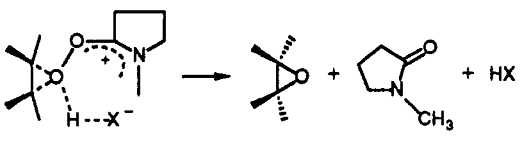
Scheme II



IV, X = PO_2Cl_2

subsequent formation of HCl.[22]

Our objective in the present study was to develop a new oxygen-transfer reagent based upon 30% H_2O_2/Vilsmeier reagent system that could compete advantageously with other ones. Since the formation of HCl during the progression of the reaction could not be avoided, we chose to pursue an approach where the generated HCl would not be available to cause undesired side reactions. Thus, we ran the reaction in a biphasic system, which removes the HCl to the aqueous phase and effects the epoxidation in the nonpolar organic phase where such reactions have been shown to be accelerated.[7] Another important factor could be the influence of the amide structure toward the reactivity of the intermediate hydroperoxyammonium salt. As anticipated, the Vilsmeier reagent III, prepared by reaction of *N*-methylpyrrolidone with $POCl_3$,[23] affords a nicely efficient oxygen-transfer reagent by reaction with 30% H_2O_2 using a phase-transfer catalysis procedure (Scheme I). Reaction times are very short and the epoxides are obtained in fair to very good yields only accompanied by dichloro byproducts. All reactions are unoptimized but give reproducible results. Results obtained are summarized in Table I, and spectral data are listed in refs 24–29. This new procedure is extremely clean and offers a distinct advantage in chemoselectivity with polyfunctional substrates over more commonly used oxidants such as MCPBA or peroxycarboximidic acids.[9] The attempted Baeyer–Villiger oxidation of cyclohexanone with 3 equiv of salt III and H_2O_2 resulted in a complete recovery of the starting material. ϵ-Caprolactone could not be detected in the crude reaction mixture. A competitive experiment between 1-methylcyclohexene and 2-butanone with 3.5 equiv of salt III and H_2O_2 resulted in a quantitative epoxidation of the olefin.

On the other hand, the oxygen transfer is extensively chemoselective, none of the other possible epoxides being observed in the reaction of polyfunctional olefins. A disubtituted double bond is epoxidized selectively in the presence of a monosubstituted one (entry 3). (−)-*trans*-Caryophyllene and (*R*)-(+)-limonene (entries 4 and 5) are selectively oxidized on the trisubstituted double bond. Finally a nonconjugated carbon–carbon double bond preferentially reacts with the salt IV to give the corresponding epoxide (entries 6 and 7). Acid-sensitive olefin (entry 16) gives no detectable amount of compounds arising from the hydrolysis of the acetal function. The rate of epoxidation for a weakly nucleophilic terminal double bond is generally lower than that for a more highly substituted one. Consequently in the case of styrene (entry 17), epoxide is formed in very low yield and decomposition of the oxidizing agent with the anion of H_2O_2 becomes the major reaction.[6a]

Although the structure of hydroperoxyammonium salt IV is not established, its formation seems fairly straightforward by the observation of facile oxirane formation (Scheme II).

On the other hand, the fact that (+)-α-3,4-epoxycarane is obtained as the unique diastereoisomer from the reaction of IV with (+)-Δ^3-carene (entries 1 and 2) implies that the epoxide results from a direct stereoselective oxygen atom transfer and is not formed by ring closure of an α-chloro, β-hydroxy intermediate, which would have given rise to the β-3,4-epoxycarane.[30]

Experimental Section

In a typical experiment, anhydrous Na_2CO_3 *(12 g, 113.2 mmol)* was suspended in 30% H_2O_2 (40 mL) and CH_2Cl_2 (40 mL). 18-Crown-6 (0.10 g, 0.378 mmol) and 1-methylcyclohexene (0.92 g, 9.6 mmol) were added to this heterogeneous biphasic system. Then the Vilsmeier reagent III[23] (24 mmol) in CH_2Cl_2 (30 mL) was added dropwise over 1 h under a nitrogen atmosphere to the well stirred reaction mixture at −20 °C. The mixture was further stirred until the temperature reached 20 °C; then it was filtered through Celite and the phases were separated. The aqueous layer was extracted with CH_2Cl_2 (20 mL) and the combined organic fractions were washed with water (30 mL), 3% $NaHSO_3$ (30 mL), and brine (30 mL) and dried over $MgSO_4$. Distillation of the solvent under atmospheric pressure gave a colorless residue constituted of 1-methylcyclohexene oxide, traces of starting material, and *N*-methylpyrrolidone. Purfication by flash chromatography on silica gel using a mixture of pentane–ether (98–2) as eluent gave pure 1-methylcyclohexene oxide (0.97 g; 90%).

Alternatively, pentane (100 mL) was added to the crude residue and the mixture washed with H_2O (3 × 60 mL) and dried over $MgSO_4$. Distillation of the solvent at atmospheric pressure gave almost pure 1-methylcyclohexene oxide by ^1H NMR.

Supplementary Material Available: Spectral data for compounds prepared including IR, ^1H NMR, ^{13}C NMR, and elemental analyses (2 pages). Ordering information is given on any current masthead page.

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(22) Rodriguez, J.; Thesis, Faculté des Sciences et Techniques de St Jérôme, Marseille, France, 1984.

(23) For preparation of the Vilsmeier reagent III, see: Bredereck, H.; Bredereck, K. *Chem. Ber.* **1961**, *94*, 2278. III: ^{13}C NMR ($CDCl_3$) 178,64, 62,10 41,27, 39,05, 18,31; ^{31}P NMR (H_3PO_4) −7,31.

(24) ^1H NMR ($CDCl_3$, 200 MHz) δ 2.84 (1 H, s), 2.30 (1 H, ddd, *J* = 16.2, 8.6, 1.4 Hz), 2.14 (1 H, dd, *J* = 16.2, 8.6 Hz), 1.53 (1 H, dt, *J* = 16.4, 2.1 Hz), 1.45 (1 H, dd, *J* = 16.4, 2.2 Hz), 1.26 (3 H, s), 1.01 (3 H, s), 0.73 (3 H, s), 0.5 (2 H, m).

(25) ^1H NMR ($CDCl_3$, 200 MHz) δ 4.90 (1 H, s), 4.79 (1 H, s), 2.81 (1 H, dd, *J* = 10.5, 3.9 Hz), 2.52 (1 H, m), 2.23 (2 H, m), 2.04 (2 H, m), 1.74–1.49 (5 H, m), 1.45–1.21 (2 H, m), 1.13 (3 H, s), 0.94 (3 H, s), 0.92 (3 H, s).

(26) ^1H NMR ($CDCl_3$, 200 MHz) δ 6.29 (1 H, dd, *J* = 17.6, 10.5 Hz) 5.15 (1 H, d, *J* = 17.6 Hz), 4.98 (1 H, d, *J* = 10.5 Hz), 4.96 (1 H, s), 2.66 (1 H, t, *J* = 6.3 Hz), 2.29 (2 H, m), 1.64 (2 H, q, = 7.7 Hz), 1.22 (3 H, s), 1.17 (3 H, s).

(27) ^1H NMR ($CDCl_3$, 200 MHz) δ 7.36–7.16 (5 H, m), 6.40–6.29 (1 H, m), 6.15–5.99 (1 H, m), 3.24–3.14 (2 H, m), 2.31–1.15 (7 H, m).

(28) ^1H NMR ($CDCl_3$, 200 MHz) δ 3.48 (1 H, m), 3.32 (1 H, d, *J* = 2.5 Hz), 2.70–2.59 (1 H, m), 2.42–2.18 (2 H, m), 1.77–1.48 (5 H, m), 1.45–1.24 (2 H, m).

(29) ^1H NMR ($CDCl_3$, 200 MHz) δ 4.77 (1 H, dd, *J* = 7.2, 4 Hz), 3.89 (2 H, m), 3.06 (1 H, m), 2.86 (1 H, m), 1.88 (1 H, m), 1.71 (1 H, m), 1.49 (4 H, m), 1.33 (4 H, m), 1.19 (15 H, m).

(30) (a) Cocker, W.; Grayson, D. H. *Tetrahedron Lett.* **1969**, 4451. (b) Brown, H. C.; Suzuki, A. *J. Am. Chem. Soc.* **1967**, *89*, 1933.

Approaches to the Preparation of Silyl Cations

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Introduction

Silicon has a lower electronegativity than carbon, and it might be expected that silylenium ions (R_3Si^+) would

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Table I. Product Compositions for the Reactions of Chlorotriphenylmethane (1) with Inorganic Salts[a]

inorganic salt	product composition (mol %)				
	C_6H_5–C_6H_5	C_6H_5OH	$(C_6H_5)_3CH$	$(C_6H_5)_3COH$	$(C_6H_5)_3CNHAc$
$AgBF_4$[b]				89[c,d]	
$NaB(C_6H_5)_4$ A[b]	24	9	6	50	3
B[d]	–	–		76	21
$AgB(C_6H_5)_4$ A[b]	28		8	55	9
B	49	7	2	24	18
C[e]	48	14	12	26	–

[a] Reactions were carried out in CH_3CN, unless otherwise stated, and at 25 °C (except –50 °C for use of $AgBF_4$ and –196 to 25 °C for $NaB(C_6H_5)_4$). [b] The reaction was carried out in CD_3CN in a sealed, degassed NMR tube with ~0.1 mmol of 1. [c] The reaction in CD_3 CN was quenched with KOD solution (40% in D_2O). [d] Isolated yields. [e] Solvent was $CDCl_3$.

form more easily and would be more stable than carbenium ions (R_3C^+).[1] Several groups have claimed that they prepared silylenium ions, either as transient intermediates or as detectible and/or isolable species.[2-11] However, in a recent critical review[12] Olah concluded that to date no silylenium ions stable in liquid solution had been prepared (see, however, refs 9 and 10 for a rebuttal). We report here several experiments designed to test whether silylenium ions could be generated and detected at low temperatures.

Results and Discussion

Our overall goal was to prepare silylenium ions in the absence of free halide ions and oxygen-containing anions, as these species are known to form strong bonds to silicon.[1] We initially chose to use tetraphenylborate ion as the counterion in the experiments. But first, to test our procedures and our approach, we followed by NMR techniques the reaction of chlorotriphenylmethane with silver tetrafluoroborate at –50 °C (eq 1). The spectrum we

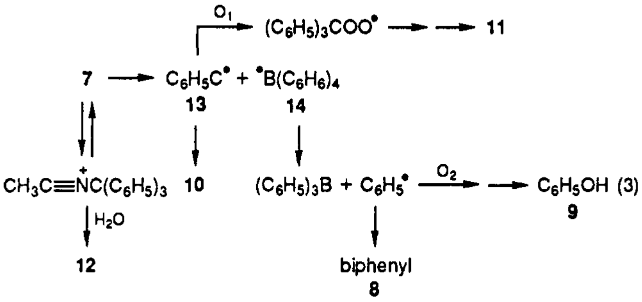
$$\underset{1}{(C_6H_5)_3CCl} + \underset{2}{AgBF_4} \rightarrow \underset{3}{(C_6H_5)_3C^+BF_4^-} \xrightarrow{D_2O} \underset{4}{(C_6H_5)_3COD} \quad (1)$$

obtained was in agreement with the published spectrum of the triphenylmethyl carbenium ion.[13] The addition of potassium deuteroxide to the reaction mixture resulted in a collapse of the aromatic proton signals to a singlet that was characteristic of triphenylmethanol, which was subsequently isolated from the reaction mixture.

Then we examined the reaction of chlorotriphenylmethane with salts of a halogen and oxygen-free counterion, the tetraphenylborate ion (sodium and silver salts). At –50 °C chlorotriphenylmethane proved to be too insoluble in acetonitrile; interestingly, the ionic salt sodium tetraphenylborate was quite soluble under those conditions. At room temperature, complex reaction mixtures were obtained (eq 2 and Table I), indicating that the

$$\begin{gathered}\underset{5}{(C_6H_5)_3CCl} + \underset{6}{(C_6H_5)_4B^-Na^+}(\text{or } Ag^+) \rightarrow \\ \underset{7}{[(C_6H_5)_3C^+][^-B(C_6H_5)_4]} \xrightarrow{H_2O} \\ \underset{8}{\text{biphenyl}} + \underset{9}{\text{phenol}} + \underset{10}{\text{triphenylmethane}} + \\ \underset{11}{\text{triphenylmethanol}} + \underset{12}{N\text{-(triphenylmethyl)acetamide}} \end{gathered} \quad (2)$$

tetraphenylborate ion was too reactive for our purposes. The products formed can be accounted for by ionic and radical reactions involving oxygen and water (eq 3).[14] It does seem possible, however, that ion pair 7 would be detectable if the temperature of the system could be made low enough.



(3)

Attention was then directed to analogous reactions of chlorotrimethylsilane. No reaction was observed with sodium tetraphenylborate at 25 °C. With silver tetraphenylborate, we obtained a complex set of products. With the more sterically hindered chlorotriisopropylsilane, we did not observe any reaction with silver tetraphenylborate at room temperature.

To avoid the reactivity of the "electron-rich" phenyl rings in the complex borate ion, we examined various silver salts of complex anions as halide abstracters from chlorotrimethylsilane (eqs 4 and 5), from iodotrimethylsilane (eqs 6 and 7), and from two related compounds (eqs 8 and 9). In all of the cases, a transfer of halide ion occurred to silicon.

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(10) Lambert, J. B.; Schulz, W. J., Jr.; McConnell, J. A.; Schilf, W. *J. Am. Chem. Soc.* **1988**, *110*, 2201–2210. It was reported that triphenylsilyl perchlorate in sulfolane exists in the covalent form in concentrated solutions and in the ionic form in dilute solutions.

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(14) Triphenylmethane may also stem from the disproportionation of the triphenylmethyl carbonium ion (Patai, S.; Dayagi, S. *J. Chem. Soc.* **1962**, 716).

$$(CH_3)_3SiCl + AgBF_4 \xrightarrow{-50\ °C} (CH_3)_3SiF \quad (4)$$

$$(CH_3)_3SiCl + Ag_2SiF_6 \xrightarrow{-50\ °C} (CH_3)_3SiF \quad (5)$$

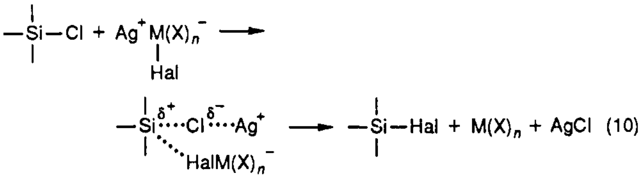
$$(CH_3)_3SiI + Ag_2PtCl_6 \xrightarrow{-50\ °C} (CH_3)_3SiCl \quad (6)$$

$$(CH_3)_3SiI + Ag_2SiF_6 \xrightarrow{-50\ °C} (CH_3)_3SiF \quad (7)$$

$$(CH_3)_2SiCl_2 + Ag_2SiF_6 \xrightarrow{-50\ °C} (CH_3)_2SiF_2 \quad (8)$$

$$CH_3(C_6H_5)_2SiCl + Ag_2SiF_6 \xrightarrow{-50\ °C} CH_3(C_6H_5)_2SiF \quad (9)$$

It is noteworthy that, in the reaction of eq 8, chlorofluorodimethylsilane was not detected; apparently this species is more reactive than dichlorosilane. In reactions 4–9, the formation of transient Si^+ ions or Si^+X^- ion pairs is likely, although ligand exchange within a complex is also a possibility (eq 10). The result that chloride ion in the hexachloroplatinate anion is stable to silver ion but rapidly transferred to silicon is impressive. The possible success of this approach to the generation of silyl cations clearly rests on the nature of the counterion employed. What is needed is a stable anion with a buried negative charge such as would occur in a substituted and sterically blocked tetraphenylborate ion,[15] or in an anion trapped inside a cage hydrocarbon.



(10)

Our results are consistent with the analysis of the problem of generating R_3Si^+ by Olah,[12] namely that R_3Si^+ ions appear to be more reactive than the corresponding carbon species, R_3C^+. Possible reasons are: (1) silicon being a larger atom than carbon, it is less able to be stabilized by hyperconjugation; (2) the high bond strengths of silicon–halogen bonds (and bonds to oxygen) and the availability of d orbitals for silicon allow a facile ligand exchange to occur, aborting the formation of free ions.

Experimental Section

General. All reactions were carried out in oven-dried (120 °C) flasks or NMR tubes (5-mm i.d.). Ethyl acetate, hexanes (from Tilley Chemical Co.), dichlorodimethylsilane, and trimethylsilyl chloride (from Aldrich Chemical Co.) were dried and distilled over CaH_2. Acetonitrile-d_3 (containing 1% tetramethylsilane) and chloroform-*d* (containing 0.03% tetramethylsilane) (from Aldrich Chemical Co.) were dried over P_2O_5 before use. Chlorodiphenylmethylsilane, chlorotriisopropylsilane, iodotrimethylsilane, chlorotriphenylmethane, deuterium oxide, potassium hexachloroplatinate, potassium hydroxide-*d* (KOD), silver nitrate, silver tetrafluoroborate, sodium hexafluorosilicate, sodium tetraphenylborate (from Aldrich Chemical Co.), and hexafluorosilic acid (60% aqueous solution) were used as received. Silver tetraphenylborate,[16] silver hexachloroplatinate,[17] and silver hexafluorosilicate[18] were prepared according to published procedures and were dried over P_2O_5 in vacuo before use.

Analytical TLC was performed on precoated plates purchased from Analtech, Inc. (silica gel GHLF). Visualization of spots on TLC plates was made by use of UV light and/or 2.5% phosphomolybdic acid in ethanol with heating. Mixtures of ethyl acetate and hexanes were used as eluants. Gas chromatography analyses were performed on a Hewlett-Packard 5794A instrument equipped with a 12.5-m cross-linked methylsilicone gum capillary column (0.2-mm i.d.). Temperature condition in GC was set up as the following: injector temperature 260 °C; column temperature program, initial temperature 70 °C, duration 2.00 min; increment rate 15 °C/min; final temperature 250 °C. Purification by gravity column chromatography was carried out by use of EM Reagents silica gel 60 (particle size 0.063–0.200 mm, 70–230-mesh ASTM). Separations by radial thin-layer chromatography were performed on a Model 7924T Chromatotron from Harrison Research. The plates were coated with EM Reagents silica gel 60 PF_{254} containing gypsum. Infrared (IR) spectra were measured on a Perkin-Elmer 599B or 710B spectrophotometer. The wavenumbers reported are referenced to the polystyrene 1601 cm^{-1} absorption. Proton NMR spectra were obtained on a Varian CFT-20 spectrometer with chloroform-*d* as solvent and tetramethylsilane as an internal standard, except where otherwise indicated. Proton NMR multiplicities are recorded by use of the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; *J*, coupling constant (hertz). High-resolution mass spectra were obtained by means of a VG Analytical 70-S mass spectrometer.

Standard Procedure for Reactions Carried Out in Sealed NMR Tubes. The inorganic salt was placed in an NMR tube, which was evacuated at 0.01 Torr for 24 h on a vacuum line bearing a side arm fitted with a stopcock and a rubber septum. For the addition of the salt, a liner-sleeve was used to keep the glass surfaces to be fused at the end of the loading procedure clean. The organic substrate, if liquid and volatile, was injected through the septum (the stopcock was opened momentarily), and the vapor was trapped in the NMR tube, which was cooled with liquid nitrogen (−196 °C). For nonvolatile liquid substrates, a capillary tube containing the compound was inserted into the NMR tube; for solid substrates, the compound was carefully layered over the inorganic salt and the tube was evacuated as described above. The deuterated solvent, which had been stored over P_2O_5 on the vacuum line, was transferred as a vapor into the NMR tube cooled with liquid nitrogen. The NMR tube was sealed off with a torch. Without being shaken, the cold reaction mixture was warmed to the melting point of the solvent and ^1H NMR spectra were run at −50 °C to obtain prereaction spectra. Spectra were then recorded after vigorous shaking of the tube, which was kept at −50 °C by frequent immersion in a cooling bath.

Reaction of Chlorotriphenylmethane (1) with Inorganic Salts: I. With Silver Tetrafluoroborate (2). The reagents added according to the standard procedure were silver salt **2** (9.4 mg, 0.048 mmol), chloride **1** (10.0 mg, 0.036 mmol), and CD_3CN (0.25 mL): ^1H NMR (CD_3CN, −50 °C, after mixing) δ 7.31 (s), 7.79 (s, br), 7.68–8.05 (m), and 8.22–8.43 (m) ppm (identical with the published spectrum of triphenylmethyl carbenium ion).[13] The NMR tube was then opened, and 100 μL of KOD solution (0.7 mmol in CD_3CN) was added at −50 °C to quench the reaction. After 3.0 min, the reaction mixture turned pale yellow. In an additional 7.0 min, it gradually became colorless and clear. A very fine precipitate was observed at the bottom of the tube. The second spectrum was then recorded at −50 °C: ^1H NMR (CD_3CN) δ 7.34 ppm (s, $(C_6H_5)_3C$). This spectrum was identical with that of an authentic sample of triphenylmethanol. The reaction mixture in the tube was worked up by extraction with diethyl ether. The organic layer was dried over $MgSO_4$, filtered, and evaporated in vacuo to give a white solid (8.3 mg, 89%): GC t_R 12.76 min; authentic sample of $(C_6H_5)_3COH$ gave the same value for t_R. Note: analysis of the reaction mixture by GC at 260 °C (injection port) showed triphenylmethane as the major signal.

II. With Sodium Tetraphenylborate (5). Procedure A. The standard procedure was followed, except that the tube was covered with a plastic cap. The reagents added were sodium salt **5** (27.3 mg, 0.082 mmol), chloride **1** (22.2 mg, 0.080 mmol), and CD_3CN (0.30 mL). A deep brown color was produced when the solvent was trapped at −196 °C. After the tube was warmed to 25 °C, dry air was introduced. The brown color faded after the

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tube was shaken at room temperature. The reaction mixture consisted of a clear yellow liquid and a small amount of a white precipitate: ^{1}H NMR (CD_3CN) (of the liquid phase) δ 6.94–7.23 (m), 7.32–7.53 (m, br), 7.74–7.99 (m, br), and 8.25–8.54 ppm (m, br). After 2 days at room temperature, the reaction mixture was extracted with diethyl ether. The composition of this product mixture was determined by GC and is listed in Table I. We cannot exclude the possibility of the formation of small amount of 9-phenylfluorene because its GC retention time (12.74 min) is close to that of triphenylmethanol, and its ^{1}H NMR spectrum overlaps with that of the reaction mixture.

Procedure B. In a one-necked, round-bottomed flask, sodium salt **5** (500.0 mg, 1.46 mmol) and chloride **1** (407.0 mg, 1.46 mmol) were mixed in CH_3CN (15.0 mL) at room temperature under an atmosphere of nitrogen. A deep brown color appeared during 3 min but faded to yellow after an additional 5 min. The solution was stirred at room temperature for 5 days. Then the reaction was quenched with an aqueous solution of sodium carbonate (pH ~9). Extraction of the mixture with diethyl ether and then toluene, followed by evaporation in vacuo, afforded a deep reddish brown oil mixed with a brown solid. The product was purified on silica gel (Chromatotron, 2-mm plate; programmed from 10% EtOAc in hexanes through 20% and 40% to 100% EtOAc as eluant). The products, biphenyl, phenol, Ph_3COH, and Ph_3CNHAc [mp 212–214 °C (lit.[19] mp 212–214 °C)], were isolated in 61-mg (0.40-mmol), 53-mg (1.63-mmol), 291-mg (1.12-mmol), and 94.0-mg quantities (0.312-mmol), respectively. Phenol: TLC (10% EtOAc in hexanes) R_f 0.27; GC t_R 2.57 min; ^{1}H NMR ($CDCl_3$) δ 5.81 (s, br, 1 H, OH), 6.72–7.46 ppm (m, 5 H, C_6H_5). Biphenyl: TLC (10% EtOac in hexanes) R_f 0.75; GC t_R 6.93 min; ^{1}H NMR ($CDCl_3$) δ 7.29–7.43 ppm (m, C_6H_5). Triphenylmethanol: TLC (10% EtOAc in hexanes) R_f 0.66; GC t_R 12.80 min; ^{1}H NMR ($CDCl_3$) δ 2.08 (s, 1 H, OH), 7.28 ppm (s, 15 H, phenyl). *N*-(Triphenylmethyl)acetamide: TLC (10% EtOAc in hexanes) R_f 0.15; GC t_R 14.59 min; ^{1}H NMR ($CDCl_3$) δ 2.06 (s, 3 H, CH_3N), 6.55 (s, br, 1 H, NH), 7.24 ppm (s, 15 H, phenyl). Tetraphenylmethane was not detected; an authentic sample gave t_R of 12.2 min.

III. With Silver Tetraphenylborate (6). Procedure A. The standard procedure was followed, except that the tube was filled with dry air and covered with a plastic cap. The reagents added were silver salt **6** (42.7 mg, 0.100 mmol), chloride **1** (27.0 mg, 0.097 mmol), and CD_3CN (0.40 mL). The tube was shaken, and the purplish reaction mixture was centrifuged at room temperature: ^{1}H NMR (CD_3CN) δ 6.95–7.15 (m), 7.39 (s, $(C_6H_5)_3CCl$), 7.24–7.65 (m), and 7.85–8.06 ppm (m, br). After 8 days of standing at room temperature, the dark green mixture was centrifuged again and decanted. The solution was treated with Na_2CO_3 (30 mg) in D_2O and extracted with ether to give a brown solution: ^{1}H NMR (CD_3CN) δ 6.78–7.21 (m), 7.35 (s, $(C_6H_5)_3COD$), 7.24–8.03 ppm (m, br). The composition of this product mixture was determined by GC and is listed in Table I.

Procedure B. In a one-necked, round-bottomed flask, silver salt **6** (579 mg, 1.36 mmol) and chloride **1** (378 mg, 1.36 mmol) were mixed in CH_3CN (10.0 mL) under an atmosphere of nitrogen. The resulting yellow mixture was stirred at room temperature in the dark for 2 days and then filtered through Celite to give a brown solution. The composition of this product mixture was determined by GC and is listed in Table I.

Procedure C. The same as procedure B, except that $CDCl_3$ was used as the solvent and the reaction mixture was allowed to stand in darkness for 10 days. The composition of this product mixture was determined by GC and is listed in Table I.

Reaction of Chlorotrimethylsilane with Inorganic Salts: I. With Sodium Tetraphenylborate (5). The reagents added according to the standard procedure were sodium salt **5** (20.0 mg, 0.058 mmol), chlorosilane (6.9 mg, 0.065 mmol), and CD_3CN (0.25 mL); they were mixed at -50 °C: ^{1}H NMR (CD_3CN) δ 0.53 (s, $(CH_3)_3SiCl$), 7.06 (m), and 7.36 ppm (m, br). The latter two peaks represent the spectrum of sodium tetraphenylborate. The reaction mixture showed the same spectrum after 20 days of standing at room temperature.

II. With Silver Tetraphenylborate (6). The reagents added according to the standard procedure were silver salt **6** (22.0 mg, 0.051 mmol), chlorosilane (5.1 mg, 0.047 mmol), and CD_3CN (0.25 mL). The thick, brown reaction mixture after mixing was centrifuged at room temperature: ^{1}H NMR (CD_3CN) δ 0.47 (s, $(CH_3)_3SiCl$), 6.90–7.43 ppm (m, br) (major signals).

III. With Silver Tetrafluoroborate (2).[20,21] The reagents added according to the standard procedure were fluoroborate **2** (26.0 mg, 0.134 mmol), chlorosilane (13.0 mg, 0.121 mmol), and CD_3CN (0.25 mL). The suspension was pale yellow before mixing: ^{1}H NMR (CD_3CN, -50 °C) δ 0.46 ppm (s, $(CH_3)_3SiCl$). After mixing at -50 °C, the reaction mixture became slightly reddish yellow with a yellow precipitate: ^{1}H NMR (CD_3CN) δ 0.26 ppm (d, *J* = 7.5 Hz, $(CH_3)_3SiF$). No peak from the starting silane was found. The spectrum of the reaction mixture did not change after 24 h of standing at room temperature.

IV. With Silver Hexafluorosilicate. The reagents added according to the standard procedure were the silicate (35.0 mg, 0.098 mmol), chlorosilane (43.1 mg, 0.39 mmol), and CD_3CN (0.25 mL): ^{1}H NMR (CD_3CN, -50 °C, before thorough mixing; some mixing had occurred during warm-up from -196 °C to -50 °C) δ 0.26 (d, *J* = 7.7 Hz, $(CH_3)_3SiF$), 0.47 ppm (s, $(CH_3)_3SiCl$) (the integration ratio of peak areas was 1:2.3); (after mixing) δ 0.26 (d, *J* = 7.4 Hz, $(CH_3)_3SiF$), 0.48 ppm (s, $(CH_3)_3SiCl$) (the integration ratio of peak areas was 1:1.5). Then the third spectrum was taken at room temperature: δ 0.27 (d, *J* = 7.4 Hz, $(CH_3)_3SiF$), 0.48 ppm (s, $(CH_3)_3SiCl$) (the ratio of integration of peak area was 1:1.4). The spectrum of the reaction mixture remained unchanged during 6 days at room temperature.

Reaction of Iodotrimethylsilane with Inorganic Salts: I. With Silver Hexachloroplatinate. The reagents added according to the standard procedure were the platinate (23.0 mg, 0.037 mmol), iodosilane (7.4 mg, 0.037 mmol), and CD_3CN (0.25 mL): ^{1}H NMR (CD_3CN, -50 °C, before thorough mixing; some surface mixing had occurred) δ 0.45 (s, $(CH_3)_3SiCl$), 0.79 (s, $(CH_3)_3SiI$); (after mixing) δ 0.43 ppm (s, $(CH_3)_3SiCl$).

II. With Silver Hexafluorosilicate. The reagents added according to the standard procedure were the silicate (22.9 mg, 0.064 mmol), iodosilane (12.0 mg, 0.058 mmol), and CD_3CN (0.25 mL): ^{1}H NMR (CD_3CN, -50 °C, before mixing) δ 0.80 (s, $(CH_3)_3SiI$): (after mixing) δ 0.28 ppm (d, *J* = 7.4 Hz, $(CH_3)_3SiF$). The spectrum of the reaction solution did not change after 4 days of standing at room temperature. The tube was opened, and the reaction was quenched with D_2O (50 μL). The doublet peak at δ 0.28 ppm remained unshifted.[21]

Reaction of Dichlorodimethylsilane with Silver Hexafluorosilicate. The reagents added according to the standard procedure were the silver salt (27.8 mg, 0.078 mmol), dichlorosilane (21.9 mg, 0.17 mmol), and CD_3CN (0.25 mL): ^{1}H NMR (CD_3CN, -50 °C, before mixing) δ 0.88 ppm (s, $Cl_2Si(CH_3)_2$); (after mixing) δ 0.40 (t, *J* = 6.4 Hz, $F_2Si(CH_3)_2$),[22] 0.88 ppm (s, $Cl_2Si(CH_3)_2$) (peak area ratio was 2:1). The third spectrum was recorded at room temperature: δ 0.40 ppm (t, *J* = 6.4 Hz, $F_2Si(CH_3)_2$); the peak at δ 0.88 had disappeared.

Reaction of Chlorodiphenylmethylsilane with Silver Hexafluorosilicate. The reagents added according to the standard procedure were the silicate (30.0 mg, 0.086 mmol), chlorosilane (44.1 mg, 0.19 mmol), and CD_3CN (0.25 mL): ^{1}H NMR (CD_3CN, -50 °C, before mixing) δ 0.97 (s, 3 H, CH_3SiCl), 7.39–7.74 (m, 10 H, $(C_6H_5)_2Si$); (after mixing) 0.84 (d, *J* = 7.2 Hz, CH_3SiF),[23] 0.99 (s, CH_3SiCl), 7.41–7.78 ppm (m, $(C_6H_5)_2Si$). The

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[19] Bacon, R. G. R.; Köchling, J. *J. Chem. Soc., Suppl. 1* **1964**, 5609. The melting point of the compound has been reported in the range of 206–218 °C. Cf.: Sanguigni, J. A.; Levine, R. *J. Med. Chem.* **1964**, *7*, 573 (206.5–207.2 °C). Cheeseman, G. W. H. *Chem. Ind.* **1954**, 281 (211–213 °C). Cristol, S. J.; Leffler, J. E. *J. Am. Chem. Soc.* **1954**, *76*, 4468 (214–218 °C).

[20] Similar experiments [$(CH_3)_3SiCl + AgBF_4 \rightarrow (CH_3)_3SiF$] have been carried out in deuterioacetone and deuterioacetonitrile at a higher temperature (-23 °C). (Bassindale, A. R.; Stout, T. *Tetrahedron Lett.* **1984**, *25*, 1631).

[21] The ^{1}H NMR spectrum of fluorotrimethylsilane was reported to be a doublet at δ 0.37 ppm (d, *J* = 7.2 Hz). (Olah, G. A.; O'Broen, D. H.; Lui, C. Y. *J. Am. Chem. Soc.* **1969**, *91*, 701. See also: Della, E. W.; Tsanaktsidis, J. *Synthesis* **1988**, 407. Olah, G. A.; Mo, Y. K. *J. Am. Chem. Soc.* **1971**, *93*, 4942).

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J. Org. Chem. **1991**, *56*, 475-476

integration ratio of the two former peaks (CH_3SiF:CH_3SiCl) was 1.6:1.

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Synthesis of Hydroxy Lactones by Bis(tributyltin) Oxide Promoted Ring Expansion of Halo Lactones

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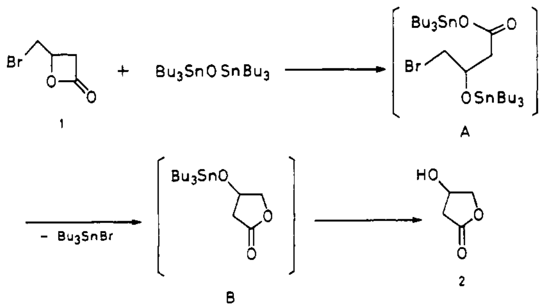
Halo lactones are easily prepared by cyclofunctionalization of unsaturated carboxylic acids on treatment with halogen under basic conditions.[1] This halolactonization had proven useful in organic synthesis because of advantages in operational convenience and high stereoselectivity. We have reported the synthesis of heterocyclic compounds by the cleavage of halo lactones with organotin alkoxide.[2] Organotin alkoxides cleave β-lactone rings easily to provide tin alkoxides, and tin has a great affinity toward halogens.[3-5]

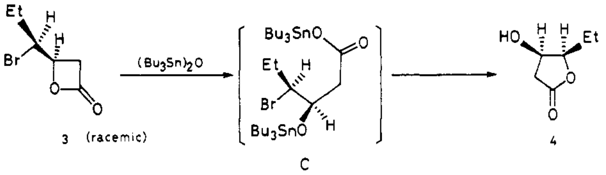
On the basis of these features, we have found a novel synthetic method for ring expansion of halo lactones with bis(tributyltin) oxide [$(Bu_3Sn)_2O$].

The reaction of $(Bu_3Sn)_2O$ with β-lactone **1** at 80 °C for 5 h gave β-hydroxy-γ-butyrolactone[6] (**2**) in 80% yield. As shown in Scheme I, the reaction course may be explained as follows. First, the β-lactone is cleaved to afford the intermediate A. Subsequently, the stannyl carboxylate moiety of A attacks the terminal organic bromide[7] to produce B, which on work up with MeOH gives the product **2**.

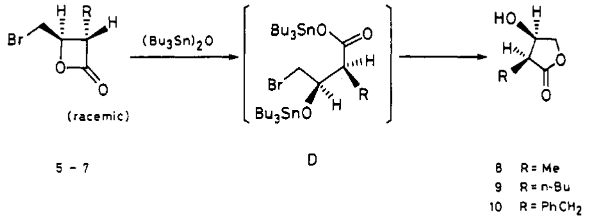
Scheme I



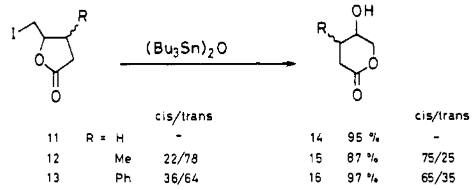
Scheme II



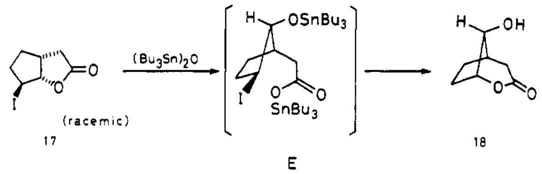
Scheme III



Scheme IV



Scheme V



When the β-lactone bearing a secondary alkyl bromide **3** is used, the stannyl carboxylate moiety of C attacks at the back side of the terminal secondary alkyl bromide in a S_N2 process to give the stereoisomerically pure product, 3,4-*cis*-substituted lactone **4** in 77% yield (Scheme II). The lactone **3** was prepared from the stereospecific bromolactonization of *trans*-hexenoic acid.[1g]

We examined the use of α,β-*trans*-substituted β-lactones, **5–7**, as substrates. These compounds were prepared from the stereoselective bromolactonization of α-substituted

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