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Synthetic Methods and Reactions. 62.[1] Transformations with Chlorotrimethylsilane/Sodium Iodide, a Convenient in Situ Iodotrimethylsilane Reagent

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A new, convenient, inexpensive alternative to iodotrimethylsilane reagent is explored. A mixture of chlorotrimethylsilane/sodium iodide in acetonitrile is found to be a better reagent than iodotrimethylsilane for the cleavage of esters, lactones, carbamates, and ethers. Cleavage of esters and lactones (10 examples) occurred somewhat slower with the present system than with iodotrimethylsilane. On the other hand, ethers (7 examples) cleaved much more readily with the present system. A feasible mechanism is proposed for this disparity. Carbamates (6 examples) also underwent facile cleavage to give the corresponding amines. The general applicability of the method has been shown using various types of substrates. The facile conversion of alcohols to iodides using the present method is also reported. Conversion of alcohols to iodides is much faster with chlorotrimethylsilane/sodium iodide than with iodotrimethylsilane, and iodides are formed in excellent yield.

The use of organosilicon reagents became significant during recent years in organic synthesis. New organosilicon reagents have been developed, and silylated synthons are being widely used in the activation of a substrate or in directing the reaction course in a specific manner.[2]

The high bond energy of the silicon-oxygen bond (90-110 kcal/mol) makes it thermodynamically very favorable to use a reagent with a weak Si-X bond and react it with an appropriate oxygen-containing organic molecule to form a silicon-oxygen bonded intermediate, which then can be transformed to another product in a subsequent step. One such reagent developed in our laboratories,[3-5] as well as independently by Jung,[6,7] is iodotrimethylsilane, which has gained use in the cleavage of esters,[3-6] ethers,[7] and carbamates,[8] as well as in conversion of alcohols to iodides.[9] We have also shown the usefulness of iodotrimethylsilane in the deoxygenation of sulfoxides to sulfides.[10] This reaction has since been applied to the synthesis of certain prostacyclin derivatives.[11] It has also been used in the cleavage of ketals,[12] although ethylene ketals are not cleaved cleanly.

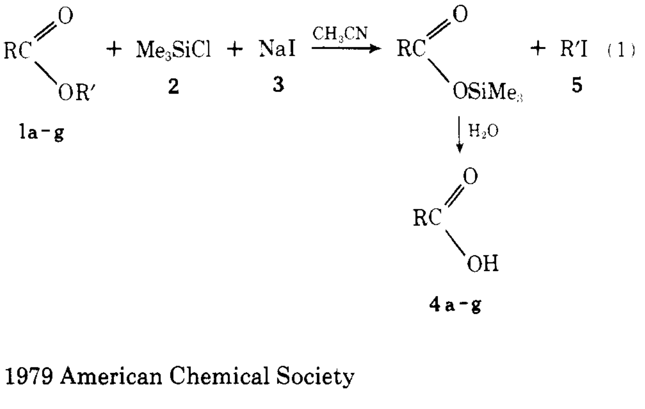
The hydrolytic susceptibility of the Si-I bond in iodotrimethylsilane could be a problem in several organic reactions containing acid sensitive compounds. In addition, iodotrimethylsilane should be prepared freshly and used under strictly anhydrous conditions, as it fumes in air and turns purple on standing, making prolonged storage undesirable. Also, it was until now a relatively expensive commercial reagent, prepared from chlorotrimethylsilane and anhydrous magnesium iodide,[13] or from phenyltrimethylsilane and iodine,[14] or from hexamethyldisiloxane/iodine/aluminum powder.[6] In each case, the reagent has to be isolated by distillation from the reaction mixture.

A comparison of the reported methods showed the phenyltrimethylsilane/iodine reagent to be most useful because iodotrimethylsilane is generated in situ.[4,5] However, under these reaction conditions, the required reaction temperature is fairly high. Also, iodine may cause side reactions, and iodobenzene can sometimes be a very inconvenient byproduct. In view of synthetic interest in iodosilane reagents, we have been interested in developing other methods to generate iodotrimethylsilane or its in situ equivalent for simplified and general use.

This led us to utilize the surprisingly simple and inexpensive alternative of chlorotrimethylsilane with sodium iodide in acetonitrile solution. When chlorotrimethylsilane is added to an acetonitrile solution of anhydrous sodium iodide, a yellow colored solution (whose spectral characteristics are similar to those of a solution obtained from iodotrimethylsilane and acetonitrile in acetone-d_6) is obtained with immediate formation of white precipitate of sodium chloride.[15]

We have, in a preliminary communication, reported our first results on the deoxygenation of sulfoxides with chlorotrimethylsilane/sodium iodide reagent.[16,17] An independent recent report by Morita et al.[18] on the cleavage of phosphonate esters with chlorotrimethylsilane/sodium iodide prompts us to report our results in full, including the cleavage of esters, lactones, carbamates, and ethers, as well as the conversion of alcohols to iodides.[19]

Cleavage of Esters and Lactones. Alkyl esters of carboxylic acids and lactones (1) undergo facile cleavage when the corresponding substrates are reacted with chlorotri-



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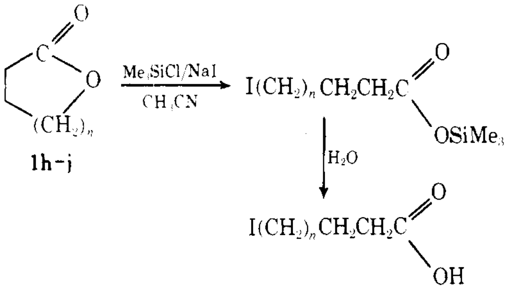
methylsilane and sodium iodide in acetonitrile. The product carboxylic acids (**4**) were isolated in excellent yield (eq 1).

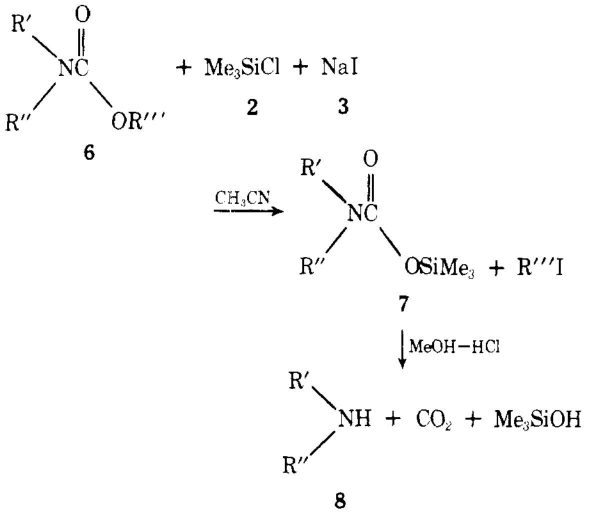
The reaction is quite facile for methyl, ethyl, and benzyl esters. Benzyl esters are cleaved at ambient temperature, whereas methyl and ethyl esters require heating under reflux. Even hindered esters [e.g., methyl pivalate (**1g**)] can be cleaved, albeit at a much slower rate. The method is applicable for esters of both aromatic and aliphatic carboxylic acids, as well as for unsaturated carboxylic acids. The cleavage is slightly slower with the present reagent than with iodotrimethylsilane. This can be due to the inevitable presence of hydroiodic acid in experiments using iodotrimethylsilane, which hydrolyzes esters very rapidly. Indeed, cleavage of esters with this reagent proceeds at a slower rate when carried out in the presence of pyridine.[6] β-, γ-, and δ-lactones (**1h–g**) undergo ready cleavage on heating under reflux with chlorotrimethylsilane/sodium iodide in acetonitrile to provide, after hydrolytic workup, the corresponding iodoalkyl carboxylic acids (**4–j**). β-Butyrolactone reacted somewhat faster than γ-butyrolactone (eq 2).



1h–j (2)

4h–j

Cleavage of Carbamates. Cleavage of carbamates is slightly more facile than that of esters. Initial acidic treatment in order to cleave the silyl carbamate **7** formed in situ and then basic workup of reaction mixture allows the isolation of the corresponding amines in good yield (eq 3). Alkyl carbamates are cleaved into the corresponding amines in a reaction analogous to that of esters and lactones under mild conditions, when treated with chlorotrimethylsilane/sodium iodide in acetonitrile, followed by the addition of methyl alcohol saturated with hydrochloric acid to the reaction mixture. As is the case with esters, benzyl and *tert*-butyl carbamates are cleaved faster than the methyl and ethyl derivatives. Benzyl carbamates are cleaved almost instantaneously at 25 °C, as are *tert*-butyl carbamates. On the other hand, methyl carbamates require heating under reflux for 24 hr for complete cleavage to the corresponding amines. The cleavage with the present reagent is, thus, slower than with iodotrimethylsilane.[8]



(3)

A particularly interesting example is the cleavage of benzyl *tert*-butyloxycarbonyl glycinate (**6f**). Treatment of **6f** with chlorotrimethylsilane/sodium iodide gave glycine (**8f**) in quantitative yield with the deprotection of both ester and carbamate functions (eq 4). Applications of the reaction in peptide chemistry are currently under investigation in our laboratories.

$$\underset{\mathbf{6f}}{(CH_3)_3COC(O)NHCH_2CO_2CH_2Ph} \xrightarrow[CH_3CN]{Me_3SiCl/NaI} (CH_3)_3CI + CO_2 + PhCH_2I + \underset{\mathbf{8f}}{NH_2CH_2CO_2H} \quad (4)$$

Cleavage of Ethers. Both dialkyl and aryl alkyl ethers (**10a–g**) cleave very readily when treated with chlorotrimethylsilane/sodium iodide in acetonitrile (eq 5). Dialkyl

$$\underset{\mathbf{10a\text{-}g}}{ROR'} + Me_3SiCl + NaI \longrightarrow ROSiMe_3 + \underset{\mathbf{12a\text{-}g}}{R'OSiMe_3} + RI + \underset{\mathbf{14}}{R'I}$$

$$\xrightarrow{H_2O} \underset{\mathbf{11a\text{-}g}}{ROH} + \underset{\mathbf{13}}{R'OH} \quad (5)$$

ethers generally cleave faster than aryl alkyl ethers. Benzyl ethers are cleaved particularly fast compared to other alkyl ethers. If the reaction is allowed to proceed for longer periods of time, the intermediate silyl ethers are converted directly to the corresponding alkyl iodides, otherwise, hydrolysis gives the alcoholic products (Table III). The reaction is completely regiospecific for benzyl and aryl alkyl ethers, and to a lesser degree in the case of dialkyl ethers. The reaction of ethers with chlorotrimethylsilane/sodium iodide proceeds faster than with iodotrimethylsilane itself.[3,7] On the other hand, as mentioned previously, esters are cleaved slower with chlorotrimethylsilane/sodium iodide than with iodotrimethylsilane. This dichotomy in behavior suggests different mechanistic paths for the hydrolysis of esters and lactones, on the one hand, and ethers, on the other. Another important feature of the present method is that compounds, such as *p*-dimethoxybenzene (**10g**), can be converted to hydroquinone (**11g**) in quantitative yield.

When anisole was demethylated with iodotrimethylsilane and sodium iodide (8–10 h for completion), the reaction proceeded faster than with iodotrimethylsilane alone (20–24 h for completion). This observation strongly suggests an ionic mechanism for the cleavage of ethers catalyzed by iodide ion, in accord with previous postulations. However, no such catalysis was observed in the case of esters and lactones, the cleavage of which consequently seems to proceed by a different reaction mechanism under the reaction conditions. In addition, we believe that two different mechanisms are operating concurrently in the case of the cleavage of esters and lactones: one via cleavage by adventitious amounts of HI, and the other via cleavage by iodotrimethylsilane, as postulated. These observations are in accord with our previous conclusions on the mechanism of cleavage of esters by iodotrimethylsilane.

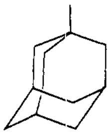
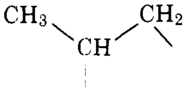
Conversion of Alcohols into Iodides. When alcohols (**15a–i**) are reacted with chlorotrimethylsilane/sodium iodide in acetonitrile solution, the corresponding alkyl iodides are obtained in high yield. Primary, secondary, and tertiary as well as allylic and benzylic alcohols can be converted into the corresponding iodides in excellent yield (eq 6, Table IV).

$$\underset{\mathbf{15a\text{–}i}}{ROH} \xrightarrow[CH_3CN]{Me_3SiCl/NaI} \underset{\mathbf{16a\text{–}i}}{RI} + Me_3SiOH + NaCl \quad (6)$$

The reaction with chlorotrimethylsilane/sodium iodide is rapid compared to that with iodotrimethylsilane.[9] Thus, for example, cyclohexanol is transformed into iodocyclohexane in 40 min. Control experiments showed that under the reac-

Table I. Dealkylative Cleavage of Esters and Lactones by Chlorotrimethylsilane/Sodium Iodide Reagent

$$\underset{1}{RCOOR'} + \underset{2}{ClSiMe_3} \xrightarrow{NaI\ (3)} \underset{4}{RCOOH}$$

compd	esters						
1	R	R′	registry no.	1:2:3 (molar ratio)	time,[a] h	% yield of carboxylic acid[b]	registry no.
a	$C_6H_5CH{=}CH-$	CH_3-	103-26-4	1:2:2	35	85[c]	621-82-9
b	C_6H_5-	$C_6H_5CH_2-$	120-51-4	1:2:2	4[d]	80[e]	65-85-0
c	o-ClC_6H_4-	CH_3-	610-96-8	1:3:2	48	87	118-91-2
d	o-FC_6H_4-	CH_3-	394-35-4	1:3:2	48	90	445-29-4
e	$C_5H_{11}-$	CH_3-	106-70-7	1:3:3	42	71	142-62-1
f		CH_3-	711-01-3	1:3:3	30	98	828-51-3
g	$(CH_3)_3C-$	CH_3-	598-98-1	1:4:4	58	79	75-98-9
h			1823-54-7	1:3:3	10	81[f]	69089-22-1
i	$-(CH_2)_3-$		96-48-0	1:3:3	24	79[f]	7425-27-6
j	$-(CH_2)_4-$		542-28-9	1:3:3	30	84[f]	19448-36-3

[a] All the experiments were carried out by heating under reflux in acetonitrile unless otherwise indicated. [b] Isolated yield. The IR, NMR, and mp or bp of the isolated products were in agreement with the authentic samples. [c] 11% of unreacted starting material was recovered in this experiment. [d] This experiment was carried out at 25 °C. [e] 90% of benzyl iodide was also isolated in this reaction. [f] The corresponding iodocarboxylic acids were formed.

Table II. Decarboxylative Cleavage of Carbamates by Chlorotrimethylsilane/Sodium Iodide Reagent

$$\underset{6}{RNHCOOR'''} \xrightarrow[2\quad 3]{ClSiMe_3\text{-}NaI} \underset{8}{RNH_2} + \underset{9}{R'''I}$$

carbamates				6:2:3 (molar ratio)	reaction conditions time, h/temp, °C	products and yields	
compd 6	R	R‴	registry no.			8	9
a	H	$PhCH_2-$	621-84-1	1:2:3	1/25	c	76[a] 100[b]
b	c-$C_6H_{11}-$	CH_3	5817-68-5	1:2:3	24/80	44[a,d]	c
c	Ph-	CH_3	2603-10-3	1:2:3	24/80	46[a,e]	c
d	$-CH_2CO_2H$	$PhCH_2$	1138-80-3	1:2:2	1/25	100[b]	100[b]
e	$-CH_2CO_2H$	$(CH_3)_3C-$	4530-20-5	1:2:2	1/25	100[b]	100[b]
f	$-CH_2CO_2CH_2Ph$	$(CH_3)_3C-$	69089-23-2	1:2:2	1/25	$NH_2CH_2CO_2H$, 100[b,f]	$CH_3C(CH_3)_2I$, 100[b,g] $PhCH_2I$ 100[b,h]

[a] Isolated yield. [b] Yield as determined by NMR. [c] Not isolated. [d] Registry no. 108-91-8. [e] Registry no. 62-53-3. [f] Registry no. 56-40-6. [g] Registry no. 558-17-8. [h] Registry no. 620-05-3.

tion conditions used by Jung et al., conversion of cyclohexanol to iodocyclohexane is slower with iodotrimethylsilane.[9] This is probably due to the use of a larger excess of chlorotrimethylsilane/sodium iodide in the reaction mixture. Also, activation due to acetonitrile cannot be totally discounted. The reaction with iodotrimethylsilane itself can be accelerated not only by using excess of the reagent, but also by using added sodium iodide in the presence of only a 10% excess of iodotrimethylsilane.

The results show that all studied synthetic transformations can be carried out by replacing iodotrimethylsilane by the more convenient and inexpensive chlorotrimethylsilane/sodium iodide reagent. This also eliminates problems connected with the instability of iodotrimethylsilane during storage and its high hydrolytic sensitivity. The inexpensive chlorotrimethylsilane/sodium iodide reagent generally can be used in excess, thereby considerably shortening the reaction times, and thus avoiding difficulties of unnecessary exposure of the substrates to acidic conditions (due to inevitable formation of HI from iodotrimethylsilane) during prolonged periods of reaction times, although in such cases propene can be used as an acid scavenger.

Experimental Section

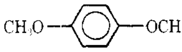
Starting Materials. All the starting materials used in this work were either commercially available in generally 98% or higher purity and used without further purification or prepared by standard literature procedures. Acetonitrile was purified by the usual methods and stored over molecular sieves.

Melting points were determined on Fisher-Johns apparatus and have not been corrected. NMR and IR spectra were obtained on Varian EM-360L and Perkin-Elmer 297 spectrometers, respectively.

General Experimental Procedure for Cleavage of Esters and Lactones by Chlorotrimethylsilane/Sodium Iodide. Reactions were normally conducted on a 20-mmol scale in a 50 mL flask fitted with a water condenser and flushed continuously with dry nitrogen as follows: To a solution of the corresponding ester or lactone (20

Table III. Dealkylation of Ethers by Chlorotrimethylsilane/Sodium Iodide Reagent

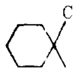
$$\underset{\mathbf{10}}{\mathrm{ROR'}} \xrightarrow[\mathbf{2}\quad\mathbf{3}]{\mathrm{ClSiMe_3\text{-}NaI}} \underset{\mathbf{11}}{\mathrm{ROH}} \longrightarrow \underset{\mathbf{12}}{\mathrm{RI}}$$

	ethers				reaction conditions	products and yields[a]	
compd **10**	R	R′	registry no.	**10:2:3**	time, h/temp, °C	**11**	**12**
a	Ph–	CH_3–	100-66-3	1:2:2	48/82	100[e]	[b]
b	4-CH_3-Ph–	CH_3–	104-93-8	1:2:2	9/82	95[f]	[b]
c	Ph	C_2H_5–	103-73-1	1:2:2	40/82	90	[b]
d	$PhCH_2$–	CH_3–	538-86-3	1:2:2	16/82	0	93
e	$PhCH_2$–	$PhCH_2$–	103-50-4	1:2:2	16/82	0	88
f	c-C_6H_{11}–	Me	931-56-6	1:2:2	16/82	35[c]	43[c]
				1:2:2	5/25	90[c,g]	10[c]
g			150-78-7	1:4:4	48/82	98[d,h]	0

[a] Isolated yield. The products were characterized by comparing IR, NMR, and bp or mp with those of the authentic samples. [b] Not isolated. [c] Isolated pure products by column chromatography on silica gel by eluting with hexane and chloroform successively. [d] Hydroquinone is formed with deprotection of both methyl groups. [e] Registry no. 108-95-2. [f] Registry no. 106-44-5. [g] Registry no. 108-93-0. [h] Registry no. 123-31-9.

Table IV. Conversion of Alcohols to Iodides with Chlorotrimethylsilane/Sodium Iodide Reagent

$$\underset{\mathbf{15}}{\mathrm{ROH}} \xrightarrow[\mathbf{2}\quad\mathbf{3}]{\mathrm{ClSiMe_3\text{-}NaI}} \underset{\mathbf{16}}{\mathrm{RI}}$$

compd **15**		registry no.	**15:2:3**	reaction conditions time, min/temp, °C	yield of iodide[a] **16**	registry no.
a	c-C_5H_9–	96-41-3	1:2:2	30/25	78	1556-18-9
b	c-C_6H_{11}–		1:2:2	40/25	98	626-62-0
c		590-67-0	1:2:2	30/25	98	40304-83-4
d	1-C_9H_{19}–	143-08-8	1:2:2	60/25	83	4282-42-2
e	2-C_9H_{19}–	628-99-9	1:2:2	40/25	80	2216-37-7
f	1-adamantyl	768-95-6	1:2:2	40/25	85[b]	768-93-4
g	$PhCH_2$–	100-51-6	1:2:2	20/25	98	
h	$PhCH{=}CHCH_2$–	104-54-1	1:2:2	20/25	93	59625-54-6
i	cholesterol	57-88-5	1:2:3	2 h/25[c]	80	2930-80-5

[a] Isolated yield. The products were characterized by comparing IR, NMR, and bp or mp with those of the authentic samples. [b] 10% of *N*-(1-adamantyl)acetamide was also isolated in this experiment. [c] Cholesterol was solubilized using a mixture of chloroform and acetonitrile as the solvent.

mmol) and sodium iodide (for specific amounts, see Table I) in acetonitrile (20 mL), chlorotrimethylsilane (for specific amounts, see Table I) was added with continuous good stirring. The reaction mixture was then heated under reflux and monitored by TLC on silica gel with benzene as eluent, for the given period of time (see Table I). Soon after the observed completion of reaction, the reaction mixture was cooled to room temperature, and the product silyl esters were hydrolyzed to the corresponding carboxylic acids by adding water (50 mL). Subsequently, the reaction mixture was taken up in ether (50 mL × 2) and washed successively with water and sodium thiosulfate solution (10%, 25 mL) to remove inorganic salts and iodine, respectively. Water-insoluble carboxylic acids were then extracted by sodium bicarbonate solution (15%, 25 mL × 2) while the ether layer contained the unreacted starting ester. Pure carboxylic acids were obtained by acidification of the bicarbonate extract, filtration, and drying (in oven) at 50–80 °C. In the case of water soluble carboxylic acids, the isolation of the products was achieved by ether extraction. The ether layer was washed with a small amount of brine and dried over Na_2SO_4. The residue obtained after evaporation of ether was further purified, if necessary, by distillation or analyzed directly (by NMR, see Table I).

Typical Procedure for Cleavage of Esters. Cinnamic Acid. To a mixture of methyl cinnamate (3.24 g, 20 mmol) and sodium iodide (6.0 g, 40 mmol) in dry acetonitrile (20 mL) was added chlorotrimethylsilane (4.32 g, 40 mmol) in dry nitrogen atmosphere. The reaction mixture was then heated under reflux and monitored by TLC periodically. The reaction was stopped after 35 h and taken up in ether (50 mL), washed successively with water (25 mL), 10% aqueous sodium thiosulfate solution (25 mL), 15% aqueous sodium bicarbonate solution (25 mL × 2), and brine, and dried over Na_2SO_4. Evaporation of ether afforded 350 mg (11%) of unreacted methyl cinnamate. Acidification of the combined bicarbonate extract precipitated cinnamic acid. It was filtered and dried in an oven at 80 °C for 30 min to afford 2.5 g (85%) of pure cinnamic acid, mp 134.5 °C.

Valeric Acid. A mixture of methyl valerate (2.6 g, 20 mmol), chlorotrimethylsilane (6.5 g, 60 mmol) and sodium iodide (9.0 g, 60 mmol) in dry acetonitrile (20 mL) was brought to reflux and maintained at this temperature for 42 h. The reaction mixture was then cooled to room temperature, taken up in ether (50 mL), washed successively with water (25 mL), 10% sodium thiosulfate solution (25 mL), and brine, and dried over Na_2SO_4. Removal of ether afforded crude valeric acid, which was further distilled to obtain pure valeric acid (bp 82–84 °C/10 mm), yield 1.65 g (71%).

Typical Procedure for the Cleavage of Methyl *N*-Phenylcarbamate. (a) Preparative Procedure with Product Isolation. A mixture of methyl *N*-phenylcarbamate (1.51 g, 10 mmol), chlorotrimethylsilane (2.16 g, 20 mmol), and sodium iodide (4.5 g, 30 mmol) in dry acetonitrile (30 mL) was heated under reflux in a nitrogen atmosphere. The progress of the reaction was monitored by TLC to check for the disappearance of the starting material. At the end of the reaction (24 h), the mixture was allowed to cool to room temperature. To the cooled mixture, 3 mL of methanol saturated with HCl was carefully added, and the mixture was stirred for 15 min. The volatile materials were then removed from the mixture under reduced pressure, and the residue was dissolved in methanol. Sufficient sodium methoxide was added to render the solution alkaline. After removal of methanol under reduced pressure, the residue was shaken with ether (20 mL) and water (20 mL). The aqueous layer was again extracted with ether (20 mL), and the combined ethereal extract was washed with water (3 × 20 mL), sodium thiosulfate solution (10%, 20 mL), and brine. It was then dried over anhydrous Na_2SO_4. Aniline obtained by distillation from the dried extract gave correct physical and spectral characteristics, yield 400 mg (43%).

(b) Following Reactions by NMR Spectroscopy. Carbamate (0.2 mmol) and 0.6 mmol of sodium iodide were dissolved in 0.5 mL of deuterated acetone and taken in a 5 mm NMR tube. Chlorotrimethylsilane (0.6 mmol) was added to the solution, and after a quick, vigorous shaking, a ^1H NMR of the solution was obtained.

General Procedure for the Dealkylation of Ethers by Chlorotrimethylsilane/Sodium Iodide. These reactions were generally carried out in 20-mmol scale in a 50-mL flask fitted with a water condenser (if necessary) and flushed continuously with dry nitrogen. To a solution of the corresponding ether (20 mmol) and sodium iodide (3 g, 20 mmol) in acetonitrile (20 mL) was added chlorotrimethylsilane (2.16 g, 20 mmol) slowly with continuous stirring. The reaction mixture was stirred at room temperature until the completion of the reaction, as monitored by TLC on silica gel with hexane as eluent (see Table III). In some cases, it was necessary to heat the reaction mixture under reflux until the completion of the reaction. On completion of the reaction, the reaction mixture was quenched with water (25 mL) and taken up in ether. The ether layer was then washed with sodium thiosulfate (to remove iodine) and brine and dried over Na_2SO_4. Evaporation of the ether layer gave pure phenolic products or, in the case of aliphatic ethers, alcohols and related products, depending on the reaction conditions (see Table II for details). The products were further purified, if necessary, by column chromatography on silica gel by eluting successively with hexane to obtain pure iodides and with chloroform to obtain pure alcohols (see Table III).

General Procedure for the Conversion of Alcohols into Iodides by Chlorotrimethylsilane/Sodium Iodide Reagent. These reactions were also carried out on a 20-mmol scale in a 50-mL flask, which was purged continuously with dry nitrogen. To a solution of the corresponding alcohol (20 mmol) and sodium iodide (3 g, 20 mmol) in acetonitrile (20 mL) was slowly added chlorotrimethylsilane (2.16 g, 20 mmol) with continuous good stirring. The reaction mixture was monitored by TLC on silica gel with hexane as eluent. The reaction was complete in less than half an hour in most of the cases as shown in Table IV. Upon completion of the reaction, the reaction mixture was taken up in ether and washed successively with water, sodium thiosulfate solution (10%, 25 mL), and brine (20 mL) and dried over Na_2SO_4. Evaporation of ether afforded pure iodides in good yields (see Table IV). Further purification of the iodides, when desired, was achieved by distillation.

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Registry No.—**2**, 75-77-4; **3**, 7681-82-5.

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(15) A solution of equimolar proportions of acetonitrile and iodotrimethylsilane in acetone-d_6 showed two absorptions at $\delta_{^1H}$ (ext tms) 2.24 and 0.27 due to methyl protons of acetonitrile and iodotrimethylsilane, respectively. Similarly, a solution of equimolar proportions of chlorotrimethylsilane, sodium iodide, and acetonitrile also gave similar absorptions at $\delta_{^1H}$ (ext tms) 2.15 and 0.15. When these two solutions were mixed together, the mixture still showed only two absorptions at $\delta_{^1H}$ (ext tms) 2.20 and 0.20, strongly suggesting the formation of similar types of complexes in both cases. Thus, we suggest the following mechanism.

$$CH_3CN + (CH_3)_3SiI \underset{}{\overset{\text{acetone}}{\rightleftharpoons}} [CH_3C{\equiv}N^+Si(CH_3)_3]I^-$$

and

$$CH_3CN + (CH_3)_3SiCl + NaI \overset{\text{acetone}}{\rightleftharpoons} \left[\underset{\mathbf{17}}{CH_3C{\equiv}N^+Si(CH_3)_3}\right] I^- + NaCl\downarrow$$

In addition, when iodotrimethylsilane is mixed with acetonitrile in the absence of acetone, a pale yellow precipitate is formed, which fumes in air, suggesting it could be due to the formation of the complex of the type **17.** Similar observations were made when chlorotrimethylsilane and sodium iodide were mixed together in acetonitrile. Further support in favor of the above mechanism is obtained from ^{13}C NMR measurements. Thus, a solution obtained from iodotrimethylsilane and acetonitrile in acetone gave three absorptions at $\delta_{^{13}C}$ (ext tms) 118.3, 2.2, and 2.8 due to nitrile carbon, methyl carbon of acetonitrile, and methyl carbon of silyl group, respectively. Similarly, a solution of sodium iodide, chlorotrimethylsilane, and acetonitrile in acetone gave three absorptions at $\delta_{^{13}C}$ (ext tms) 118.5, 2.2, and 2.7, whereas authentic samples of iodotrimethylsilane, chlorotrimethylsilane, and acetonitrile gave absorptions respectively at δ ^{13}C (ext tms) 3.4, 4.1, and 118.5, and 2.0.

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(17) We thank one of the referees for bringing to our attention the use of chlorotrimethylsilane/sodium iodide reagent by Russ et al. See, A. H. Schmidt and M. Russ, *Chem.-Z.*, **102**, 26 (1978); **102**, 65 (1978).

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(19) After submission of this manuscript, another publication has appeared on the in situ generation of iodotrimethylsilane. See M. E. Jung and T. A. Blumenkopf, *Tetrahedron Lett.*, 3657 (1978). In our own laboratory, the reaction of hexamethyldisilane with iodine

$$(CH_3)_3SiSi(CH_3)_3 + I_2 \rightarrow 2(CH_3)_3SiI$$

giving iodotrimethylsilane without any byproduct is also utilized in certain cases.