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Anodic Oxidation of (Trimethylsilyl)methanes with π-Electron Substituents in the Presence of Nucleophiles

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It was found that oxidation potentials of methanes with π-electron substituents were decreased by introduction of a trimethylsilyl group. The anodic oxidation of benzyl-, allyl-, aryl(or alkyl)thiomethyl-, and aryloxymethyl-substituted trimethylsilanes smoothly proceeded in the presence of nucleophiles, e.g. alcohols and carboxylic acids, to eliminate the trimethylsilyl groups giving the corresponding alkoxylated and carboxylated products in moderate or high yields without full optimization of electrolytic conditions, while aminomethylsilanes did not undergo such a kind of anodic oxidation.

Anodic oxidation of organic compounds involves mostly a proton elimination step which sometimes governs overall efficiency and/or selectivity of the reaction. For instance, the anodic substitution of toluene involves the proton elimination from the methyl or phenyl group which is substituted by a nucleophile. The proton elimination step is generally influenced by reaction conditions, and in fact it has been found that the product selectivity of the toluene oxidation is sensitively affected by electrolytic conditions such as acidity/basicity of anolyte and anode material.[1—6]

In this work, it was attempted to control the proton elimination on the basis of a different principle in which the methyl group of toluenes was modified by a cationic leaving group. As leaving species more favorable than proton, NO^+, RCO^+, and I^+ have sometimes been used.[7] However, these are electron-withdrawing groups, which cause increases in the oxidation potential of the mother compounds. This should be a disadvantage for efficient anodic oxidation. In this work, a trimethylsilyl group was used as a cationic leaving group for the following reasons:[8] (a) A trimethylsilyl substituent increases HOMO energy level of π-electron system at β-position,[14—17] (b) a C-Si bond is more easily cleaved than a C-H one[18] (Bonding energy: CH_3-$SiMe_3$, 89.4 kcal mol^{-1}; CH_3-H, 104.8 kcal mol^{-1}[19]), (c) a silicon atom is more easily attacked by nucleophiles than a hydrogen one,[18] (d) silyl substituents contribute to stabilize β-carbocations, comparably to alkoxy ones,[18,20] (e) a C-Si bond is chemically stable,[18] and (f) trimethylsilyl compounds are easily prepared using trimethylsilyl chloride.[21]

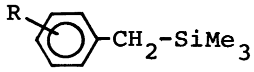
The following anodic substitution reaction of (trimethylsilyl)methanes with π-electron substituents was examined in the presence of nucleophiles, e.g. alcohols and carboxylic acids.

$$\mathrm{A{-}\overset{|}{\underset{|}{C}}{-}SiMe_3 + NuH \xrightarrow{-2e} A{-}\overset{|}{\underset{|}{C}}{-}Nu + {}^{+}SiMe_3 + H^+}$$

A: π-Electron substituent
NuH: Nucleophile

Results and Discussion

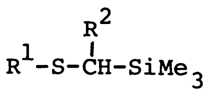
Trimethylsilylated compounds[(trimethylsilyl)methanes] such as benzyl-, allyl-, thiomethyl-, oxymethyl-, and aminomethyl-trimethylsilane (**1**—**5**), and related unsilylated compounds were used as the starting materials of the anodic oxidation.



1a: R=H
1b: R=*p*-Me
1c: R=*o*-Me

R-CH=CH-CH_2-$SiMe_3$

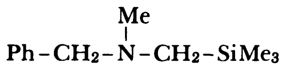
2a: R=H
2b: R=Ph



$$R^1\text{-S-}\overset{R^2}{\overset{|}{C}}\text{H-SiMe}_3$$

3a: R^1=Ph, R^2=H
3b: R^1=*p*-Me-C_6H_4, R^2=H
3c: R^1=Me, R^2=Ph

Ph-O-CH_2-$SiMe_3$ **4**



$$\text{Ph-CH}_2\text{-}\overset{\text{Me}}{\overset{|}{N}}\text{-CH}_2\text{-SiMe}_3$$

5

Oxidation Potentials of Trimethylsilanes. Benzyl- and thiomethyl-trimethylsilanes (**1a**, **b**, and **3a**, **c**) gave irreversible cyclic voltammetric waves at a platinum anode in 0.1 M (1 M=1 mol dm^{-3}) Bu_4NBF/MeCN (Scan rate, 100 mV s^{-1}). As shown in Table 1, their oxidation peak potentials (E_p^{ox}) are significantly less noble than those of the unsilylated parent compounds. Similar decreases in oxidation potentials of allyl- and aminomethyl-silanes have been found by Yoshida et al.[11] and Cooper and Owen,[22] respectively. These facts suggest that the decreases in oxidation potentials of the π-electron compounds can be induced by introduction of silyl groups to the α-positions.

Anodic Oxidation of Benzylsilanes (1a—c). Oxidation in Methanol: Benzylsilanes (**1a**, **b**) were oxidized at platinum and graphite anodes in methanol containing $NaClO_4$ to give mixtures of α-monomethoxy-

Table 1. Oxidation Potentials of Benzyl- and [Aryl(or alkyl)thiomethyl]trimethylsilanes, and Their Unsilylated Parent Compounds

Trimethylsilane	E_p^{ox}/V[a]	Unsilylated parent compound	E_p^{ox}/V[a]
1a	1.38	Ph-CH_3	1.98
1b	1.17	*p*-Me-C_6H_4-CH_3	1.70
3a	0.92	Ph-S-CH_3	1.05
3c	0.99	Me-S-CH_2-Ph	1.25

a) vs. Ag/$AgNO_3$ sat.

Table 2. Anodic Oxidation of Benzyltrimethylsilanes in Methanol[a]

Run	Benzyltrimethylsilane	Anode	Charge passed/×96500 C mol^{-1}	Yield[b]/% **6a/b**	Yield[b]/% **7a/b**
1	**1a**	Pt	2.8	56	35
2	**1a**	Graphite	2.8	49	30
3	**1a**	Pt	4.7	38	52
4	**1a**	Graphite	4.7	44	49
5	**1b**	pt	3.0	47	32
6	**1b**	Graphite	3.0	25	39
7	**1b**	pt	5.0	8	65
8	**1b**	Graphite	5.0	0	61

a) Silanes (5 mmol) were electrolyzed at 1.0 A dm^{-2} of constant current in 0.57 M $NaClO_4$/MeOH (35 cm^3) in a divided cell. b) Determined by GLC.

toluenes (**6a**, **b**) and α,α-dimethoxytoluenes (**7a**, **b**) in good combined yields (Table 2). Any nucleus-methoxylated products were not formed. At smaller amounts of charge passed, the platinum anode seems somewhat favorable to the formation of **6**. Increases in charge passed resulted in evident decreases and increases in the yields of **6** and **7**, respectively. This fact suggests that **7** forms via **6**.

$$\mathbf{1a,b} \xrightarrow{-2e\ +\ \mathrm{MeOH}} \mathrm{R{-}C_6H_4CH_2{-}OMe}$$

6a: R=H

6b: R=*p*-Me

$$\xrightarrow{-2e\ +\ \mathrm{MeOH}} \mathrm{R{-}C_6H_4CH(OMe)_2}$$

7a: R=H

7b: R=*p*-Me

It is interesting to note that Yoshida et al.[11] have obtained **6** (R=H and *p*-Cl) as single products in high yields in the anodic oxidation of **1** at a graphite anode in Et_4NOTs/MeOH, though any reasoning for such a difference from the above result can not be made at present.

Oxidation in Dichloromethane: Allyl alcohol is easily oxidized because of its low oxidation potential.[23] Therefore, the anodic allyloxylation hardly takes place in general, since the oxidation of allyl alcohol itself occurs preferably to substrates to be allyloxylated. However, the benzylsilanes, of which the oxidation potentials are decreased by the introduction of trimethylsilyl groups, could be anodically allyloxylated in moderate yields under unoptimized conditions (Table 3: Runs 9 and 10).

The anodic substitution is reasonably affected by natures of nucleophiles used. In fact 2,2,2-trifluoroethanol, whose nucleophilicity should be extremely low due to the strongly electron-withdrawing CF_3 group, did not give the corresponding trifluoroethoxylated product (Run 11). On the other hand, somewhat nucleophilic trifluoroacetate ion gave benzyl trifluoroacetate along with benzyl alcohol as a by-product in the oxidation of **1a** (Run 12). The formation of benzyl alcohol may be due to water as a contaminant in the electrolyte or to hydrolysis of the main prodct during the work-up procedure. In Run 13 without any nucleophile added, **1a** itself played a role of nucleophile and benzyl(trimethylsilylmethyl)benzene was formed in 30% yield. In a quaternary ammonium tosylate solution (Run 14), tosylate ion did not act as a nucleoplile, but products such as bibenzyl and toluene were formed, probably, via benzyl radical intermediate species.

From the above results, a mechanistic scheme (Scheme 1) can be postulated as below. In the scheme, the elimination of trimethylsilyl cation from the cation radical intermediate species occurs superiorly to that of protons and the radical coupling process proceed under certain conditions.

In an acetonitrile solution (Run 15), **1a** was anodically acetamidated to give *N*-benzylacetamide in a low yield.

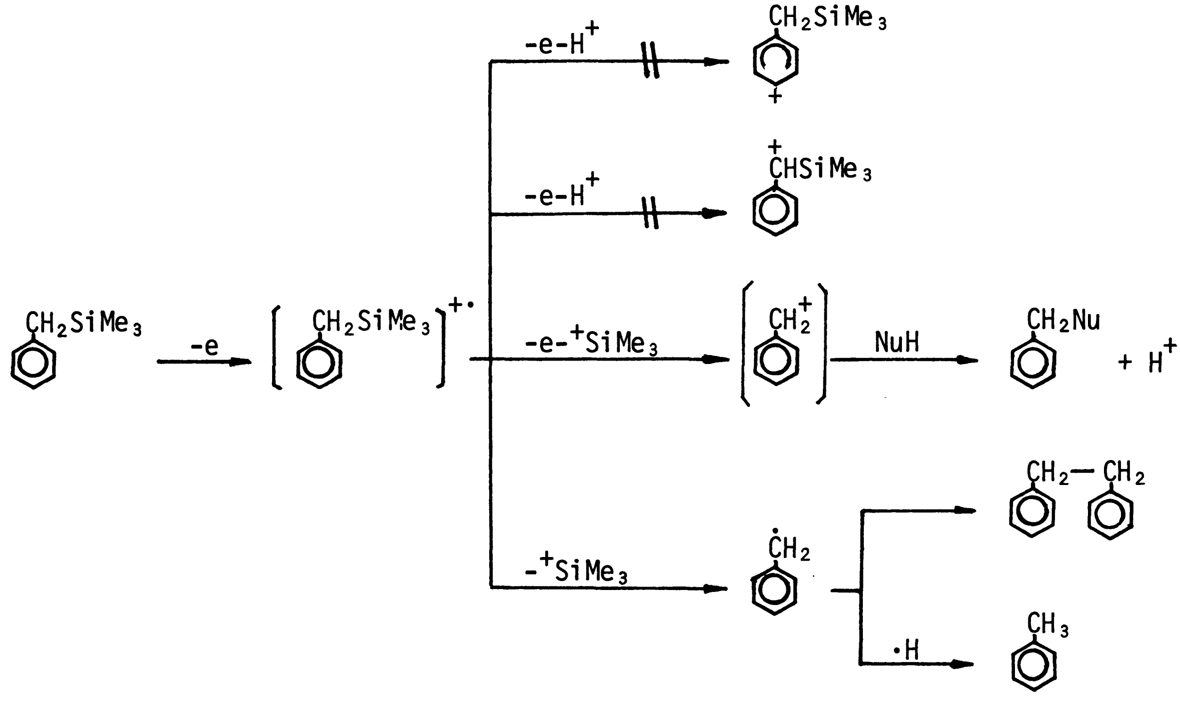
Anodic Oxidation of Allylsilanes (2a, b). Allyltrimethylsilane (**2b**) was anodically trifluoroethoxylated in a low yield in a divided cell (Table 4: Run 16), while benzyltrimethylsilane (**1b**) was not in an undivided cell (Run 11). Reasoning for this difference has not been clearly made, but it is likely that the trifluoroethoxylation is accelerated by acid electrogenerated in the anode chamber of the divided cell. In fact, the yield was increased by addition of TsOH (Run 17).

Although benzylsilane (**1a**) did not give the corresponding tosylate but underwent the radical process as described above (Run 14), allyl tosylate was formed in the oxidation of allylsilane (**2a**) under similar conditions (Run 18). This may be rationalized due to a stronger electrophilicity of allyl cation than benzyl one

Table 3. Anodic Oxidation of Benzyltrimethylsilanes in Dichloromethane in the Presence and Absence of Nucleophiles[a]

Run	Benzyltrimethylsilane	Nucleophile	Electrolyte	Anode	Charge passed/X96500 C mol^{-1}	Product (Yield/%)
9[b]	**1c**	$CH_2{=}CHCH_2OH$[c]	0.60 M Et_4NOTs	Graphite	2.0	o-Me-C_6H_4-O-$CH_2CH{=}CH_2$ (36[d])
10[b]	**1b**	$CH_2{=}CHCH_2OH$[c]	0.60 M Et_4NOTs	Graphite	2.0	p-Me-C_6H_4-O-$CH_2CH{=}CH_2$ (34[d])
11[b]	**1b**	CF_3CH_2OH[c]	0.60 M Et_4NOTs	Graphite	2.0	p-Me-C_6H_4-O-CH_2CF_3 (Not formed)
12[b]	**1a**	CF_3COO^-	0.57 M $CF_3COONBu_4$	Pt	3.0	$PhCH_2$-$OOCCF_3$ (24[e]) $PhCH_2$-OH (8[e])
13[f]	**1a**	—	0.57 M Bu_4NClO_4	Pt	1.5	$PhCH_2$-$C_6H_4SiMe_3$ (30[e])
14[f]	**1a**	—	0.46 M Et_4NOTs	Graphite	2.4	$PhCH_2CH_2Ph$ (9[d]) $PhCH_3$ (trace)
15[f]	**1a**	MeCN[g] + H_2O	0.57 M Bu_4NBF_4	Pt	2.0	$PhCH_2$-NHCOMe[h] (17[d])

a) Silanes (5 mmol) were electrolyzed at 1.0 A dm^{-2} of constant current. b) An undivided cell was used. c) 20 mmol. d) Isolated yield. e) Determined by GLC. f) A divided cell was used. g) Used as solvent. h) Unknown products were also formed.



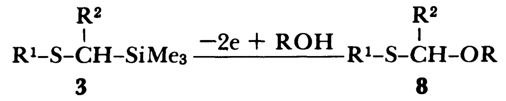
Scheme 1.

Table 4. Anodic Oxidation of Allylsilanes in the Presence of Nucleophiles[a]

Run	Allylsilane	Nucleophile	Electrolyte	Product (Yield[b]/%)
16	**2b**	CF_3CH_2OH (20 eq)	0.30 M Et_4NOTs	$PhCH=CHCH_2-OCH_2CF_3$ (10)
17[c]	**2b**	CF_3CH_2OH (20 eq)	0.30 M Et_4NOTs	$PhCH=CHCH_2-OCH_2CF_3$ (19)
18[d]	**2a**	TsO^-	0.30 M Et_4NOTs	$CH_2=CHCH_2-OTs$ (20)
19[d]	**2a**	CF_3COO^-	0.50 M $CF_3COONBu_4$	$CH_2=CHCH_2-OOCCF_3$ (Formed[e])

a) Electrolysis was carried out by passing 2X96500 C mol^{-1} of charge at 0.8 A dm^{-2} using a graphite anode in acetonitrile in a divided cell. b) Isolated yield. c) TsOH (1 equiv) was added to the anolyte. d) CH_2Cl_2 was used as solvent. e) Confirmed by GLC-MS.

Table 5. Anodic Oxidation of Thiomethylsilanes in the Presence of Alcohols[a]



$$\underset{\mathbf{3}}{R^1\text{-S-}\overset{R^2}{\overset{|}{C}}\text{H-SiMe}_3} \xrightarrow{-2e\ +\ ROH} \underset{\mathbf{8}}{R^1\text{-S-}\overset{R^2}{\overset{|}{C}}\text{H-OR}}$$

Run	**3**	ROH	Yield[b] of **8**/%
20[c]	**3a**	MeOH[d]	50[e]
21	**3a**	MeOH[d]	66[e]
22[f]	**3a**	MeOH[d]	56
23	**3a**	EtOH	65
24	**3a**	Me_2CHOH	49
25	**3a**	Me_3COH	25
26	**3a**	$CH_2=CHCH_2OH$	59[e]
27	**3a**	$CH_2=CHCH(Me)OH$	54[e]
28	**3a**	$Me_2C=CHCH_2OH$	58[e]
29	**3a**	PhOH	0
30	**3b**	$CH_2=CHCH_2OH$	42[e]
31	**3c**	CF_3CH_2OH	6[g]
32	**3c**	$CH_2=CHCH_2OH$	66[e]
33	**3c**	$Me_2C=CHCH_2OH$	77[e]

a) 2.5 mmol of **3** was electrolyzed by passing 2X 96500 C mol^{-1} of charge at 1.0 A dm^{-2} of current density at a graphite anode in 0.60 M Et_4NOTs/MeCN containing 50 mmol of ROH in an undivided cell. b) Isolated yield. c) At 0.5 A dm^{-2} of current density. d) Used as solvent. e) Determined by GLC. f) At 1.5 A dm^{-2} of current density. g) By-products: $(CF_3CH_2O)_2CHPh$ (16%) and $(MeS)_2CHPh$ (32%).

whose positive charge is more highly delocalized. The anodic trifluoroacetoxylation of **2a** (Run 19) occurred as well as that of **1a**.

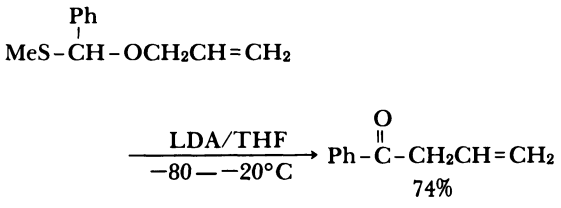
The reaction scheme of allylsilanes can be presented similarly to that of benzylsilanes (Scheme 1). Yoshida et al. reported interesting results from a mechanistic aspect and proposed a more detailed mechanism.[11]

Anodic Oxidation of [Aryl(or alkyl)thiomethyl]silanes (3a—c). Oxidation in the Presence of Alcohols: It is known that α-methoxylated sulfides can be obtained by the anodic methoxylation of sulfides.[24,25] However, the existence of electron-withdrawing groups at the α-positions of sulfide molecules seems to be necessary to accelerate deprotonation from cation radical intermediate species and to result in successful methoxylation. In fact, it was confirmed that methyl phenyl sulfide was anodically methoxylated in only 1% yield.

As shown in Table 5, [aryl(or alky)lthiomethyl]trimethylsilanes (**3a—c**) could be alkoxylated in the anodic oxidation in the presence of a variety of alcohols such as primary (Runs 20—23, 26, 28, 30—33), secondary (Runs 24, 27) and tertiary (Run 25) alcohols. In most cases, the yields were considerably good, though reaction conditions were not fully optimized. Phenol (Run 29) and trifluoroethanol (Run 31) did not give satisfactory results due to their low nucleophilicities.

Although arylthiometyl ethers (**8**) are versatile synthetic reagents for C_1 homologation,[26] it is not so easy to prepare them except for methyl and aryl arylthiomethyl ethers.[27] The anodic alkoxylation should provide an efficient and useful method for the preparation of **8**.

It is noteworthy that the allyloxylation of (thiomethyl)silanes can be performed by the anodic method, though allyl alcohols have considerably less noble oxidation potentials. The anodic methoxylation of phenyl trifluoroethyl sulfide proceeds very efficiently (in 93% yield) by contribution of the electron-withdrawing trifluoromethyl group,[24] while the allyloxylation did not. This fact should clearly indicate a sufficient effect of the modification of sulfides by trimethylsilyl groups on the allyloxylation. It is expected that **8** with allyl groups are converted into the corresponding β,γ-unsaturated ketones by the [2,3]Wittig rearrangement using bases. In fact, **8** derived from **3c** and allyl alcohol in Run 32 gave the ketone in a good yield as follows:



$$\text{MeS-}\overset{Ph}{\overset{|}{C}}\text{H-OCH}_2\text{CH=CH}_2 \xrightarrow[-80\text{—}-20^\circ C]{LDA/THF} \text{Ph-}\overset{O}{\overset{\|}{C}}\text{-CH}_2\text{CH=CH}_2\ \ 74\%$$

Oxidation in the Presence of Carboxylic Acids: As shown in Table 6, the anodic carboxylation of **3a** could smoothly proceed using a few kinds of aliphatic carboxylic acids. It is interesting to note that an unsilylated

Table 6. Anodic Oxidation of Phenylthiomethylsilane in the Presence of Carboxylic Acids[a]

$$\underset{\textbf{3a}}{\text{Ph-S-CH}_2\text{-SiMe}_3} \xrightarrow{-2e\,+\,\text{RCOOH}} \underset{\textbf{9}}{\text{Ph-S-CH}_2\text{OCOR}}$$

Run	RCOOH	Yield[b] of **9**/%
34	MeCOOH	66
35[c]	MeCOOH	20
36	$Me_2CHCOOH$	61

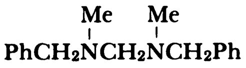
a) 2.5 mmol of **3a** was electrolyzed by passing 2× 96500 C mol^{-1} of charge at 1.0 A dm^{-2} of current density at a graphite anode in 0.60 M Et_4NOTs/MeCN containing 50 mmol of RCOOH in an undivided cell. b) Isolated yield. c) At a Pt anode in 0.6 M MeCOONa/MeCOOH.

sulfide, $PhSCH_2CH_3$, was not acetoxylated at all under the same conditions.

A reaction scheme involving sulfenium ions as key intermediates would be written for the anodic alkoxylation and carboxylation of **3** analogously to Scheme 1.

Anodic Oxidation of Aryloxymethyl (4) and Aminomethyl (5) Silanes. (Phenoxymethyl)trimethylsilane (**4**), which is an oxygen analogue of **3a**, was anodically methoxylated (52% yield) under conditions presented in Table 5.

[(*N*-Methylbenzylamino)methyl]trimethylsilanes (**5**) did not undergo the alkoxylation,[28] but gave a diamine (**10**) in 40—68% yields in the presence of either methanol or ethanol. The diamine (**10**) was also formed chemically from *N*-methylbenzylamine and formaldehyde along with dimethyl or diethyl ether.



$$\text{PhCH}_2\overset{\text{Me}}{\overset{|}{\text{N}}}\text{CH}_2\overset{\text{Me}}{\overset{|}{\text{N}}}\text{CH}_2\text{Ph}$$

10

Experimental

Materials. Anodes: Platinum and graphite anodes were polished with fine alumina powder and emery paper, respectively, and then washed with acetone.

Solvents: Acetonitrile, dichloromethane, and methanol were dried using P_2O_5-CaH_2, CaH_2, and sodium metal, respectively, and then distilled in an atmosphere of nitrogen.

Benzyltrimethylsilanes (1a—c): A general method developed for preparing aryltrimethylsilanes[29] was applied. **1a**: Bp 84—85 °C (26 mmHg) (1 mmHg=133.322 Pa) [lit,[30] 93 °C) (35 mmHg)]. **1b**: Bp 84—85 °C (14 mmHg) (lit,[31] 211.5 °C). **1c**: Bp 82—83 °C (9 mmHg) (lit,[32] 210—211 °C.

Allyltrimethylsilanes (2a, b): The silane **2a** was prepared by the method of literature.[29] Bp 86—87 °C (lit,[29] 85 °C). The silane **2b** was also prepared similarly to **2a**. Bp 103—105 °C (10 mmHg); ^{1}H NMR [$CDCl_3$, relative to $Si(CH_3)_3$] δ=0.00 (s, 9H, $Si(CH_3)_3$), 1.5—1.7 (m, 2H, CH_2-Si), 6.1—6.4 (m, 2H, CH=CH), and 7.0—7.4 (m, 5H, C_6H_5).

[Aryl(or alkyl)thiomethyl]trimethylsilanes (3a—c): The silanes were prepared by methods of literatures. **3a**:[33,34] Bp 136—137 °C (32 mmHg) [lit,[35] 158.5 °C (52 mmHg)]. **3b**:[35] Bp 150—151 °C (30 mmHg) [lit,[35] 83—85 °C (1 mmHg)]. **3c**:[37] Bp 99—100 °C (8 mmHg); ^{1}H NMR ($CDCl^3$, relative to $Si(CH_3)_3$) δ=0.00 (s, 9H, $Si(CH_3)_3$), 1.87 (s, 3H, S-CH_3), 3.31 (s, 1H, CH), and 7.1—7.3 (m, 5H, C_6H_5).

Phenoxymethyltrimethylsilane (4): The silane was prepared by the method of literature.[38] Bp 86—87 °C (9 mmHg) (lit,[38] 83—84 °C (8 mmHg)).

[*N*-(Methylbenzylamino)methyl]trimethylsilane (5): The silane was prepared by the method of literature[39] and purified by column chromatography (Silica gel, hexane–ether (1 : 1)).

Electrolysis. The electrolysis was galvanostatically carried out at room temperature using a platinum (7.7 cm^2) or graphite (5.0 cm^2) anode in a divided (anolyte, 35—50 cm^3) or undivided (electrolyte, 15 cm^3) cell. Detailed electrolytic conditions are shown in the text.

Separation and Analysis of Products. After electrolysis, the electrolytic solution was poured into a saturated sodium chloride solution and extracted with ether or dichloromethane. The extract was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The products were analyzed by GLC (2 m PEG 20 M and 2.25 m Silicone HV grease columns) and isolated by column chromatography (silica gel, hexane–dichloromethane (4:1) or benzene). Molecular structures of all the products were determined by ^{1}H NMR, MS and IR spectra, and/or elemental analysis. Data for the identification of some special products are given below.

[(Benzylphenyl)methyl]trimethylsilane: IR (neat) 3070, 3030, 2960, 2900, 1600, 1505, 1490, 1450, 1250, 1215, 1155, 850, 725, and 690 cm^{-1}; ^{1}H NMR ($CDCl_3$, relative to $SiCH_3$) δ=0.00, 0.02 (s, 9H, $Si(CH_3)_3$), 2.07, 2.13 (s, 2H, -CH_2-Si), 3.95 (s, 2H, C_6H_5-$C\underline{H}_2$-C_6H_4), and 6.47—6.77 (m, 9H, $C_6\underline{H}_5$-CH_2-$C_6\underline{H}_4$); MS (70 eV) *m/z* (M^+); GLC 2 peaks with almost equal area, probably for *o*- and *p*-benzyl isomers.

3-Phenylallyl 2,2,2-Trifluoroethyl Ether: ^{1}H NMR ($CDCl_3$, TMS) δ=3.90 (q, 2H, CH_2CF_3), 4.35 (d, 2H, =CH-$C\underline{H}_2$-O), 6.1—6.7 (m, 2H, CH=CH) and 7.2—7.6 (m, 5H, C_6H_5).

Methyl Phenylthiomethyl Ether:[40] IR (neat) 3070, 3000, 2940, 2900, 2830, 1590, 1480, 1440, 1185, 1080, and 900 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS) δ=3.47 (s, 3H, O-CH_3), 5.00 (s, 2H, S-CH_2-O), and 7.2—7.6 (m, 5H, C_6H_5); MS (70 eV) *m/z* 154 (M^+).

Ethyl Phenylthiomethyl Ether: IR (neat) 3070, 2990, 2940, 2900, 1590, 1480, 1440, 1080, 1015, 840, and 740 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS) δ=1.22 (t, 3H, $CH_2C\underline{H}_3$), 3.67 (q, 2H, $C\underline{H}_2CH_3$), 4.98 (s, 2H, S-CH_2-O), and 7.1—7.5 (m, 5H, C_6H_5); MS (70 eV) *m/z* 168 (M^+). Found: C, 64.29; H, 7.25%. Calcd for $C_9H_{12}SO$: C, 64.25; H, 7.19%.

Isopropyl Phenylthiomethyl Ether: ^{1}H NMR ($CDCl_3$, TMS) δ=1.17 (d, 6H, CH_3), 3.8—4.3 (m, 1H, CH), 5.00 (s, 2H, S-CH_2-O), 7.1—7.6 (m, 5H, C_6H_5); MS (70 eV) *m/z* 182 (M^+). Found: C, 65.58; H, 7.60%. Calcd for $C_{10}H_{14}SO$: C, 65.89; H, 7.74%.

***t*-Butyl Phenylthiomethyl Ether:** IR (neat) 3070, 2980, 2930, 1585, 1480, 1440, 1395, 1365, 1055, 1025, and 740 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS) δ=1.25 (s, 9H, CH_3), 4.87 (s, 2H, S-CH_2-O), and 7.1—7.5 (m, 5H, C_6H_5); MS (70 eV) *m/z* 196 (M^+). Found: C, 67.20; H, 8.18; S, 16.39%. Calcd for $C_{11}H_{16}SO$: C, 67.30; H, 8.22; S, 16.33%.

Allyl Phenylthiomethyl Ether: IR (neat) 3070, 3030, 2990, 2900, 2860, 1585, 1480, 1440, 1060, 1000, and 930 cm^{-1}; ^{1}H NMR (CDCl$_3$, TMS) δ=4.17 (d, 2H, O-C$\underline{H}_2$-CH=), 5.00 (s, 2H, S-CH$_2$-O), 5.0—5.5 (m, 2H, CH=C$\underline{H}_2$), 5.6—6.2 (m, 1H, C$\underline{H}$=CH$_2$), and 7.2—7.6 (m, 5H, C$_6$H$_5$); MS (70 eV) *m/z* 180 (M$^+$). Found: C, 66.32; H, 6.86; S, 18.25%. Calcd for C$_{10}$H$_{12}$SO: C, 66.63; H, 6.71; S, 17.79%.

1-Methylallyl Phenylthiomethyl Ether: IR (neat) 3070, 2990, 2940, 2910, 1740, 1585, 1480, 1440, 1060, 1040, 1025, 995, and 930 cm^{-1}; ^{1}H NMR (CDCl$_3$, TMS) δ=1.26 (d, 3H, CH$_3$), 4.35 (quintet, 1H, O-C$\underline{H}$(CH$_3$)CH=), 4.91 (s, 2H, S-CH$_2$-O), 5.1—5.3 (m, 2H, =CH$_2$), 5.5—5.9 (m, 1H, -CH=), and 7.2—7.5 (m, 5H, C$_6$H$_5$); MS (70 eV) *m/z* 194 (M$^+$). Found: C, 68.01; H, 7.30; S, 16.47%. Calcd for C$_{11}$H$_{14}$SO: C, 68.00; H, 7.26; H, 16.50%.

3-Methyl-2-butenyl Phenylthiomethyl Ether: IR (neat) 3060, 3030, 2980, 2910, 2880, 1670, 1585, 1480, 1440, 1200, 1060, 900, and 735 cm^{-1}; ^{1}H NMR (CDCl$_3$, TMS) δ=1.69 (s, 3H, CH$_3$), 1.75 (s, 3H, CH$_3$) 4.17 (d, 2H, O-C$\underline{H}_2$-CH=), 5.00 (s, 2H, S-CH$_2$-O), 5.36 (t, 1H, CH$_2$-C$\underline{H}$=), and 7.2—7.7 (m, 5H, C$_6$H$_5$). Found: C, 69.11; H, 7.79%. Calcd for C$_{12}$H$_{16}$SO: C, 69.19; H, 7.74%.

Allyl (*p*-Methylphenylthio)methyl Ether: IR (neat) 3075, 3030, 2980, 2920, 2900, 2860, 1640, 1595, 1490, 1060, 1000, and 920 cm^{-1}; ^{1}H NMR (CDCl$_3$, TMS) δ=2.33 (s, 3H, CH$_3$), 4.20 (d, 2H, O-C$\underline{H}_2$-CH=), 5.00 (s, 2H, S-CH$_2$-O), 5.1—5.5 (m, 2H, CH=C$\underline{H}_2$), 5.6—6.3 (m, 1H, C$\underline{H}$CH$_2$), 7.08 (d, 2H, C$_6$H$_4$), and 7.38 (d, 2H, C$_6$H$_4$); MS (70 eV) *m/z* 194 (M$^+$). Found: C, 68.29; H, 7.68%. Calcd for C$_{11}$H$_{14}$SO: C, 68.00; H, 7.26%.

2,2,2-Trifluoroethyl Phenyl(methylthio)methyl Ether: ^{1}H NMR (CDCl$_3$, TMS) δ=1.98 (s, 3H, CH$_3$), 3.90 (q, 2H, -CH$_2$-), 5.73 (s, 1H, S-CH-O), and 7.4—7.8 (m, 5H, C$_6$H$_5$).

[Di(methylthio)]phenylmethane: ^{1}H NMR (CDCl$_3$, TMS) δ=2.10 (s, 6H, CH$_3$), 4.77 (s, 1H, S-CH-S), and 7.4—7.8 (m, 5H, C$_6$H$_5$).

Di(2,2,2-trifluoroethoxy)phenylmethane: ^{1}H NMR (CDCl$_3$, TMS) δ=3.90 (q, 2H, -CH$_2$-), 5.87 (s, 1H, O-CH-O), 7.12 (s, 5H, C$_6$H$_5$).

Allyl Phenyl(methylthio)methyl Ether: IR (neat) 3080, 3040, 3000, 2930, 2870, 1640, 1600, 1490, 1455, 1070, 1010, and 915 cm^{-1}; ^{1}H NMR (CDCl$_3$, TMS) δ=1.87 (s, 3H, CH$_3$), 4.1—4.3 (m, 2H, O-C$\underline{H}_2$CH=), 5.1—5.6 (m, 2H, CH=C$\underline{H}_2$), 5.60 (s, 1H, S-CH-O), 5.7—6.4 (m, 1H, C$\underline{H}$=CH$_2$), and 7.1—7.6 (m, 5H, C$_6$H$_5$); MS (70 eV) *m/z* 194 (M$^+$). Found: C, 68.59; H, 7.53%. Calcd for C$_{11}$H$_{14}$SO: C, 68.00; H, 7.26%.

3-Methyl-2-butenyl Phenyl(methylthio)methyl Ether: IR (neat) 3075, 3040, 2995, 2930, 2870, 1670, 1605, 1495, 1455, 1080, 1060, 1030, and 725 cm^{-1}; ^{1}H NMR (CDCl$_3$, TMS) δ=1.70 (s, 3H, =C-CH$_3$), 1.78 (s, 3H, =C-CH$_3$), 1.90 (s, 3H, S-CH$_3$), 4.22 (d, 2H, O-C$\underline{H}_2$-CH=), 5.47 (t, 1H, CH$_2$-C$\underline{H}$=), 5.63 (s, 1H, S-CH-O), and 7.2—7.7 (m, 5H, C$_6$H$_5$). Found: C, 70.12; H, 8.27%. Calcd for C$_{13}$H$_{18}$SO: C, 70.23; H, 8.16%. The product **10** was also identified with an independently synthesized sample[41] by comparing their physical properties.

[2,3]Wittig Rearrangement Reaction of Allyl Phenyl(methylthio)methyl Ether. A THF solution (1 cm^3) of the titled ether (0.203 g, 1.0 mmol) was dropwise added to a mixed solution of diisopropylamine (2.2 mmol), 1.50 M butyllithium/hexane (1.5 cm^3, 2.2 mmol) and THF (5 cm^3) at −80 °C. The temperature was gradually elevated and reached to −20 °C after 4 h. The reaction mixture was poured into a saturated ammonium chloride solution and extracted with ether. The extract was dried over anhydrous sodium sulfate and evaporated under reduced pressure. Allyl phenyl ketone was isolated from the residue by preparative thin layer chromatography (Silica gel, hexane–chloroform (1 : 1)): Yield 0.108 g (74%). The ketone was converted into the 2,4-dinitrophenylhydrazone to be identified. IR (KBr) 3300, 3090, 1610, 1595, 1580, 1505, 1485, 1330, 1310, 1135, 1100, 980, and 920 cm^{-1}; MS (70 eV) *m/z* 326 (M$^+$). Found: C, 58.79; H, 4.18; N, 17.06%. Calcd for C$_{16}$H$_{14}$N$_4$O$_4$: C, 58.89; H, 4.32; N, 17.17%.

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