu_4NClO_4	CH_2Cl_2	−78	0.07	92 (1314)	(86/14)
6	$LiClO_4$	CH_2Cl_2-THF (10:1)	−78	0.02	84 (4200)	(84/16)
7	$Mg(ClO_4)_2$	CH_2Cl_2-THF (10:1)	−78	0.05	70 (1400)	(81/19)
8	$LiBF_4$	CH_2Cl_2-THF (10:1)	−78	0.30	24 (80)	(75/25)
9	Et_4NOTs	CH_2Cl_2	−78	0.30	—	
10	Et_4NBr	CH_2Cl_2	−78	0.30	—	

a) Carried out by using **1a** (1.2 mmol) and **3a** (1.0 mmol) with Pt electrodes (1.5 cm^2) at a constant current density of 2.67 mA cm^{-2} in an undivided cell. b) 0.1 Mol equivalent of the electrolyte to the substrate **3a** was used. c) 3 Ml was used. d) Electricity consumed (based on **3a** as an one-electron process). e) Based on isolated products. f) Current efficiency on the basis of one electron reaction. g) Determined based on isolated materials.

such as $LiClO_4$, n-Bu_4NClO_4, and $Mg(ClO_4)_2$. A combination of $LiClO_4$ and n-Bu_4NClO_4 (1/1 mixture), employed to get enough electric conductivity through the electrolysis media, gave the best conversion yield of **5a** (Entry 4). Other supporting electrolytes such as lithium tetrafluoroborate, tetraethylammonium tosylate, and tetraethylammonium bromide are less useful for this purpose (Entries 8—10). Halogenated solvents such as dichloromethane and 1,2-dichloroethane are highly effective for the formation of the aldol **5a**, while AcOEt, hexane, and THF are less effective. In order to increase the solubility of $LiClO_4$, $Mg(ClO_4)_2$, and $LiBF_4$ in CH_2Cl_2, THF was added to the solution in approximately 10 vol% (Entries 6—8). As shown in Table 1, Entries 1—4, the yield and erythro/threo selectivity of **5a** increase with lowering the temperature from 20 to −78 °C, although the current efficiency decreases. Meanwhile, feasibility of the present reaction at wide temperature range enables to raise the reactivity of rather less reactive acetals and unmasked carbonyl compounds (Entries 4 and 26 in Table 2). The yield and erythro/threo (e/t) selectivity of **5a** obtained by an EG acid-catalyzed reaction are comparable to the literature data obtained by other reagents such as TMSOTf (−75 °C/10 h, 89% yield, e/t=93 : 7),[2] $TrClO_4$ (−75 °C/0.25 h, 96% yield, e/t=88 : 12),[3a] and $TiCl_4$ (1 equiv) (−75 °C/2 h, 95% yield, e/t=50 : 50).[15a] The erythro selectivity of this reaction can be rationalized in terms of an acyclic extended transition state of Type **A** (Scheme 2), in good accordance with the results obtained with TMSOTf[2] or $TrClO_4$[3a] as a catalyst. This EG acid-catalyzed procedure could be applied to aldol reaction of a variety of acetals **1** and enol silyl ethers **3**, and the results are shown in Table 2, Entries 1—12. Acetals of aromatic aldehydes generally gave reasonable results, whereas acetals of saturated aliphatic aldehydes and ketones provided the corresponding adducts slightly lower yields or lower current efficiencies.



Scheme 2.

Aldols derived from 1,2-bis(trimethylsiloxy)cycloalkenes **4** and acetals **1** are synthetically valuable as precursors of 1,3-cycloalkanediones by rearrangement.[16a] Keto esters can also be prepared from these aldol products by oxidative or reductive ring cleavage.[16] These aldol reactions of **4** with acetals **1** have been carried out by using a stoichiometric amount of Lewis acid such as $TiCl_4$ and $BF_3 \cdot OEt_2$. However, aldol products derived from 1,2-bis(trimethylsiloxy)-cyclobutene **4c** are susceptible to undergo further rearrangement with acid-catalyst such as TMSOTf, TFA, and p-TsOH to give 1,3-cyclopentanediones. We have succeeded in the EG acid-catalyzed aldol reaction of **4** with acetals **1**, giving the corresponding adducts **6**, selectively (Table 2, Entries 13—20). Any by-products due to acid-catalyzed rearrangement have not been observed in the reaction products, except for the free alcohols which is due to partial hydrolysis of the trimethylsiloxy group of **6** (4—6%).

On the other hand, it is noted that the aldol reaction of enol silyl ethers **3** with unmasked ketones and aldehydes **2** is unsuccessful with a catalytic amount of TMSOTf[14a] as an acid-catalyst, while $TrClO_4$ effects this condensation, smoothly.[3] Stimulated by these findings, we attempted the EG acid-catalyzed aldol reaction of aldehydes **2** with enol silyl ethers **3** to compare the stereochemical outcome of the product with that obtained from **1** and **3**. The electrolysis of benzaldehyde **2a** and **3a** in CH_2Cl_2 containing an 1 : 1 mixture of $LiClO_4$ and n-Bu_4NClO_4 produced the desired aldol product **7a** in 85% yield. However, erythro/threo ratio of the product **7a** decreased to 69 : 31 in comparison with the ratio 86 : 14 obtained from the acetal **1a** and **3a**. In this reaction, aldols **7** are isolated as a silyl ether. The aldol reaction with ketones required a higher temperature than that for the reaction with aldehydes. Typical results of electrochemical aldol reaction of unmasked **2** with enol silyl ethers **3** are summarized in Table 2, Entries 21—26.

In order to gain an insight into the behavior of the EG acid in this aldol reaction, an electrolysis procedure different from that above mentioned was examined. Thus, electrolysis of the solution in the absence of **1a** and **3a** by passing about 0.05 F mol^{-1} of electricity was followed by the addition of the substrates **1a** and **3a** at −78 °C (stirring was continued for 10 min) to give the following results. The desired aldol adducts **5a** were obtained in almost identical yields with those obtained in the concurrent electrolysis. However, the electrolysis in the presence of a small amount of bases such as pyridine and triethylamine prevents the condensation, completely. These results along with erythro-selectivity of the adducts suggest the formation of EG acid of Brønsted acid character like as $HClO_4$[7]

Table 2. Aldol Reaction of Enol Silyl Ethers **3** and **4** with Acetals **1**, Aldehydes, and Ketones **2** Catalyzed by Electrogenerated Acid (EG Acid)[a]

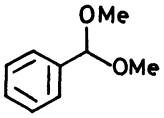
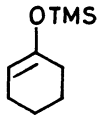
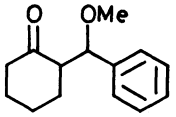
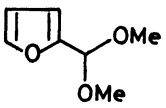
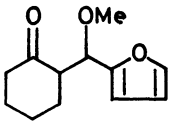
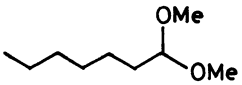
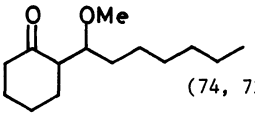
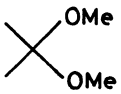
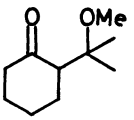
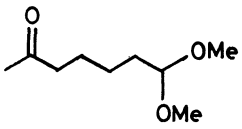
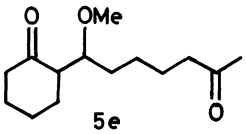
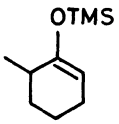
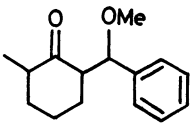
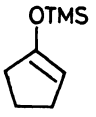
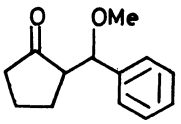
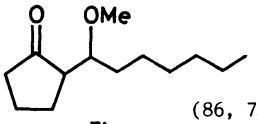
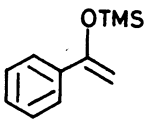
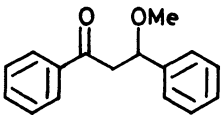
Entry	Acetal or Aldehyde	Enol Silyl Ether	Electricity / F mol^{-1}[b]	Product[c] (Yield[d]/%, erythro/threo)[e]
1	 **1a**	 **3a**	0.07	 **5a** (93, 86:14)
2	 **1b**	**3a**	0.05	 **5b** (82, 93: 7)
3	 **1c**	**3a**	0.075	 **5c** (74, 72:28)
4	 **1d**	**3a**	0.15	 **5d** (52)
5		**3a**	0.11	 **5e** (60, ca, 60:40)
6	**1a**	 **3b**	0.15	 **5f** (64, 44:56)
7	**1a**	 **3c**	0.065	 **5g** (88, 75:25)
8	**1c**	**3c**	0.075	 **5h** (86, 73:27)
9	**1a**	 **3d**	0.075	 **5i** (85)

Table 2. (Continued)

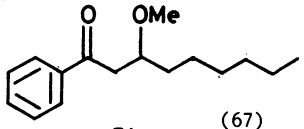
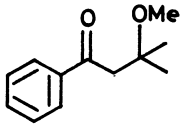
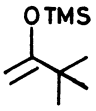
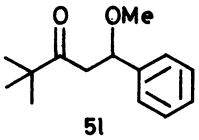
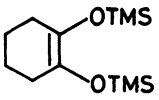
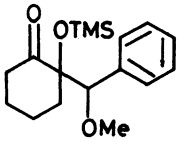
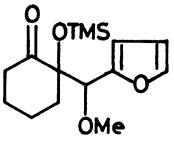
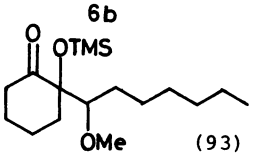
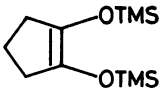
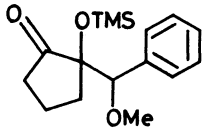
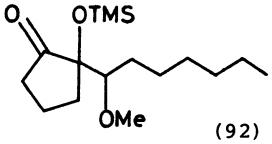
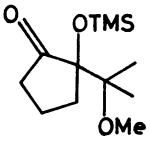
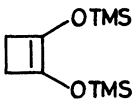
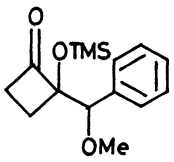
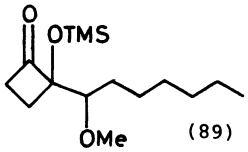
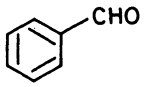
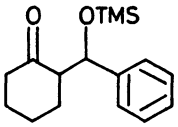
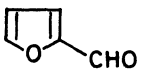
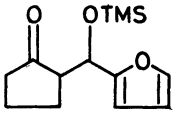
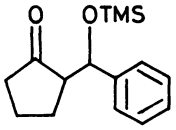
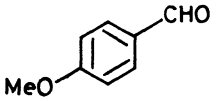
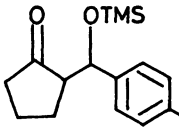
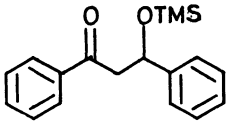
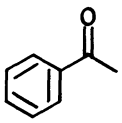
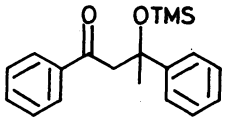
Entry	Acetal or Aldehyde	Enol Silyl Ether	Electricity / F mol^{-1} [b]	Product [c] (Yield [d]/%, erythro/threo) [e]
10	**1c**	**3d**	0.18	 **5j** (67)
11	**1d**	**3d**	0.15	 **5k** (73)
12	**1a**	 **3e**	0.15	 **5l** (33)
13	**1a**	 **4a**	0.87	 **6a** (91)
14	**1b**	**4a**	0.112	 **6b** (66)
15	**1c**	**4a**	0.124	 **6c** (93)
16	**1a**	 **4b**	0.01	 **6d** (82)
17	**1c**	**4b**	0.174	 **6e** (92)
18	**1d**	**4b**	0.174	 **6f** (74)

Table 2. (Continued)

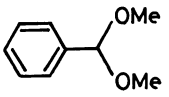
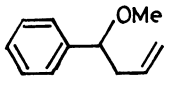
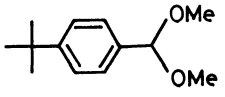
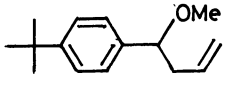
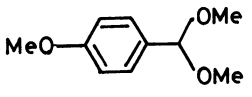
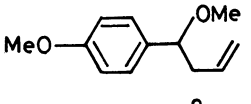
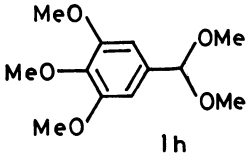
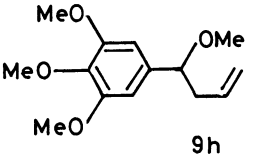
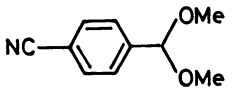
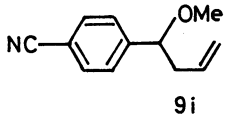
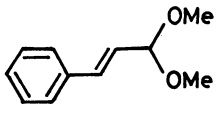
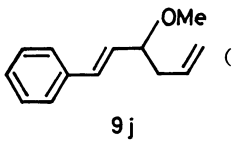
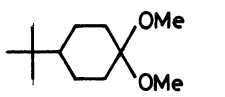
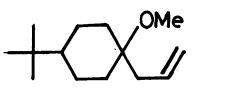
Entry	Acetal or Aldehyde	Enol Silyl Ether	Electricity / F mol^{-1} [b]	Product [c] (Yield [d]/%, erythro/threo) [e]
19	1a	 4c	0.087	 (81) 6g
20	1c	4c	0.137	 (89) 6h
21	 2a	3a	0.124	 (85, 69:31) 7a
22	 2b	3a	0.124	 (88, 83:17) 7b
23	2a	3c	0.114	 (87, 97: 3) 7c
24	 2c	3c	0.075	 (84, 99: 1) 7d
25	2a	3d	0.150	 (80) 7e
26	 2d	3d	0.224	 (84) 7f

a) Unless otherwise noted electrolyses were carried out under a constant current of 2.67 mA cm^{-2} with two platinum electrodes (1.5 cm^2) in an undivided cell under argon at −78 to −60 °C (for unmasked aldehyde as well as acetals derived from aldehydes) or at 0 °C (for unmasked ketone as well as acetal derived from ketone). b) Faradays/mole during preparative run. c) Products from **1** and **4** (Entries 13—20) are contaminated with 4—6% of the free alcohol due to the partial hydrolysis of silyl protecting group. d) Based on isolated products in complete conversion of 1.0—1.2 mmol of the substrates. e) Determined either by direct separation of isomers by SiO_2 column chromatography or by ^{1}H NMR spectra.

during the electrolysis in a CH_2Cl_2-$LiClO_4$-*n*-Bu_4NClO_4-(Pt) system. The EG acid could be concentrated at the vicinity of the anode during the electrolysis so that the aldol condensation proceeds even with EG acid generated with a catalytic amount of electricity.

Allylation with Allyltrimethylsilane. Addition of an allyl group to carbonyl compounds using allyltrimethylsilane (**8**) is of value due to the versatility of adducts in organic transformation.[17] The activation of the carbonyl function for this transformation has been effected by a stoichiometric amount of Lewis acid[18] such as $TiCl_4$, $BF_3 \cdot OEt_2$, and $AlCl_3$ and a catalytic amount of TMSOTf.[19] We attempted to use the EG acid as a catalyst for this allylation. Thus, allyltrimethylsilane was reacted with acetals **1** at 0 °C in CH_2Cl_2 with the aid of the EG acid to give the corresponding homoallylic alcohol methyl ethers **9** in high yields. However, the reaction of aldehyde **2** with allyltrimethylsilane was unsuccessful. The reaction of 4-*t*-butylcyclohexanone dimethyl acetal **1k** at 0 °C furnished a mixture of equatorial:axial adducts **9k** in 90 : 10 ratio (80% yield).[2] Some additional results are given in Table 3.

Table 3. Preparation of Homoallyl Ethers **9** from Allylsilane **8** and Acetals **1**[a]

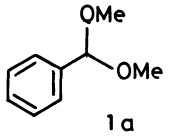
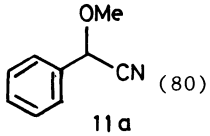
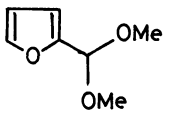
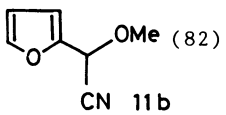
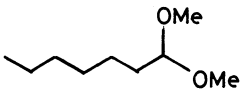
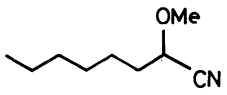
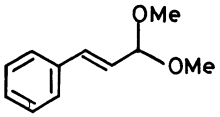
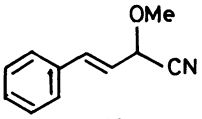
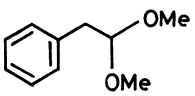
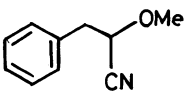
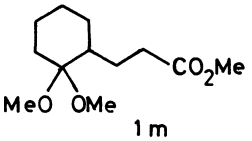
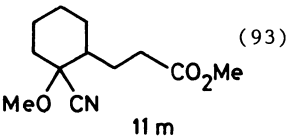
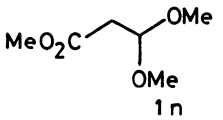
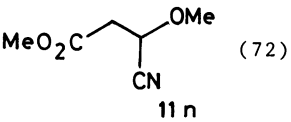
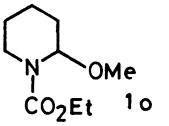
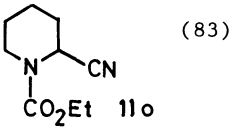
Entry	Acetal **1**	Electricity / F mol^{-1}[b]	Homoallyl ether **9** (Yield/%)[c]
1	 **1a**	0.07	 (82) **9a**
2	 **1f**	0.06	 (98) **9f**
3	 **1g**	0.04	 (93) **9g**
4	 **1h**	0.03	 (95) **9h**
5	 **1i**	0.03	 (79) **9i**
6	 **1j**	0.12	 (78) **9j**
7	 **1k**	0.21	 (80) **9k**

a) Unless otherwise noted electrolyses were carried out under a constant current of 2.67 mA cm^{-2} with two platinum electrodes (1.5 cm^2) in an undivided cell under argon at 0 °C. b) Faradays/mole during preparative run. c) Based on isolated products in complete conversion of 1.0—1.2 mmol of the substrates.

Cyanation of Acetals with Trimethylsilyl Cyanide. α-Alkoxyalkanenitriles **11**, a protected form of cyanohydrins, are synthetically useful compounds as precursors of 3-amino-2-alkenenitriles,[20] α-alkoxy ketone[21] and are accepted as synthons of acyl carbanion equivalents.[22] Although the preparation of α-alkoxy nitriles by cyanation of acetals with trimethylsilyl cyanide (**10**) using Lewis acid has been reported,[4,24] a highly convenient procedure is still in demand. We have succeeded in a facile cyanation of dimethyl acetals **1** with trimethylsilyl cyanide (**10**) by using EG acid, giving **11**.

The reaction procedure is similar to that of the aldol reaction. Thus, a mixture of heptanal dimethyl acetal (**1c**) and trimethylsilyl cyanide (**10**) in CH_2Cl_2 containing $LiClO_4$ and Et_4NClO_4 (1 : 1) was electrolyzed with plat-

Table 4. Preparation of Cyanohydrin Methyl Ether **11** from Acetal **1** and Trimethylsilyl Cyanide (**10**)[a]

Entry	Acetal **1**	Electricity[b] / F mol^{-1}	Cyanohydrin Methyl Ether **11** (Yield/%)[c]
1	 **1a**	0.04	 (80) **11a**
2	 **1b**	0.01	 (82) **11b**
3	 **1c**	0.08	 (89) **11c**
4	 **1j**	0.40	 (81) **11j**
5	 **1l**	0.03	 (87) **11l**
6	 **1m**	0.06	 (93) **11m**
7	 **1n**	0.15	 (72) **11n**
8	 **1o**	0.28	 (83) **11o**

a) Unless otherwise noted electrolyses were carried out at an applied voltage of 15 V (current: 12 mA) with two platinum electrodes (1.5 cm^2) in an undivided cell under argon at room temperature. b) Faradays/mole during preparative run. c) Based on isolated products in complete conversion of 1.0—1.2 mmol of the substrates.

inum electrodes at an applied voltage of 15 V (current: 12—13 mA). After electrolysis for 32 min (electricity: 0.077 F mol^{-1} based on acetal **1c** as one electron process) and an additional stirring for 5 min, the reaction was quenched with pyridine (2 drops). Concentration in vacuo followed by either column chromatography (SiO_2, hexane-AcOEt, 50:1) or bulb to bulb distillation gave the cyanide **11c** in 89% yield. Electrolysis with either $LiBF_4$ or Et_4NOTs as a supporting electrolyte resulted only in the recovery of the starting acetal **1c**.

As shown in Table 4, most of the acetals **1** could be smoothly converted into the corresponding cyanohydrin methyl ethers **11** with a catalytic amount of electricity. Cyclic α-methoxy amine **1o** underwent smooth cyanation through the replacement of the methoxyl group to give 2-cyanopiperidine **11o**.

Alternatively, the EG acid-catalyzed cyanation of unprotected aldehydes and ketones with trimethylsilyl cyanide (**10**) was examined. Cyanohydrin derived from ketones were obtained as a form of trimethylsilyl ethers **12**, while adducts of aldehydes were isolated as a cyanohydrins **13** due to the instability of the corresponding silyl ether to moisture. The reaction of α,β-enone **2i** with trimethylsilyl cyanide gave 1,2-adducts **12i**, predominantly (Table 5).

Table 5. Preparation of Cyanohydrin Derivatives from Ketones and Aldehydes **2**[a)]

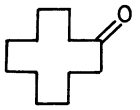
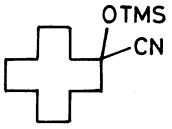
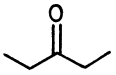
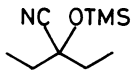
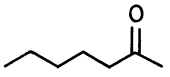
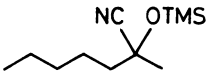
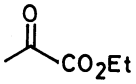
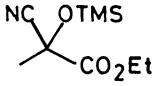
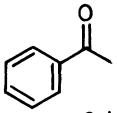
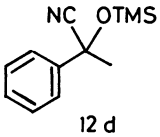
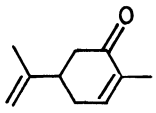
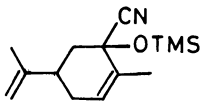
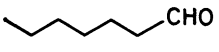
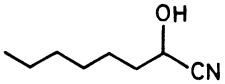
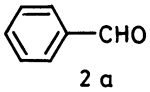
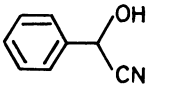
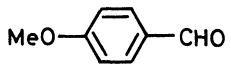
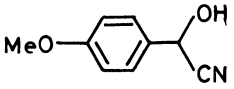
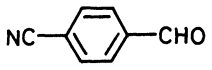
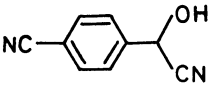
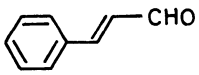
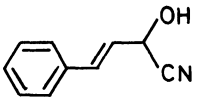
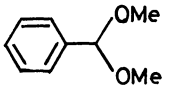
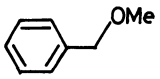
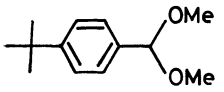
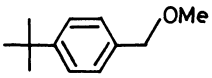
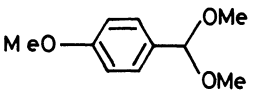
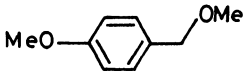
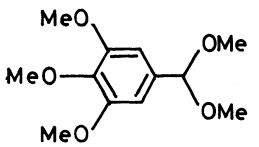
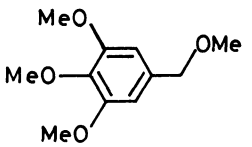
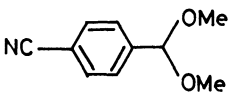
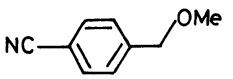
Entry	Ketone or Ardehyde **2**	Electricity[b)] / F mol^{-1}	Product, **12**, **13** (Yield/%)[c)]
1	 **2e**	0.28	 **12e** (95)
2	 **2f**	0.15	 **12f** (93)
3	 **2g**	0.15	 **12g** (97)
4	 **2h**	0.38	 **12h** (82)
5	 **2d**	0.47	 **12d** (88)
6	 **2i**	0.30	 **12i** (88)
7	 **2j**	0.37	 **13j** (82)
8	 **2a**	0.16	 **13a** (88)

Table 5. (Continued)

Entry	Ketone or Ardehyde **2**	Electricity[b] / F mol^{-1}	Product, **12**, **13** (Yield/%)[c]
9	 **2 c**	0.03	 **13 c** (97)
10	 **2 k**	0.13	 **13 k** (66)
11	 **2 l**	0.33	 **13 l** (91)

a) Unless otherwise noted electrolyses were carried out under a constant current of 20 mA cm^{-2} (for ketones) or 6.67 mA cm^{-2} (for aldehydes) with two platinum electrodes (1.5 cm^2) in an undivided cell under argon at room temperature. b) Faradays/mole during preparative run. c) Based on isolated products in complete conversion of 1.0—1.2 mmol of the substrates.

Table 6. Preparation of Methyl Ether **15** by the Reaction of Acetal **1** and Triethylsilane (**14**)[a]

Entry	Acetal **1**	Electricity[b] / F mol^{-1}	Methyl Ether **15** (Yield/%)[c]
1	 **1 a**	0.02	 **15 a** (88)
2	 **1 f**	0.06	 **15 f** (87)
3	 **1 g**	0.02	 **15 g** (95)
4	 **1 h**	0.02	 **15 h** (95)
5	 **1 i**	0.04	 **15 i** (74)

a) Unless otherwise noted electrolyses were carried out under a constant current of 2.67 mA cm^{-2} with two platinum electrodes (1.5 cm^2) in an undivided cell under argon at 0 °C. b) Faradays/mole during preparative run. c) Based on isolated products in complete conversion of 1.0—1.2 mmol of the substrates.

Hydride Addition to Acetals. Trialkylsilanes have attracted a considerable interest because of their utility as a mild hydrogen doner in modern synthetic reaction.[23] Acetals have been reduced to ethers with this reagent by the aid of TMSOTf.[24] We have also succeeded in this transformation using EG acid as a catalyst. Thus, the electrolysis of acetals **1** in the presence of a slightly excess of triethylsilane (**14**), performed in a similar manner as described for the aldol reaction, resulted in the replacement of methoxyl group with hydrogen to give the corresponding ethers **15** in good yields. Some examples of this reaction are listed in Table 6.

In this paper the EG acid has been shown to be a viable alternative as a catalyst for silicon-mediated cationic reaction in terms of its easy and clean operation, short reaction time, and high current efficiency. By analogy with the reactions catalyzed by TMSOTf[2] and $TrClO_4$,[3,5,6] the present EG acid catalyzed reactions of acetals **a** and Me_3SiNu are rationalized as depicted in Scheme 3. Thus, the EG acid generated from perchlorate salts is strong enough to activate **a** to allow the carbenium ion **b** buffered by perchlorate ion. The cation **b** undergoes smoothly nucleophilic attack of Me_3SiNu to produce the desired **c**. In this step, the intermediacy of trimethylsilyl perchlorate (Me_3SiClO_4) is considered, but the Me_3SiClO_4 is quickly hydrolyzed by methoxide ion to stable methoxytrimethylsilane **d**, allowing to regenerate the EG acid. Although the nature of EG acid was not unveiled completely, its electrophilic character to the oxygen function was demonstrated, resembling with that of conventional catalyst such as TMSOTf and $TrClO_4$ especially in the aldol reactions. As noted above briefly, if EG acid, generated in a CH_2Cl_2-$LiClO_4$-n-Bu_4NClO_4-(Pt) system, has a character of Brønsted acid like $HClO_4$, the results accomplished in this paper are the first example, to our knowledge, that is achieved by the acid not having Lewis acid character. Further study aimed at the extended application of the EG acid for organic transformation is currently under investigation.

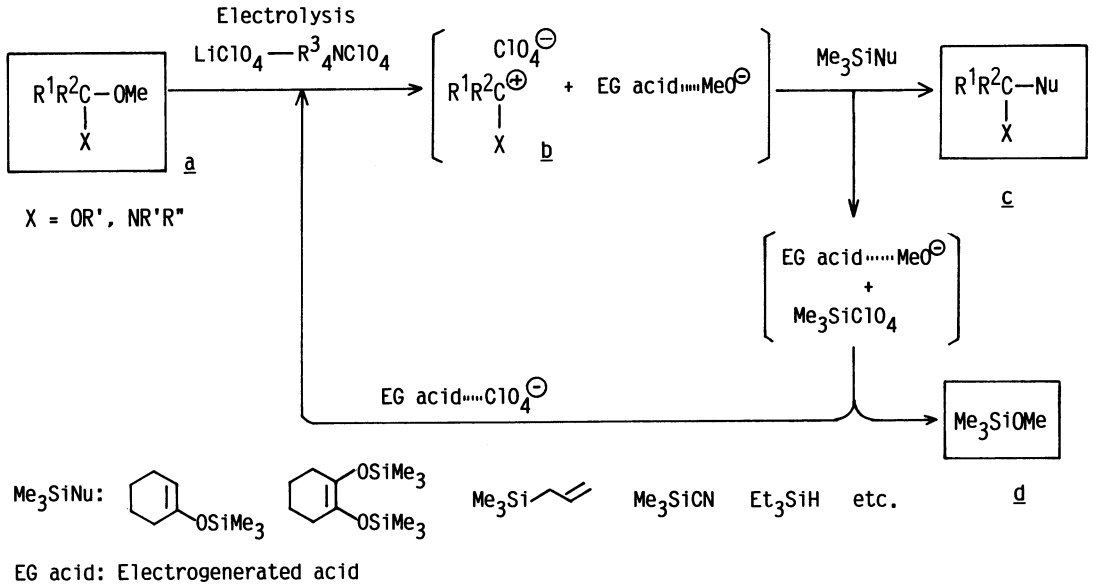
Experimental

General. Melting points are uncorrected and boiling points are indicated by an air-bath temperature without correction. IR spectra were recorded with a JASCO IRA-1 grating spectrometer. Unless otherwise noted, ^1H NHR spectra were determined at 60 MHz with either a Hitachi R-24 or a JEOL JNM-PMX 60 and ^{13}C NMR spectra were recorded with a JEOL FX-100 (25.05 MHz) spectrometer. Samples were dissolved in $CDCl_3$ and the chemical shifts are expressed in δ values (ppm) relative to Me_4Si as an internal standard. Satisfactory elemental analyses were obtained for the new compounds: C ±0.29, H ±0.29.

Materials. Enol silyl ethers **3**[25] and 1,2-bis(trimethylsiloxy)-cycloalkenes **4**[26] were prepared by the reported methods. Commercially available allyltrimethylsilane (**8**), trimethlsilyl cyanide (**10**), triethylsilane (**14**) were used as received. $LiClO_4$, n-Bu_4NClO_4, and Et_4NClO_4 purchased from Tokyo Kasei Kogyo (Japan) were used without further purification. Dichloromethane and 1,2-dichloroethane were distilled once over P_2O_5 before use.

Electrolysis Apparatus. A simple cylindrical glass tube (1.5 cm diameter×10.5 cm height) was equipped with a gas inlet tube, stirring bar, and two platinum foil electrodes (1.5 cm^2) placed parallel to each other 3 mm apart. The vessel was immersed in a cooling bath as indicated in the Experimental. The reactions were usually carried out under argon.

Typical Procedure for the Aldol Condensation of Acetal 1 with Enol Trimethylsilyl Ether 3. Into the electrolysis vessel were added $LiClO_4$ (10.6 mg, 0.1 mmol) and n-Bu_4NClO_4 (34.2 mg, 0.1 mmol) and the resulting mixture was dried at about 100 °C under vacuum for 1 h and then purged with argon. To this mixture was added a solution of cyclohexanone enol trimethylsilyl ether (**3a**, 170.3 mg, 1.0 mmol), benzaldehyde dimethyl acetal (**1a**, 182.6 mg, 1.2 mmol) in



Scheme 3.

CH_2Cl_2 (3 ml). The entire mixture was electrolyzed under a constant current of 2.67 mA cm^{-2} (applied voltage: 8—10 V) at −78 °C. Soon after electric current was communicated, the surface of the cathode was covered with a black deposite (presumably with lithium metal). The progress of reaction was monitored by TLC and the reaction was quenched with Et_3N (3 drops) when the starting **3a** was completely consumed (about 30 min and after 0.07 F mol^{-1} of electricity has been passed). The volatiles were removed on a rotary evaporator and the residue was subjected to purification by column chromatography (SiO_2, hexane-AcOEt 5 : 1) to give 174 mg (80 %) of *erythro*-**5a** (R_f 0.5, Merck Silica Gel 60 F-254, hexane-AcOEt 5 : 1) and 29 mg (13 %) of *threo*-**5a** (R_f 0.3). *erythro*-**5a**:[3a] bp 56—58 °C/0.009 Torr (1 Torr=133.322 Pa); IR (neat) 3040, 3010, 2920, 2840, 2800, 1710 (C=O), 1610 (C=C), 1500, 1450, 1140, 1125 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.2—2.1 (m, 6, CH_2), 2.27—2.93 (m, 3, CH_2CO, CHCO), 3.27 (s, 3, OCH_3), 4.78 (d, J=5 Hz, 1, CH-O), 7.3 (s, 5, PhH); ^{13}C NMR ($CDCl_3$) δ=24.6 (t), 26.4 (t), 27.0 (t), 42.2 (t), 57.2 (q), 57.4 (d), 80.1 (d), 126.9 (d, 2c), 127.2 (d), 128.2 (d, 2c), 140.9 (s), 210.4 (s). *threo*-**5a**: bp 56—58 °C/0.009 Torr; IR (neat) 3040, 3010, 2920, 2840, 2800, 1710 (C=O), 1610 (C=C), 1500, 1450, 1140, 1125 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.05—2.20 (m, 6, CH_2), 2.27—2.93 (m, 3, CH_2CO, CHCO), 3.18 (s, 3, OCH_3), 4.55 (d, J=9 Hz, 1, CH-O), 7.25 (s, 5, PhH).

The electrolysis of **1a** and **3a** in 1,2-dichloroethane was carried out in the same manner as that in dichloromethane, giving the adducts in 90% yield.

The procedure for the aldol reaction by using a circulating flow cell system: Into a flow cell as dipicted in Fig. 1 were added consecutively a solution of benzaldehyde dimethyl acetal (**1a**, 4.87 g, 35 mmol), trimethylsiloxycyclohexene (**3a**, 5.1 g, 30 mmol), $LiClO_4$ (0.32 g, 3 mmol), and n-Bu_4NClO_4 (0.34 g, 1 mmol) in THF (2 ml) and 1,2-dichloroethane (60 ml). These stuffs were mixed by circulating at a linear rate of ca. 15 cm min^{-1} by flowing pump. The mixture was then electrolyzed at a current of 15 mA with stainless steels (SUS-27, anode area: 0.5×32 cm^2) as electrodes. During the electrolysis, temperature of the solution was maintained at −20 °C by cooling externally from heat-exchanger. The electrolysis was continued until 0.02 F mol^{-1} of electricity (based on **3a**) has been passed. The mixture was then treated with triethylamine (0.5 ml) and then concentrated. The crude product thus obtained was purified by column chromatography (SiO_2, hexane-AcOEt 10 : 1) to give 5.5 g (84%, erythro/threo 71 : 29) of **5a** (based on **3a**).

Preparation of **6g** from 1,2-Bis(trimethylsiloxy)cyclobutene (**4c**). A similar electrolysis of **1a** (152.2 mg, 1.0 mmol) and **4c** (277 mg, 1.2 mmol) in CH_2Cl_2 (3 ml) in the presence of $LiClO_4$ (10.6 mg, 0.1 mmol) and n-Bu_4NClO_4 (34.2 mg, 0.1 mmol) at −78 °C for 30 min (0.087 F mol^{-1} of electricity being passed) provided **6g** in 81% yield.

Spectral data for the adducts **5—7** listed in the Table 2 are as follows.

***erythro*-2-[(2-Furyl)methoxymethyl]cyclohexanone (5b):** IR (neat) 3100, 2840, 2800, 1710 (C=O), 1500, 1450, 1190, 1120, 1005, 950, 920, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.40—2.15 (m, 6, CH_2), 2.15—3.00 (m, 3, CH_2CO, CHCO), 3.30 (s, 3, OCH_3), 4.73 (d, J=5 Hz, 1, CH-O), 6.30 (m, 2, CH=C), 7.35 (m, 1, CH=C). Found: C, 69.37; H, 7.63%. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74%.

***threo*-5b**: IR (neat) 3100, 2840, 2800, 1710 (C=O), 1500, 1450, 1320, 1230, 1150, 1125, 1117, 1090, 1010, 920, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.20—2.20 (m, 6, CH_2), 2.30—3.20 (m, 3, CH_2CO, CHCO), 3.25 (s, 3, OCH_3), 4.58 (d, J=9 Hz, 1, CH-O), 6.32 (m, 2, CH=C), 7.40 (m, 1, CH=C).

***erythro*-2-(1-Methoxyheptyl)cyclohexanone (5c):** Bp 51—53 °C/0.013 Torr; IR (neat) 2850, 2800, 1715 (C=O), 1470, 1455, 1380, 1320, 1190, 1150, 1135, 1130, 1105, 1190 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (m, 3, CH_3), 1.30 (br, 10, CH_2), 1.60—2.15 (m, 6, CH_2), 2.15—2.60 (m, 3, CH_2CO, CHCO), 3.36 (s, 3, OCH_3), 3.55—3.90 (m, 1, CH-O); ^{13}C NMR ($CDCl_3$) δ=14.0 (q), 20.9 (t), 22.6 (t), 22.6 (t), 23.0 (t), 25.9 (t), 29.4 (t), 31.8 (t), 32.7 (t), 39.1 (t), 52.7 (d), 58.3 (q), 79.6 (d), 220.9 (s). Found: C, 74.37; H, 11.33%. Calcd for $C_{14}H_{26}O_2$: C, 74.29; H, 11.58%.

***threo*-5c**: IR (neat) 2810, 1716 (C=O), 1470, 1455, 1380, 1370, 1320, 1135, 1105, 1085, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (m, 3, CH_3), 1.32 (br, 10, CH_2), 1.55—2.20 (m, 6, CH_2), 2.20—2.90 (m, 3, CH_2CO, CHCO), 3.32 (s, 3, OCH_3), 3.50—3.80 (m, 1, CH=O).

2-(1-Methoxy-1-methylethyl)cyclohexanone (5d):[3a] Bp 53—55 °C/3.5 Torr; IR (neat) 2820, 1715(C=O), 1455, 1385, 1370, 1320, 1150, 1130, 1080, 1035, 995, 915, 900, 850, 840, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.20, 1.28 (s, 6, CH_3), 1.40—2.76 (m, 9, CH_2, CH_2CO, CHCO), 3.16 (s, 3, OCH_3); ^{13}C NMR ($CDCl_3$) δ=21.2 (q), 23.2 (q), 25.4 (t), 28.5 (t), 29.0 (t), 43.8 (t), 48.3 (q), 58.3 (d), 75.2 (s), 211.6 (s).

2-(1-Methoxy-6-oxoheptyl)cyclohexanone (5e): Bp 76—77 °C/0.005 Torr; IR (neat) 2805, 1710 (C=O), 1450, 1365, 1160, 1120, 1090 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.30—2.70 (m, 17, CH_2, CH_2CO, CHCO), 2.11 (s, 3, CH_3CO), 3.29, 3.31 (s, 3, OCH_3), 3.60 (m, 1, CH-O).

***erythro*-2-(1-Methoxy-1-phenylmethyl)-6-methylcyclohexanone (5f):** Mp 58—61 °C (from hexane); IR (Nujol) 3040, 3023, 2820, 1705 (C=O), 1602 (C=C), 1580, 1485, 1443, 1355, 1310, 1280, 1215, 1120, 1094, 1020, 995, 956, 917, 862, 760, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.91, 1.01 (d, J=6 Hz, 3, CH_3), 1.30—2.30 (m, 6, CH_2), 2.35—2.80 (m, 2, CHCO), 3.21 (s, 3, OCH_3), 4.67 (d, J=6 Hz, 1, CH-O), 7.28 (s, 5, PhH). Found: C, 77.34; H, 8.71%. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68%.

***threo*-5f**: IR ($CHCl_3$) 3040, 3020, 2822, 1706 (C=O), 1601 (C=C), 1440, 1370, 1238, 1203, 1083, 1000, 860, 760, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.12, 1.21 (d, J=6 Hz, 3, CH_3), 1.30—2.30 (m, 6, CH_2), 2.50—2.90 (m, 2, CHCO), 3.13 (s, 3, OCH_3), 4.58 (d, J=10 Hz, 1, CH-O), 7.35 (s, 5, PhH).

***erythro*-2-(1-Methoxy-1-phenylmethyl)cyclopentanone (5g):**[3a] Bp 69—71 °C/0.02 Torr; IR (neat) 3080, 3020, 2880, 2805, 1745 (C=O), 1602 (C=C), 1590, 1495, 1450, 1403, 1380, 1370, 1200, 1150, 1140, 1120, 1080, 1030, 950, 875, 844, 782, 740, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.20—2.40 (m, 7, CH_2, CH_2CO, CHCO), 3.19 (s, 3, OCH_3), 4.70 (d, J=1.5 Hz, 1, CH-O), 7.22 (s, 5, PhH). Found: C, 76.37; H, 8.03%. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90%.

***threo*-5g**: IR (neat) 3080, 3055, 3020, 2805, 1740 (C=O), 1602 (C=C), 1590, 1495, 1450, 1405, 1370, 1150, 1100, 960, 740, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.30—2.40 (m, 6, CH_2, CH_2CO), 2.50—2.90 (m, 1, CHCO), 3.25 (s, 3, OCH_3), 4.63 (d, J=5 Hz, 1, CH-O), 7.25 (s, 5, PhH).

***erythro*-2-(1-Methoxyheptyl)cyclopentanone (5h):** Bp 47—50 °C/0.01 Torr; IR (neat) 2840, 2810, 1740 (C=O), 1460, 1402, 1375, 1260, 1150, 1095 cm^{-1}; ^1H NMR ($CDCl_3$, 100 MHz) δ=0.88 (m, 3, CH_3), 1.29 (br, 10, CH_2), 1.70—2.40 (m, 7, CH_2, CH_2CO, CHCO), 3.22 (s, 3, OCH_3), 3.65 (m, 1, CH-O). Found: C, 73,58; H, 11.24%. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39%.

***threo*-5h:** IR (neat) 2840, 2810, 1735 (C=O), 1465, 1405, 1264, 1090 cm^{-1}; ^1H NMR ($CDCl_3$, 100 MHz) δ=0.88 (m, 3, CH_3), 1.30 (br, 10, CH_2), 1.70—2.70 (m, 7, CH_2, CH_2CO, CHCO), 3.32 (s, 3, OCH_3), 3.45 (m, 1, CH-O).

3-Methoxy-1,3-diphenyl-1-propanone (5i):[3a] Bp 150—153 °C/3 Torr; IR (neat) 3040, 3020, 2810, 1690 (C=O), 1600 (C=C), 1580, 1490, 1450, 1360, 1265, 1200, 1100, 1055, 1000, 985, 750, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.81—3.82 (m, 2, CH_2), 3.22 (s, 3, OCH_3), 4.87 (dd, J=8, 4.5 Hz, 1, CH-O), 7.20—7.60 (m, 8, PhH), 7.80—8.10 (m, 2, PhH).

3-Methoxy-1-phenyl-1-nonanone (5j): Bp 83—85 °C/0.015 Torr; IR (neat) 3040, 2840, 2800, 1690 (C=O), 1600 (C=C), 1580, 1460, 1442, 1360, 1100, 1000, 750, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (m, 3, CH_3), 1.30 (m, 10, CH_2), 2.60—3.50 (m, 2, CH_2CO), 3.31 (s, 3, OCH_3), 3.87 (m, 1, CH-O), 7.20 (m, 5, PhH). Found: C, 77.38; H, 9.74%. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74%.

3-Methoxy-3-methyl-1-phenyl-1-butanone (5k): Bp 62—64 °C/0.007 Torr; IR (neat) 3080, 3000, 2840, 1690 (C=O), 1610, 1600 (C=C), 1480, 1460, 1080, 770, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.31 (s, 6, CH_3), 3.14 (s, 2, CH_2CO), 3.20 (s, 3, OCH_3), 7.30—8.10 (m, 5, PhH); ^{13}C NMR ($CDCl_3$) δ=25.0 (q, 2C), 48.0 (t), 49.3 (q), 74.8 (s), 128.4 (d, 3c), 132.8 (d, 2c), 138.3 (s), 198.9 (s).

5-Methoxy-2,2-dimethyl-5-phenyl-3-pentanone (5l): IR (neat) 3070, 3050, 3020, 2810, 1710 (C=O), 1602 (C=C), 1495, 1480, 1450, 1370, 1105, 1043, 995, 840, 760, 740, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.07 (s, 9, CH_3), 2.40—3.45 (m, 2, CH_2CO), 3.20 (s, 3, OCH_3), 4.72 (dd, J=8, 5.5 Hz, 1, CH-O), 7.30 (s, 5, PhH); ^{13}C NMR ($CDCl_3$) δ=25.9 (q, 3C), 44.2 (s), 45.4 (t), 56.8 (q), 79.4 (d), 126.6 (d), 127.7 (d, 2c), 128.4 (d, 2c), 141.6 (s), 212.8 (s). Found: C, 76.18; H, 9.09%. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15%.

2-(1-Methoxy-1-phenylmethyl)-2-(trimethylsiloxy)cyclohexanone (6a): (Less polar component on SiO_2 column chromatography): Bp 65—66 °C/0.007 Torr; IR (neat) 3080, 3060, 3020, 2820, 1730 (C=O), 1605 (C=C), 1498, 1455, 1340, 1310, 1250, 1180, 1150, 1130, 1100, 1075, 996, 843, 760, 704 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.04 (s, 9, $OSiMe_3$), 1.20—2.40 (m, 6, CH_2), 2.50—2.80 (m, 2, CH_2CO), 3.29 (s, 3, OCH_3), 4.53 (s, 1, CH-O), 7.39 (s, 5, PhH). Found: C, 66.33; H, 8.43%. Calcd for $C_{17}H_{26}O_3Si$: C, 66.62; H, 8.55%.

(More polar component on SiO_2 column chromatography): IR (neat) 3075, 3040, 3010, 2800, 1720 (C=O), 1600 (C=C), 1485, 1443, 1250, 1180, 1150, 1127, 1110, 1080, 1000, 890, 850, 760, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.06 (s, 9, $OSiMe_3$), 1.10—2.30 (m, 6, CH_2), 2.40—2.75 (m, 2, CH_2CO), 3.15 (s, 3, OCH_3), 3.68 (s, 1, CH-O), 7.30 (s, 5, PhH).

2-[(2-Furyl)methoxymethyl]-2-(trimethylsiloxy)cyclohexanone (6b): (Less polar component on SiO_2 column chromatography): IR (neat) 3100, 2850, 2805, 1725 (C=O), 1507, 1455, 1250, 1190, 1150, 1130, 1115, 1100, 1015, 912, 845, 790, 760, 738 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.04 (s, 9, $OSiMe_3$), 1.45—2.20 (m, 6, CH_2), 2.30—2.70 (m, 2, CH_2CO), 3.26 (s, 3, OCH_3), 4.60 (s, 1, CH-O), 6.33 (m, 2, CH=C), 7.36 (m, 1, CH=C). Found: C, 64.42; H, 8.46%. Calcd for $C_{15}H_{24}O_3Si$: C, 64.24; H, 8.63%.

(More polar component on SiO_2 column chromatography): IR (neat) 3100, 2855, 2810, 1730 (C=O), 1505, 1450, 1250, 1180, 1143, 1130, 1100, 1070, 980, 915, 840, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.12 (s, 9, $OSiMe_3$), 1.40—2.20 (m, 6, CH_2), 2.30—2.80 (m, 2, CH_2CO), 3.20 (s, 3, OCH_3), 4.73 (s, 1, CH-O), 6.37 (m, 2, CH=C), 7.38 (m, 1, CH=C).

2-(1-Methoxyheptyl)-2-(trimethylsiloxy)cyclohexanone (6c): (Less polar component on SiO_2 column chromatography): Bp 64—66 °C/0.008 Torr; IR (neat) 2820, 1720 (C=O), 1470, 1450, 1380, 1250, 1100, 1022, 940, 900, 840, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.11 (s, 9, $OSiMe_3$), 0.88 (m, 3, CH_3), 1.33 (br, 10, CH_2), 1.60—2.62 (m, 8, CH_2, CH_2CO), 3.42 (s, 3, OCH_3), 3.50 (m, 1, CH-O). Found: C, 65.14; H, 11.02%. Calcd for $C_{17}H_{34}O_3Si$: C, 64.92; H, 10.90%.

(More polar component on SiO_2 column chromatography): IR (neat) 2875, 1720 (C=O), 1460, 1250, 1180, 1140, 1120, 1100, 1070, 1050, 937, 840, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.11 (s, 9, $OSiMe_3$), 0.88 (m, 3, CH_3), 1.32 (br, 10, CH_2), 1.65—2.66 (m, 8, CH_2, CH_2CO), 3.32 (s, 3, OCH_3), 3.50 (m, 1, CH-O).

2-(1-Methoxy-1-phenylmethyl)-2-(trimethylsiloxy)cyclopentanone (6d): (Less polar component on SiO_2 column chromatography): Bp 57—59 °C/0.008 Torr; IR (neat) 3080, 3055, 3025, 2820, 1750 (C=O), 1602 (C=C), 1590, 1500, 1458, 1404, 1360, 1336, 1250, 1200, 1145, 1100, 1080, 982, 900, 843, 760, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.03 (s, 9, $OSiMe_3$), 1.30—2.50 (m, 6, CH_2, CH_2CO), 3.18 (s, 3, OCH_3), 4.34 (s, 1, CH-O), 7.33 (s, 5, PhH); ^{13}C NMR ($CDCl_3$) δ=1.93 (q), 17.7 (t), 33.3 (t), 36.4 (t), 57.3 (q), 83.5 (s), 85.9 (d), 127.9 (d, 3c), 128.5 (d, 2c), 136.7 (s), 216.8 (s).

(More polar component on SiO_2 column chromatography): IR (neat) 3075, 3040, 3020, 2810, 1742 (C=O), 1600 (C=C), 1495, 1450, 1400, 1255, 1200, 1150, 1105, 1080, 990, 900, 850, 760, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.08 (s, 9, $OSiMe_3$), 1.20—2.30 (m, 6, CH_2, CH_2CO), 3.22 (s, 3, OCH_3), 4.36 (s, 1, CH-O), 7.24 (s, 5, PhH).

2-(1-Methoxyheptyl)-2-(trimethylsiloxy)cyclopentanone (6e): Bp 56—58 °C/0.01 Torr; IR (neat) 2820, 1750 (C=O), 1470, 1405, 1250, 1155, 1104, 1080, 962, 900, 844, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.09 (s, 9, $OSiMe_3$), 0.90 (m, 3, CH_3), 1.30 (br, 10, CH_2), 1.80—2.45 (m, 6, CH_2, CH_2CO), 3.29 (s, 3, OCH_3), 3.33 (m, 1, CH-O). Found: C, 63.67; H, 10.71%. Calcd for $C_{16}H_{32}O_3Si$: C, 63.95; H, 10.73%.

2-(1-Methoxy-1-methylethyl)-2-(trimethylsiloxy)cyclopentanone (6f): Bp 44—46 °C/0.005 Torr; IR (neat) 2830, 1750 (C=O), 1470, 1410, 1380, 1365, 1253, 1160, 1115, 1060, 920, 890, 842, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.05 (s, 9, $OSiMe_3$), 1.16 (s, 6, CH_3), 1.55—2.70 (m, 6, CH_2, CH_2CO), 3.12 (s, 3, OCH_3); ^{13}C NMR ($CDCl_3$) δ=1.9 (q, 3C), 17.9 (t), 18.7 (q), 19.5 (q), 34.1 (t), 38.5 (t), 49.3 (q), 80.4 (s), 83.3 (s), 219.6 (s). Found: C, 58.76; H, 9.97%. Calcd for $C_{12}H_{24}O_3Si$: C, 58.97; H, 9.90%.

2-(1-Methoxy-1-phenylmethyl)-2-(trimethylsiloxy)cyclobutanone (6g):[19] IR (neat) 3080, 3060, 3020, 2815, 1790 (C=O), 1500, 1460, 1390, 1250, 1220, 1178, 1104, 1070, 1016, 875, 850, 760, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.04 (s, 9, $OSiMe_3$), 1.52—3.00 (m, 4, CH_2, CH_2CO), 3.28 (s, 3, OCH_3), 4.30 (s, 1, CH-O), 7.37 (s, 5, PhH).

2-(1-Methoxyheptyl)-2-(trimethylsiloxy)cyclobutanone (6h): IR (neat) 2840, 2810, 1780 (C=O), 1460, 1385, 1255, 1174, 1110, 850, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.12 (s, 9, $OSiMe_3$), 0.88 (m, 3, CH_3), 1.29 (br, 10, CH_2), 1.60—2.95 (m, 4, CH_2, CH_2CO), 3.15 (m, 1, CH-O), 3.30 (s, 3, OCH_3). Found: C, 62.85; H, 10.43%. Calcd for $C_{15}H_{30}O_3Si$: C, 62.88; H, 10.55%.

***erythro*-2-[(Trimethylsiloxy)phenylmethyl]cyclohexanone (7a):**[3b] IR (neat) 3055, 3040, 3020, 2840, 1710 (C=O), 1602 (C=C), 1495, 1450, 1370, 1250, 1130, 1100, 1065, 1010, 905, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.05 (s, 9, $OSiMe_3$),

1.07—2.07 (m, 6, CH_2), 2.07—2.67 (m, 3, CH_2CO, CHCO), 5.30 (d, J=4 Hz, 1, CH-O), 7.17 (s, 5, PhH).

***threo*-7a:** IR (neat) 3040, 3020, 2845, 1716 (C=O), 1600 (C=C), 1497, 1450, 1307, 1250, 1205, 1123, 1080, 1060, 1030, 880, 840, 765, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.01 (s, 9, $OSiMe_3$), 1.00—2.10 (m, 6, CH_2), 2.20—3.00 (m, 3, CH_2CO, CHCO), 5.05 (d, J=8 Hz, 1, CH-O), 7.22 (s, 5, PhH).

***erythro*-2-[(2-Furyl)(trimethylsiloxy)methyl]cyclopentanone (7b):** IR (neat) 2960, 2880, 1745 (C=O), 1250, 1155, 1120, 1050, 1005, 955, 915, 860, 845, 755, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.05 (s, 9, $OSiMe_3$), 1.60—2.50 (m, 7, CH_2, CH_2CO, CHCO), 5.20 (d, J=1 Hz, 1, CH-O), 6.10 (m, 1, CH=C), 6.21 (m, 1, CH=C), 7.25 (m, 1, CH=C); ^{13}C NMR ($CDCl_3$) δ=0.2 (q), 21.1 (t), 23.3 (t), 39.4 (t), 54.2 (d), 67.3 (d), 106.3 (d), 110.2 (d), 141.7 (d), 156.4 (s), 219.0 (s).

***threo*-7b:** IR (neat) 2920, 2880, 1740 (C=O), 1503, 1405, 1250, 1160, 1044, 1015, 924, 890, 840, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.10 (s, 9, $OSiMe_3$), 1.60—2.70 (m, 7, CH_2, CH_2CO, CHCO), 5.12 (d, J=4.5 Hz, 1, CH-O), 6.22 (m, 2, CH=C), 7.26 (m, 1, CH=C).

***erythro*-2-[(Trimethylsiloxy)phenylmethyl]cyclopentanone (7c):** Bp 53—54 °C/0.005 Torr; IR (neat) 3080, 3050, 3025, 1740 (C=O), 1600 (C=C), 1585, 1495, 1450, 1405, 1370, 1250, 1200, 1150, 1120, 1050, 1030, 990, 915, 862, 840, 755, 735, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.40 (s, 9, $OSiMe_3$), 1.35—2.40 (m, 7, CH_2, CH_2CO, CHCO), 5.25 (d, J=1 Hz, 1, CH-O), 7.20 (s, 5, PhH). Found: C, 68.79; H, 8.41%. Calcd for $C_{15}H_{22}O_2Si$: C, 68.65; H, 8.45%.

***threo*-7c:** IR (neat) 3080, 3050, 3025, 1740 (C=O), 1605, 1585, 1495, 1450, 1400, 1365, 1250, 1203, 1150, 1122, 1050, 1030, 990, 860, 840, 740, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.70 (s, 9, $OSiMe_3$), 1.40—2.40 (m, 7, CH_2, CH_2CO, CHCO), 5.12 (d, J=5 Hz, 1, CH-O), 7.20 (s, 5, PhH).

2-[(4-Methoxyphenyl)(trimethylsiloxy)methyl]cyclopentanone (7d): IR (neat) 2840, 2815, 1740 (C=O), 1619, 1590, 1515, 1462, 1405, 1250, 1050, 990, 915, 870, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.05 (s, 9, $OSiMe_3$), 1.35—2.55 (m, 7, CH_2, CH_2CO, CHCO), 3.70 (s, 3, OCH_3), 5.15 (m, 1, CH-O), 6.11, 6.71 (d, J=9 Hz, 4, PhH). Found: C, 65.55; H, 8.48%. Calcd for $C_{16}H_{24}O_3Si$: C, 65.71; H, 8.27%.

3-Trimethylsiloxy-1,3-diphenyl-1-propanone (7e): IR (neat) 3080, 3050, 3020, 1695 (C=O), 1600, 1581, 1498, 1363, 1255, 1207, 1180, 1100, 1075, 1050, 1030, 980, 958, 925, 890, 845, 750, 700cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.05 (s, 9, $OSiMe_3$), 2.98 (dd, J=16, 4 Hz, 1, CH_2CO), 3.57 (dd, J=16, 8 Hz, 1, CH_2CO), 5.31 (dd, J=8, 4 Hz, 1, CH-O), 7.03—7.98 (m, 10, PhH); ^{13}C NMR ($CDCl_3$) δ=2.0 (q), 27.6 (q), 54.3 (t), 76.9 (s), 125.1 (d, 2c), 126.9 (d), 128.0 (d, 4c), 129.1 (d, 2c), 132.5 (d), 138.5 (s), 148.4 (s), 198.9 (s).

3-(Trimethylsiloxy)-1,3-diphenyl-1-butanone (7f): IR (neat) 3045, 3020, 1680 (C=O), 1600 (C=C), 1582, 1495, 1450, 1380, 1320, 1300, 1250, 1210, 1080, 1040, 1000, 840, 760, 738, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.1 (s, 9, $OSiMe_3$), 1.85 (s, 3, CH_3), 3.30 (AB_q, J=13 Hz, Δ_{AB}=30.3 Hz, 2, CH_2), 7.10—8.10 (m, 10, PhH); ^{13}C NMR ($CDCl_3$) δ=2.0 (q), 27.5 (q), 54.1 (t), 76.8 (s), 125.0 (d, 2c), 126.8 (d), 128.0 (d, 4c), 128.9 (d, 2c), 132.5 (d), 138.4 (s), 148.2 (s), 198.9 (s). Found: C, 72.89; H, 7.76%. Calcd for $C_{19}H_{24}O_2Si$: C, 73.03; H, 7.74%.

Preparation of Homoallyl Alcohol Methyl Ether 9 from Acetal 1 and Allyltrimethylsilane (8); General Procedure. A mixture of $LiClO_4$ (11 mg, 0.10 mmol) and n-Bu_4NClO_4 (35 mg, 0.10 mmol) in the same electrolysis vessel as described above was dried under reduced pressure over P_2O_5 for 1 h and then purged with argon. To this mixture were added acetal **1a** (154 mg, 1.0 mmol), allyltrimethylsilane (117 mg, 1.0 mmol), and CH_2Cl_2 (3 ml). The mixture was electrolyzed using platinum foil electrodes (1.5 cm^2) at a constant current of 4 mA (applied voltage: 9—11 V) with external cooling at 0 °C. After passing 0.07 F mol^{-1} of electricity (for about 27 min), the reaction was quenched with Et_3N (2 drops), and the resulting mixture was concentrated in vacuo. The residue was purified by column chromatography (SiO_2, hexane-AcOEt 5:1) to give 135 mg (82%) of **9a**[2] as an oil: bp 75.0 °C/2.5 Torr; IR (neat) 3060, 2830, 2810, 1638 (C=C), 1475, 1460, 1362, 1080, 993, 913, 850, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.45 (m, 2, CH_2), 3.19 (s, 3, OCH_3), 4.12 (t, J=6.5 Hz, 1, CH-O), 4.72—6.10 (m, 3, CH_2=CH), 7.22 (s, 5, PhH).

4-(4-*t*-Butylphenyl)-4-methoxy-1-butene (9f): Bp 110.5 °C/4 Torr; IR (neat) 3060, 2855, 2802, 1640 (C=C), 1616 (C=C), 1507, 1460, 1362, 1262, 1190, 1100, 920, 834 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.32 (s, 9, CH_3), 2.49 (m, 2, CH_2), 3.20 (s, 3, OCH_3), 4.12 (t, J=6.5 Hz, 1, CH-O), 4.80—6.25 (m, 3, CH_2=CH), 7.05—7.40 (m, 4, PhH). Found: C, 81.51; H, 10.19%. Calcd for $C_{15}H_{22}O$: C, 82.52: H, 10.16%.

4-Methoxy-4-(4-methoxyphenyl)-1-butene (9g): Bp 105.5 °C/4.5 Torr; IR (neat) 3050, 2820, 2800, 1639 (C=C), 1610 (C=C), 1580, 1504, 1460, 1440, 1350, 1300, 1242, 1163, 1030, 990, 917, 826, 803 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.20—2.65 (m, 2, CH_2), 3.15 (s, 3, OCH_3), 3.75 (s, 3, OCH_3), 4.15 (t, J=6.5 Hz, 1, CH-O), 4.70—6.10 (m, 3, CH_2=CH), 6.77, 7.13 (d, J=9 Hz, 4, PhH).

4-Methoxy-4-(3,4,5-trimethoxyphenyl)-1-butene (9h): Bp 142.0 °C/3 Torr; IR (neat) 3075, 2815, 1644 (C=C), 1600 (C=C), 1505, 1463, 1420, 1358, 1330, 1240, 1191, 1130, 1110, 1024, 934, 843 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.42 (m, 2, CH_2), 3.20 (s, 3, OCH_3), 3.81, 3.82 (s, 9, OCH_3), 4.15 (t, J=6.5 Hz, 1, CH-O), 4.72—6.00 (m, 3, CH_2=CH), 6.45 (s, 2, PhH); ^{13}C NMR ($CDCl_3$) δ=42.6 (t), 56.1 (q, 2c), 56.7 (q), 60.7 (q), 83.9 (d), 103.5 (d, 2c), 116.8 (t), 134.9 (d), 137.3 (s), 137.6 (s), 153.3 (s, 2c). Found: C, 66.80; H, 7.95%. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99%.

4-(4-Cyanophenyl)-4-methoxy-1-butene (9i): Bp 118.0 °C/4 Torr; IR (neat) 3080, 2810, 2242 (C≡N), 1640 (C=C), 1615 (C=C), 1502, 1415, 1360, 1310, 1282, 1240, 1200, 1110, 1100, 920, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.44 (m, 2, CH_2), 3.21 (s, 3, OCH_3), 4.19 (t, J=6 Hz, 1, CH-O), 4.70—6.10 (m, 3, CH_2=CH), 7.32, 7.60 (d, J=7 Hz, 4, PhH); ^{13}C NMR ($CDCl_3$) δ=42.1 (t), 57.0 (q), 83.0 (d), 117.7 (t), 118.7 (s), 127.4 (d, 2C), 132.2 (d, 2C), 133.6 (s), 133.6 (d), 147.4 (s).

3-Methoxy-1-phenyl-1,5-hexadiene (9j):[19] Bp 100.5 °C/2.5 Torr; IR (neat) 3072, 3014, 2805, 1640 (C=C), 1600 (C=C), 1579, 1492, 1448, 1360, 1190, 1100, 965, 916, 747, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.39 (m, 2, CH_2), 3.30 (s, 3, OCH_3), 3.75 (m, 1, CH-O), 4.81—5.22 (m, 2, CH_2=C), 5.52—6.68 (m, 3, CH=C, CH=CH), 7.00—7.50 (m, 5, PhH).

3-(1-Methoxy-4-*t*-butylcyclohexyl)-1-propene (9k):[19] IR (neat) 3060, 2820, 2810, 1638 (C=C), 1390, 1360, 1080, 993, 910, 850, 810, 738 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.83 (s, 9, CH_3), 0.95—2.00 (m, 8, CH_2), 2.15 (d, J=6 Hz, 2, CH_2), 3.13 (s, 3, OCH_3), 4.75—6.10 (m, 3, CH=C).

Cyanation of Acetals 1 with Trimethylsilyl Cyanide (10) to α-Alkoxyalkanenitriles 11; General Procedure. A mixture of heptanal dimethyl acetal (**1c**, 541 mg, 3.38 mmol), trimethylsilyl cyanide (**10**, 0.7 ml, 5.26 mmol), $LiClO_4$ (23 mg, 0.22 mmol), and Et_4NClO_4 (52 mg, 0.18 mmol) in CH_2Cl_2 (5 ml) was electrolyzed with platinum electrodes (1.5 cm^2) in an

undivided cell at an applied voltage of 15 V (current: 12—13 mA). After electrolysis for 32 min (passed electricity: 0.077 F mol^{-1} based on the acetal **1c**) and an additional stirring for 5 min at room temperature, the reaction was quenched with pyridine (2 drops). Concentration of the mixture under vacuum followed by either column chromatography (SiO_2, hexane-AcOEt, 50 : 1) or bulb to bulb distillation gave 430 mg (89%) of **11c** as an oil.

2-Methoxy-2-phenylethanenitrile (11a):[4] Bp 105 °C/9 Torr; IR (neat) 3060, 3040, 3005, 2835, 2260 (C≡N), 1601 (C=C), 1590, 1500, 1458, 1320, 1284, 1207, 1100, 1037, 1008, 975, 918, 843, 760, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.50 (s, 3, OCH_3), 5.17 (s, 1, CH-O), 7.40 (br, 5, PhH).

2-(2-Furyl)-2-methoxyethanenitrile (11b): Bp 105 °C/9 Torr; IR (neat) 3153, 3120, 3000, 2830, 1500, 1460, 1390, 1320, 1303, 1243, 1235, 1195, 1180, 1150, 1140, 1080, 1018, 962, 958, 910, 890, 880, 822, 797, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.47 (s, 3, OCH_3), 5.30 (s, 1, CH-O), 6.41 (m, 1, CH=C), 6.62 (d, J=4 Hz, 1, CH=C), 7.47 (d, J=2 Hz, 1, CH=C).

2-Methoxyoctanenitrile (11c):[4] Bp 85 °C/9 Torr; IR (neat) 2970, 2900, 2810, 2800, 1465, 1370, 1330, 1130, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.97 (m, 3, CH_3), 1.31 (br, 10, CH_2), 3.46 (s, 3, OCH_3), 3.95 (t, J=6 Hz, 1, CH-O).

2-Methoxy-4-phenyl-3-butenenitrile (11j): Bp 90 °C/3 Torr; IR (neat) 3040, 3020, 3002, 2800, 2240 (C≡N), 1598, 1570, 1485, 1440, 1330, 1190, 1120, 1090, 960, 900, 740, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.50 (s, 3, OCH_3), 4.81 (dd, J=6, 1 Hz, 1, CH-O), 6.13 (dd, J=16, 6 Hz, 1, CH=C), 6.92 (dd, J=16, 1 Hz, CH=C), 7.33 (br, 5, PhH).

2-Methoxy-3-phenylpropanenitrile (11l):[4] Bp 110 °C/9 Torr; IR (neat) 3075, 3040, 3005, 2840, 1600 (C=C), 1500, 1460, 1340, 1120, 1080, 750, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.06 (d, J=7 Hz, 2, CH_2), 3.44 (s, 3, OCH_3), 4.18 (t, J=7Hz, 1, CH-O), 5.25 (s, 5, PhH).

2-(2-Methoxycarbonylethyl)-1-methoxycyclohexanecarbonitrile (11m): Bp 91 °C/3 Torr; IR (neat) 2840, 2803, 2240 (C≡N), 1730 (C=O), 1442, 1430, 1130, 1250, 1195, 1170, 1100, 1070, 1050, 1010, 980, 945, 922, 910, 884, 840, 725 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.00—2.08 (m, 10, CH_2), 2.08—2.60 (m, 3, CH_2CO, CH), 3.40 (s, 3, OCH_3), 3.65 (s, 3, CO_2CH_3).

3-Methoxycarbonyl-2-methoxypropanenitrile (11n): Bp 75 °C/5 Torr; IR (neat) 2815, 1740 (C=O), 1435, 1367, 1280, 1202, 1165, 1115, 1010, 982 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.87 (d, J=6 Hz, 2, CH_2), 3.51 (s, 3, OCH_3), 3.74 (s, 3, CO_2CH_3), 4.48 (t, J=6 Hz, 1, CH-O).

***N*-Ethoxycarbonyl-2-cyanopiperidine (11o):** Bp 83 °C/3 Torr; IR (neat) 2945, 2860, 1710 (C=O), 1420, 1260, 1180, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.25 (t, J=7 Hz, 3, CH_3), 1.30—2.20 (m, 7, CH_2, N-CH_2), 2.95 (m, 1, N-CH_2), 4.12 (q, J=7 Hz, 2, CO_2CH_2), 5.22 (m, 1, N-CH).

1-(Trimethylsiloxy)cyclododecanecarbonitrile (12e):[27] IR (neat) 2245 (C≡N), 1473, 1450, 1255, 1100, 1045, 1008, 863, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.25 (s, 9, $OSiMe_3$), 1.36 (m, 18, CH_2), 1.61—2.11 (m, 4, CH_2).

2-Ethyl-2-(trimethylsiloxy)butanenitrile (12f):[26] IR (neat) 2240 (C≡N), 1460, 1250, 1160, 1130, 1077, 1018, 880, 845, 757 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.22 (s, 9, $OSiMe_3$), 1.11 (t, δ=7 Hz, 6, CH_3), 1.75 (q, J=7 Hz, 4, CH_2).

2-Methyl-2-(trimethylsiloxy)heptanenitrile (12g):[28] IR (neat) 2245 (C≡N), 1466, 1380, 1257, 1195, 1142, 1105, 1080, 1033, 850, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.23 (s, 9, $OSiMe_3$), 0.90 (m, 3, CH_3), 1.30—1.85 (m, 8, CH_2), 1.55 (s, 3, CH_3).

Ethyl 2-Cyano-2-(trimethylsiloxy)propionate (12h): Bp 58—60 °C/2 Torr; IR (neat) 2280(C≡N), 1774 (C=O), 1458, 1383, 1262, 1200, 1156, 1008, 926, 860, 742 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.25 (s, 9, $OSiMe_3$), 1.32 (t, J=8 Hz, 3, CH_3), 1.75 (s, 3, CH_3), 4.26 (q, J=8 Hz, CH_2). Found: C, 49.96; H, 8.20; N, 6.34%. Calcd for $C_9H_{17}NO_3Si$: C, 50.20; H, 7.96; N, 6.51%.

2-Trimethylsiloxy-2-phenylpropanenitrile (12d):[28] IR (neat) 3043, 3010, 2240 (C≡N), 1600, 1490, 1445, 1370, 1250, 1223, 1150, 1120, 1000, 910, 843, 760, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.17 (s, 9, $OSiMe_3$), 1.83 (s, 3, CH_3), 7.20—7.65 (m, 5, PhH).

5-Isopropenyl-2-methyl-1-trimethylsiloxy-2-cyclohexene-1-carbonitrile (12i): Bp 79—81 °C/2 Torr; IR (neat) 3070, 3020, 2960, 2240 (C≡N), 1645, 1450, 1260, 1135, 1055, 960, 910, 850, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.20 (s, 9, $OSiMe_3$), 1.73 (s, 3, CH_3), 1.77 (s, 3, CH_3), 1.10—2.60 (m, 5, CH_2, CH), 4.72 (m, 2, CH_2=C), 5.60 (m, 1, CH=C). Found: C, 67.41; H, 7.96; N, 6.34%. Calcd for $C_{14}H_{23}NOSi$: C, 67.41; H, 9.29; N, 5.61%.

2-Hydroxyoctanenitrile (13j): IR (neat) 2920, 2840, 2240 (C≡N), 1460, 910, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90 (m, 3, CH_3), 1.10—2.10 (m, 10, CH_2), 2.60—3.40 (brs. 1, OH), 4.48 (t, J=6 Hz, 1, CH-O).

2-Hydroxy-2-phenylethanenitrile (13a): IR (neat) 3390 (OH), 3050, 2255 (C≡N), 1500, 1455, 1200, 1040, 1025, 940, 760, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.72 (brs , 1, OH), 5.43 (s, 1, CH-O), 7.41 (s, 5, PhH).

2-Hydroxy-2-(4-methoxyphenyl)ethanenitrile (13c): IR (neat) 3400 (OH), 2840, 2235 (C≡N), 1620, 1595, 1520, 1260, 1180, 1035, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.74 (s, 3, OMe), 3.50—4.00 (brs, 1, OH), 6.82 (d, J=10 Hz, 2, PhH), 7.32 (d, J=10Hz, 2, PhH).

2-Hydroxy-2-(4-cyanophenyl)ethanenitrile (13k): Mp 71—73 °C; IR ($CHCl_3$) 3400 (OH), 2245 (C≡N), 1420, 1200, 920, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.5—4.5 (brs, 1, OH), 5.60 (s, 1, CH-O), 7.62 (s, 4, PhH). Found: C, 68.18; H, 3.80; N, 17.57%. Calcd for $C_9H_6N_2O$: C, 68.35, H, 3.82; N, 17.71%.

2-Hydroxy-4-phenyl-3-butenenitrile (13l): IR (neat) 3400 (OH), 3040, 3020, 2250 (C≡N), 1495, 1450, 970, 750, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.70—4.30 (brs, 1, OH), 5.07 (d, J=6 Hz, 1, CH-O), 6.15 (dd, J=15, 6 Hz, 1, C=CH), 6.82 (d, J=15 Hz, 1, C=CH), 7.29 (s, 5, PhH).

Reaction of Acetals 1 with Triethylsilane (14); General Procedure. A mixture of acetal (**1a** 922 mg, 5.06 mmol) and Et_3SiH (**14**, 605.6 mg, 5.21 mmol) in CH_2Cl_2 (5 ml) containing $LiClO_4$ (42 mg, 0.39 mmol) and n-Bu_4NClO_4 (135.7 mg, 0.40 mmol) was electrolyzed at a constant current of 4 mA (applied voltage: 7—8 V) with platinum electrodes (1.5 cm^2) at 0 °C under argon. After passing 0.07 F mol^{-1} of electricity (it took about 25 min), the reaction was quenched with Et_3N (3 drops). Concentration followed by column chromatography (SiO_2, hexane-AcOEt, 5 : 1) gave 543 mg (88%) of **15a**[2] as an oil: IR (neat) 3080, 3060, 3020, 1605, 1450, 1380, 1100, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.36 (s, 3, OCH_3), 4.43 (s, 2, CH_2-O), 7.29 (s, 5, PhH).

1-*t*-Butyl-4-(methoxymethyl)benzene (15f): Bp 88.5 °C/2 Torr; IR (neat) 2960, 2860, 2810, 1630, 1515, 1478, 1460, 1412, 1380, 1365, 1270, 1215, 1195, 1185, 1112, 1100, 1020, 970, 920, 855, 838, 818, 670, 660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.30 (s, 9, CH_3), 3.35 (s, 3, OCH_3), 4.38 (s, 2, CH_2-O), 7.20—7.40 (m, 4, PhH).

1-Methoxy-4-(methoxymethyl)benzene (15g): Bp 91.5 °C/4 Torr; IR (neat) 2950, 2900, 2870, 2830, 1618, 1590, 1515, 1465, 1440, 1412, 1380, 1365, 1300, 1270, 1250, 1170, 1100, 1038, 1018, 1005, 960, 910, 850, 820, 740, 660 cm^{-1}; ^1H NMR

($CDCl_3$) δ=3.29 (s, 3, OCH_3), 3.72 (s, 3, OCH_3), 4.31 (s, 2, CH_2-O), 6.77, 7.16 (d, J=8.5 Hz, 4, PhH).

1,2,3-Trimethoxy-5-(methoxymethyl)benzene (15h): Bp 127.0 °C/4.5 Torr; IR (neat) 2930, 2830, 1600, 1510, 1470, 1430, 1390, 1370, 1340, 1240, 1190, 1130, 1110, 1050, 1020, 995, 925, 845, 795, 740, 705, 675 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.39 (s, 3, OCH_3), 3.82 (s, 9, OCH_3), 4.35 (s, 2, CH_2-O), 6.50 (s, 2, PhH).

4-(Methoxymethyl)benzonitrile (15i): Bp 104.0 °C/3.5 Torr; IR (neat) 2980, 2930, 2880, 2820, 2250 (C≡N), 1615, 1505, 1470, 1452, 1415, 1385, 1245, 1210, 1200, 1108, 1058, 1022, 990, 975, 925, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.40 (s, 3, OCH_3), 4.47 (s, 2, CH_2-O), 7.35, 7.60 (d, J=8 Hz, 4, PhH).

References

1) a) T. H. Chan and I. Fleming, *Synthesis,* **1979**, 761; b) E. W. Colvin, "Silicon in Organic Synthesis," Butterworths, London (1981); c) W. R. Weber, "Silicon Reagents for Organic Synthesis," Springer-Verlag, Berlin, Heiderberg (1983).

2) R. Noyori, S. Murata, and M. Suzuki, *Tetrahedron,* **37**, 3899 (1981).

3) a) T. Mukaiyama, S. Kobayashi, and M. Murakami, *Chem. Lett.,* **1984**, 1759; b) *ibid.,* **1985**, 447.

4) K. Utimoto, Y. Wakabayashi, T. Horiie, M. Inoue, Y. Shishiyama, M. Obayashi, and H. Nozaki, *Tetrahedron,* **39**, 967 (1983).

5) S. Kobayashi, M. Murakami, and T. Mukaiyama, *Chem. Lett.,* **1985**, 953.

6) Preparation of $TrClO_4$: H. J. Dauben Jr., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.,* **25**, 1442 (1960).

7) a) S. Torii, "Electroorganic Syntheses: Oxidations Methods and Applications;" Kodansha+Verlag Chemie: Tokyo+Weinheim, 1985; Part I, Chapter 13; b) K. Uneyama, *Yuki Gosei Kagaku Kyokai Shi,* **43**, 557 (1985).

8) a) K. Uneyama, A. Isimura, K. Fujii, and S. Torii, *Tetrahedron Lett.,* **24**, 2857 (1983); b) K. Uneyama, N. Nisiyama, and S. Torii, *ibid.,* **25**, 4137 (1984).

9) S. Torii, T. Inokuchi, K. Kondo, and H. Ito, *Bull. Chem. Soc. Jpn,* **58**, 1347 (1985).

10) K. Uneyama, Y. Masatsugu, T. Ueda, and S. Torii, *Chem. Lett.,* **1984**, 529.

11) K. Uneyama, A. Isimura, and S. Torii, *Bull. Chem. Soc. Jpn,* **58**, 1859 (1985).

12) S. Torii and T. Inokuchi, *Chem. Lett.,* **1983**, 1349.

13) T. Mukaiyama, *"Organic Reactions,"* Wiley & Sons, New York (1982), Vol. 28, p. 203.

14) a) S. Murata, M. Suzuki, and R. Noyori, *J. Am. Chem. Soc.,* **102**, 3248 (1980); b) E. Nakamura, M. Shimizu, I. Kuwajima, J. Sakata, Y. Yokoyama, and R. Noyori, *J. Org. Chem.,* **48**, 932 (1983).

15) a) T. Mukaiyama and M. Hayashi, *Chem. Lett.,* **1974**, 15; b) T. Mukaiyama and A. Ishida, *ibid.,* **1975**, 319; c) T. Mukaiyama, H. Ishihara, and K. Inomata, *ibid.,* **1975**, 527; d) *ibid.,* **1975**, 531.

16) a) J. Simada, K. Hashimoto, B. H. Kim, E. Nakamura, and I. Kuwajima, *J. Am. Chem. Soc.,* **106**, 1759 (1984); b) I. Kuwajima, "Gendai Kagaku Zokan;" Tokyo-Kagaku Dojin, (1985), Vol. 3, p. 108.

17) a) A. Hosomi and H. Sakurai, *Yuki Gosei Kagaku Kyokai Shi,* **43**, 406 (1985); b) Z. N. Parnes and G. I. Bolestova, *Synthesis,* **1984**, 991.

18) a) A. Hosomi, H. Sakurai, and M. Endo, *Chem. Lett., Gosei* **1976**, 941; b) A. Hosomi, M. Endo, and H. Sakurai, *ibid.,* **1978**, 499.

19) T. Tsunoda, M. Suzuki, and R. Noyori, *Tetrahedron Lett.,* **1980**, 71.

20) K. Kobayashi and T. Hiyama, *Tetrahedron Lett.,* **24**, 3509 (1983).

21) W. P. Wallace and H. R. Henze, *J. Am. Chem. Soc.,* **64**, 2882 (1942).

22) G. Stork and L. Maldonado, *J. Am. Chem. Soc.,* **93**, 5286 (1971).

23) M. Hudlický, "Reductions in Organic Chemistry;" Ellis Horwood Limited, Chichester, England (1984).

24) T. Tsunoda, M. Suzuki, and R. Noyori, *Tetrahedron Lett.,* **1979**, 4679.

25) a) H. O. House, L. J. Czuba, M. Gall, and H. D. Olmsted, *J. Org. Chem.,* **34**, 2324 (1969); b) J. K. Rasmussen, *Synthesis,* **1977**, 91.

26) K. Rühlmann, *Synthesis,* **1971**, 236.

27) D. A. Evans, G. L. Carroll, and L. K. Truesdale, *J. Org. Chem.,* **39**, 914 (1974).

28) D. A. Evans and L. K. Truesdale, *Tetrahedron Lett.,* **1973**, 4929.