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Synthetic Methods and Reactions. 112.[1] Synthetic Transformations with Trichloromethylsilane/Sodium Iodide Reagent

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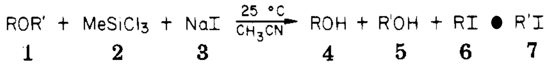
A new, convenient, and inexpensive alternative to the in situ equivalent of iodotrimethylsilane was developed. A mixture of trichloromethylsilane/sodium iodide in dry acetonitrile is found to be a more selective reagent than chlorotrimethylsilane/sodium iodide for the cleavage of ethers, esters, and lactones. Ethers are cleaved regioselectively by this reagent. Cleavage of esters and lactones also occurred more readily with the present system. Conversion of alcohols, particularly tertiary and benzylic alcohols, to corresponding iodides is achieved in very short times at ambient temperatures. Deoxygenation of sulfoxides to sulfides is found to be instantaneous. Reductive dehalogenation of alicyclic α-halo ketones to the corresponding ketones has also been studied. The reagent is also used for the deprotection of acetals to carbonyl compounds.

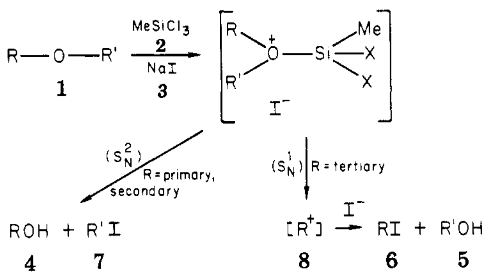
In recent years organosilicon reagents have been used extensively in organic syntheses. Many new silicon reagents have been developed, and silylated synthons are being widely used. One such reagent developed in our laboratories,[2-4] as well as independent by Jung et al.,[5,6] is iodotrimethylsilane, which has gained wide use for different transformations.[2-11] However, its hydrolytic susceptibility, sensitivity in air, and decomposition on prolonged storage are undesirable. Due to these difficulties, several convenient alternative methods for in situ generation of iodotrimethylsilane have been reported. These methods include use of trimethylphenylsilane/iodine,[2,4] hexamethyldisilane/iodine,[12] allyltrimethylsilane/iodine,[13] 3,6-bis(trimethylsilyl)-1,4-cyclohexadien/iodine,[13] as well as chlorotrimethylsilane/sodium iodide[12b,14] in dry acetonitrile. The use of the latter reagent for different organic transformations including deoxygenation of sulfoxides to sulfides,[15] cleavage of esters, lactones, ethers, and carbamates,[12b] conversion of alcohols to iodide,[12b] as well as dehalogenation of α-halo ketones[16] to ketones was explored. In general, this reagent was found to be more reactive than iodotrimethylsilane in these transformations, but the reactions were generally unselective. Interested in finding a selective new in situ equivalent of iodotrimethylsilane for different organic transformations, we now report the successful development of such a reagent from trichloromethylsilane/sodium iodide in dry acetonitrile. When trichloromethylsilane is added to an acetonitrile solution of anhydrous sodium iodide, a yellow solution is slowly obtained with simultaneous formation of a white precipitate of sodium chloride.[17]

Scheme I

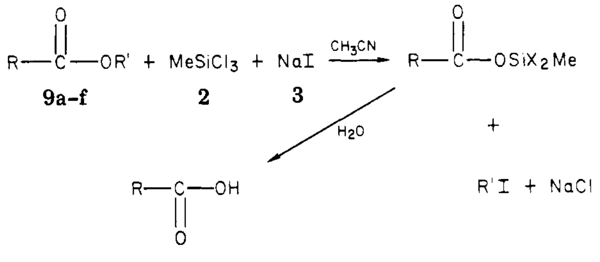


$$\underset{1}{ROR'} + \underset{2}{MeSiCl_3} + \underset{3}{NaI} \xrightarrow[CH_3CN]{25\ ^\circ C} \underset{4}{ROH} + \underset{5}{R'OH} + \underset{6}{RI} \bullet \underset{7}{R'I}$$

Scheme II

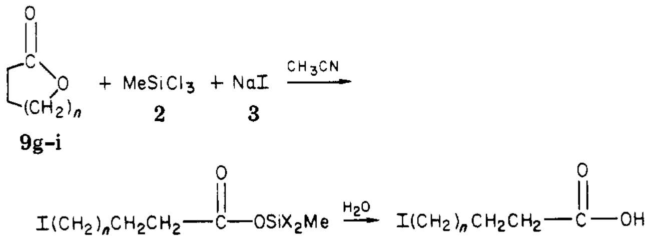


Scheme III



10a-f

Scheme IV



10g-i

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[1] For part 111, see: Olah, G. A.; Karpeles, R.; Narang, S. C. *Synthesis*, in press.

[2] Ho, T. L.; Olah, G. A. *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 774.

[3] Ho, T. L.; Olah, G. A. *Synthesis* **1977**, 417.

[4] Ho, T. L.; Olah, G. A. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 4.

[5] Jung, M. E.; Lyster, M. A. *J. Am. Chem. Soc.* **1977**, *99*, 968.

[6] (a) Jung, M. E.; Lyster, M. A. *J. Org. Chem.* **1977**, *42*, 3761. (b) Minamikawa, J.; Brassi, A. *Tetrahedron Lett.* **1978**, 3085. (c) Jung, M. E.; Mazurel, M. A.; Lim, R. M. *Synthesis* **1978**, 588.

[7] Jung, M. E.; Lyster, M. A. *J. Chem. Soc., Chem. Commun.* **1978**, 315.

[8] Jung, M. E.; Ornstein, P. L. *Tetrahedron Lett.* **1977**, 2659.

[9] Olah, G. A.; Gupta, B. G. B.; Narang, S. C. *Synthesis* **1977**, 583.

[10] Nicolaou, K. C.; Barnette, W. E.; Magolda, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 2567.

[11] Jung, M. E.; Andrus, W. A.; Orstein, P. L. *Tetrahedron Lett.* **1977**, 4175.

[12] (a) Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *Angew. Chem.* **1979**, *91*, 648; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 612. (b) *J. Org. Chem.* **1979**, *44*, 1247. (c) Seitz, D. E.; Ferreira, L. *Synth. Commun.* **1979**, *9*, 931.

[13] Jung, M. E.; Blumenkopf, T. A. *Tetrahedron Lett.* **1978**, 3657.

[14] Morita, T.; Okamoto, Y.; Sakurai, H. *Tetrahedron Lett.* **1978**, 2523; *J. Chem. Soc., Chem. Commun.* **1978**, 874.

[15] Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *Synthesis* **1979**, 61.

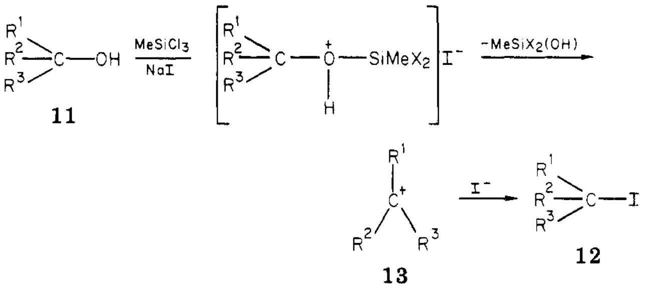
[16] Olah, G. A.; Arvanaghi, M.; Vankar, Y. D. *J. Org. Chem.* **1980**, *45*, 3531.

0022-3263/83/1948-3667$01.50/0

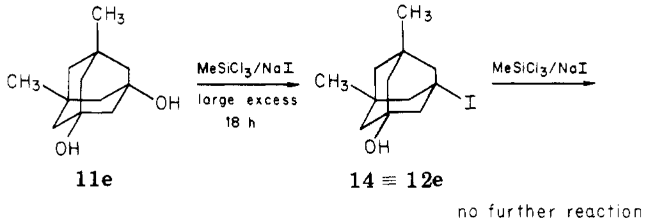
In a preliminary communication from our laboratory, we have recently reported that trichloromethylsilane/sodium iodide is a useful reagent for the regioselective cleavage of ethers.[18] Trichloromethylsilane/sodium iodide was found to be milder and more regioselective than chlorotrimethylsilane/sodium iodide. This initial observation prompted us to investigate in detail its use in synthetic transformations. We now report our results in full, including cleavage of ethers, esters, and lactones, conversion of alcohols to iodides, reductive dehalogenation of α-halo ketones to parent ketones, deoxygenation of sulfoxides to sulfides, and deprotection of acetals to ketones.

Cleavage of Ethers. Cleavage of ethers is conveniently carried out with trichloromethylsilane/sodium iodide in acetonitrile solution at ambient temperature (Scheme I). The reaction takes place readily with high regioselectivity (Table I). The reagent was found to be more selective than chlorotrimethylsilane/sodium iodide. From Table I, it is clear that for methyl ethers (**1a,f,h,o**) demethylation is the major reaction, affording alcohols as the sole products, provided the alkyl groups are either primary or secondary. If the alkyl group is tertiary as (**1n**) in Table I, the resulting product is solely the corresponding iodide. These results suggest that in cases of *tert*-alkyl methyl ethers, the reaction predominantly takes place via an S_N1 pathway through a carbocation intermediate (**8**) producing iodides (**6**) as the major products. Primary and secondary alkyl methyl ethers, however, prefer an S_N2 pathway resulting in alcohols (**4**) as major products (Scheme II).

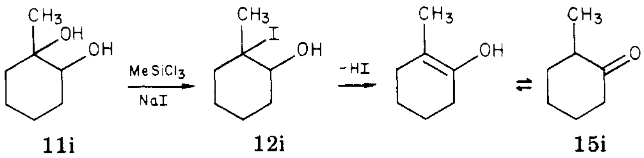
Scheme V



Scheme VI



Scheme VII



Benzyl ethers (**1c,l**), trityl ethers (**1d,k**), and tetrahydropyranyl ethers (**1e,m**) were also found to cleave regioselectively at ambient temperature to give quantitative yields of alcohols (Table I). In the case of ethyl alkyl ethers, however, depending on the nature of the alkyl group, the product varies in yields of alcohols (**4**) and iodides (**6**). The *sec*-alkyl ethyl ethers (**1b,g,p**) cleaved regioselectively to the corresponding alcohols, but primary alkyl ethyl ethers (**1i,j**) gave approximately 1:1 mixtures of alcohols (**4**) and iodides (**6**) (Table I).

Cleavage of Esters and Lactones. Methyl esters of carboxylic acids are stable to trichloromethylsilane/sodium iodide reagent at ambient temperature. When refluxed in acetonitrile methyl esters of aliphatic carboxylic acids (**9a–c**) gave good yield of the corresponding free carboxylic acids (Scheme III). Methyl esters of aromatic acid **9d**, however, reacted slowly, giving a ~50% yield, with the balance of the ester recovered unreacted. On the other hand *tert*-butyl ester **9e** cleaved at room temperature (5 h). Under these conditions benzyl benzoate gave less then 20% conversion. However, when refluxed for 6 h benzyl benzoate (**9f**) gave near quantitative conversion to benzoic acid. These results are summarized in Table II.

Lactones (**9g–i**) also undergo ready cleavage when refluxed with the reagent in acetonitrile to provide, after hydrolytic workup, a good yield of the corresponding iodo carboxylic acids (**10g–i**). Lactones react somewhat faster than esters (Scheme IV).

Conversion of Alcohols to Iodides. All alcohols are converted to their corresponding iodides with trichloro-

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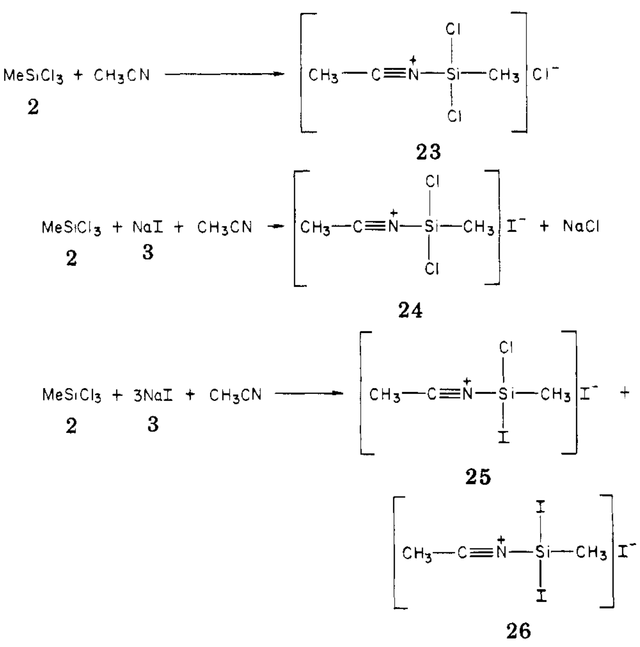
[17] A solution of trichloromethylsilane in acetonitrile shows a ^{29}Si NMR peak at 13.14 ppm with respect to Me$_4$Si. Addition of an equimolar quantity of anhydrous sodium iodide results in precipitation of sodium chloride but no appreciable change in the ^{29}Si spectrum. However, when 3 equiv of sodium iodide is added, the peak at $^{\delta}$Si$_{29}$ 13.14 disappears and two new peaks at $^{\delta}$Si$_{29}$ 10.98 and −115.98 appear in the ^{29}Si NMR. These observations can be rationalized if a complex **23** is formed between trichloromethylsilane **2** and acetonitrile. With 1 equiv of sodium iodide added, the complex **24** differs from **23** in only the counterion; as such there is no appreciable difference in ^{29}Si absorption. However, with 3 equiv of sodium iodide two distinctively different species, **25**, and **26**, are formed, corresponding to the two peaks at $^{\delta}$Si$_{29}$ 10.98 and −115.98 ppm, respectively. This type of complexes has been reported previously when iodotrimethylsilane or chlorotrimethylsilane/sodium iodide is dissolved in acetonitrile.[21]



[18] Olah, G. A.; Husain, A.; Gupta, B. G. B.; Narang, S. C. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 690.

[19] "Dictionary of Organic Compounds", Oxford University Press: New York, 1965.

[20] "Handbook of Tables for Organic Compounds Identification", Chemical Rubber Co.: Cleveland, OH, 1978. "Handbook of Chemistry and Physics", 57th ed.; Chemical Rubber Co., Cleveland, OH.

[21] Olah, G. A.; Narang, S. C. *Tetrahedron* **1982**, *38*, 2225.

[22] A mixture of triphenylmethanol and triphenylmethane were obtained in these cases, presumably due to the facile hydrolysis and reduction of trityl iodide formed during the reaction. For deoxygenation of triphenylmethanol using diiodomethylsilane, see Ando, W.; Ikeno, M. *Tetrahedron Lett.* **1979**, 4941.

Table I. Dealkylation of Ethers (1) by the Trichloromethylsilane/Sodium Iodide Reagent

$$\underset{1}{\mathrm{ROR'}} + \underset{2}{\mathrm{MeSiCl_3}} + \underset{3}{\mathrm{NaI}} \xrightarrow[\mathrm{CH_3CN}]{25\ ^\circ\mathrm{C}} \underset{4}{\mathrm{ROH}} + \underset{5}{\mathrm{R'OH}} + \underset{6}{\mathrm{RI}} + \underset{7}{\mathrm{R'I}}$$

				products and yields, %[a,b]			
1	R	R'	time, h	4	5	6	7
a	c-C_6H_{11}	CH_3	7	81	0	0	*c*
b	c-C_6H_{11}	C_2H_5	8	85	0	0	*c*
c	c-C_6H_{11}	$PhCH_2$	4	90	0	0	85
d	c-C_6H_{11}	CPh_3	4	75	0	0	100[d]
e	c-C_6H_{11}	THP[e]	3	88	0	0	*c*
f	*n*-C_3H_7CH-*n*-C_4H_9	CH_3	10	85	0	0	*c*
g	*n*-C_3H_7CH-*n*-C_4H_9	C_2H_5	8	75	0	0	*c*
h	*n*-C_9H_{19}	CH_3	9	100	0	0	*c*
i	*n*-C_9H_{19}	C_2H_5	36	57	*c*	43	*c*
j	*n*-$C_{11}H_{23}$	C_2H_5	36	55	*c*	45	*c*
k	*n*-$C_{11}H_{23}$	CPh_3	3	87	0	0	100[d]
l	c-$C_7H_{13}CH_2$	$C_6H_5CH_2$	4	100	0	0	95
m	c-$C_7H_{13}CH_2$	THP[e]	16	98	0	0	*c*
n	$(CH_3)_2C$-*n*-C_7H_{15}	CH_3	6	0	*c*	100	0
o	3-stigmastanyl	CH_3	16	97	0	0	*c*
p	3-stigmastanyl	C_2H_5	36	86	0	0	*c*

[a] Isolated yield of the products unless otherwise noted. [b] All products gave satisfactory physical and spectral (IR and NMR) characteristics. [c] Not isolated. [d] Isolated as a mixture of triphenylmethanol and triphenylmethane.[22] [e] THP = tetrahydropyranyl.

Table II. Dealkylative Cleavage of Esters and Lactones

$$\underset{9}{\mathrm{RCOOR'}} + \underset{2}{\mathrm{MeSiCl_3}} + \underset{3}{\mathrm{NaI}} \xrightarrow{\mathrm{CH_3CN}} \underset{10}{\mathrm{RCOOH}}$$

9	R	R'	time, h[a]	yields of 10, %[b,e]	bp/mp, °C (torr)	lit.[19,20] bp/mp, °C (torr)
a	$(CH_3)_2CH$	CH_3	12	70	152-154 (760)	154.3 (760)
b	PhCH=CH	CH_3	12	85	135	133
c	c-C_6H_5	CH_3	12	86	119-121 (12-13)	120-121 (13)
d	Ph	CH_3	12	51	122	122
e	$(CH_3)_3C$	$(CH_3)_3C$	5[d]	71	75-78 (20-21)	75-78 (20)
f	Ph	$PhCH_2$	6	95	122	122
g	-$(CH_2)_5$-		3	90[e]	43	42.5-44
h	-$(CH_2)_3$-		3	86[e]	39	40-41
i	CH_3CHCH_2-		4	85[e]	38.5	39

[a] All the experiments were carried out by heating under reflux in acetonitrile unless otherwise indicated. [b] Isolated yields. [c] All the products gave satisfactory NMR, which were compared with authentic samples. [d] Reaction was done at room temperature. [e] Products are the corresponding iodocarboxylic acids.

methylsilane/sodium iodide reagent in acetonitrile solution (Table III). Again the reagent was found to be milder and more selective for this transformation than chlorotrimethylsilane/sodium iodide.[12a] Primary alcohols were found to react extremely slowly. Thus 1-undecanol (**11h**) gave less than 20% conversion to 1-undecyl iodide when refluxed with trichloromethylsilane/sodium iodide in acetonitrile for 72 h. Secondary alcohols (**11f,g**) have moderate reactivity but still require refluxing in acetonitrile for appreciable conversion. On the other hand tertiary and benzylic alcohols (**11a–c**) are almost instantly converted to the corresponding iodides when treated with the reagent at room temperature. It should be noted that under these mild conditions secondary alcohols do not show appreciable reactivity. Thus, 5-nonanol stirred with trichloromethylsilane/sodium iodide in acetonitrile for 30 min shows no trace of 5-iodononane, and cyclohexanol gave less than 4% iodocyclohexane.

These observations suggest that the tertiary and benzylic alcohols (**11**) react via the corresponding carbocationic species **13** to the iodide **12** (Scheme V).

Bridgehead alcohols such as 1-adamantanol (**11d**) are also converted quantitatively to the corresponding iodide. An interesting observation is the reaction of 1,3-dimethyladamantane-5,7-diol (**11e**) with this reagent system. Even with a large excess of trichloromethylsilane/sodium iodide and long reaction time only the monoiodide **14** is formed (Scheme VI). Subjecting the monoiodide **14** to the same reagent failed to convert the second alcohol group to the iodide. The identity of the monoiodide **14** was confirmed by ^{1}H NMR and elemental analysis. Anal. Calcd: for C, 47.07; H, 6.26; I, 41.45. Found: C, 47.21; H, 6.03; I, 41.46.

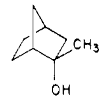
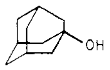
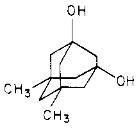
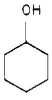
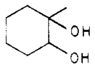
In the case of vicinal dihydroxy compounds, such as 1-methyl-*trans*-1,2-cyclohexanediol (**11i**), treatment with trichloromethylsilane/sodium iodide results in the formation of ketone **15i**. This is presumably due to the elimination of HI from the initially formed monoiodide, resulting in the formation of enol, which is then converted to the keto form (Scheme VII).

A number of alcohols were studied with this reagent system. The results of these experiments are summarized in Table III. An added advantage of this reagent is that only $^1/_2$ molar equiv of the silyl reagent is required per mol of hydroxyl group. Thus, in a typical experiment 20 mmol of a tertiary alcohol is treated with 10–12 mmol of trichloromethylsilane and 25 mmol of sodium iodide in ~30 mL of dry acetonitrile to complete the reaction.

Reductive Dehalogenation of α-Halo Ketones. Dehalogenation of α-halo ketone **16** to parent ketones **17** is

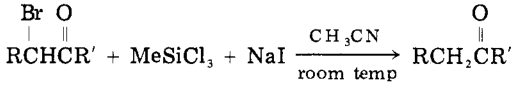
Table III. Conversion of Alcohols to Iodides

$$\underset{11}{\mathrm{ROH}} + \underset{2}{\mathrm{MeSiCl_3}} + \underset{3}{\mathrm{NaI}} \xrightarrow[25\text{-}80\ ^\circ\mathrm{C}]{\mathrm{CH_3CN}} \underset{12}{\mathrm{R{-}I}}$$

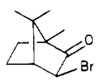
11	alcohol	11:2:3	time, h[a]	yield of iodide 12, %[b,c]	mp/bp, °C (torr)
a	$CH_3(CH_2)_6C(CH_3)_2OH$	1:0.6:1	0.25	95	81-82 (2)
b	$C_6H_5CH_2OH$	1:0.6:1	0.25	95	83-84 (3)
c		1:0.6:1	0.25	96	80-81 (20)
d		1:1:1	2.00	80	73.6
e		1:2.5:2.5	12[d]	60[e]	140.7
f		1:1.2:1.2	18[d]	54	38 (1.5)
g	5-$C_9H_{19}OH$	1:1.2:1.2	18[d]	73	55 (1.5)
h	*n*-$C_{11}H_{23}OH$	1:1.2:1.2	72[d]	19	105 (1.5)
i		1:0.6:0.6	0.5	90[f]	

[a] Reactions carried out at room temperature unless otherwise noted. [b] Isolated yield of purified product. [c] All products gave satisfactory IR and NMR characteristics. [d] Reaction carried out at refluxing temperature of solvents. [e] Product is the monoiodide. [f] Product is 2-methylcyclohexanone.

Table IV. Reductive Dehalogenation of α-Halo Ketones

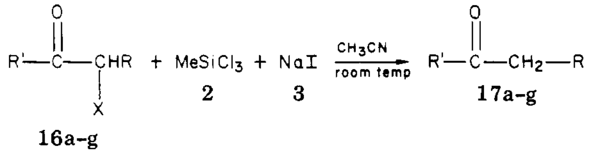


$$\underset{16}{\mathrm{RCH(Br)C(=O)R'}} + \underset{2}{\mathrm{MeSiCl_3}} + \underset{3}{\mathrm{NaI}} \xrightarrow[\text{room temp}]{\mathrm{CH_3CN}} \underset{17}{\mathrm{RCH_2C(=O)R'}}$$

16	R	R'	time,[a] h	yield of product 17,[b,c] %	mp/bp, °C (torr)	lit.[19,20] mp/bp, °C (torr)
a	H	C_6H_5	2	90	79-81 (12-13)	83-85 (12)
b	H	*p*-ClC_6H_5	2	98	105-107 (9-10)	99 (7)
c	H	*p*-BrC_6H_5	2	98	49	51
d	H	*p*-PhC_6H_5	2	90	116	120-121
e			18[d]	60	176	178.8
f	Ph	Ph	3	92	55	55-56
g	CH_3	CH_3	2	95	79.5	80

[a] Reactions were carried out at room temperature unless otherwise noted. [b] Yield of isolated purified product. [c] All products gave satisfactory NMR characteristics. [d] The reaction was carried out at refluxing temperature of the solvent.

Scheme VIII

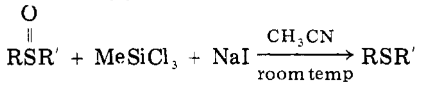


carried out smoothly with trichloromethylsilane/sodium iodide in acetonitrile solution at room temperature (Scheme VIII). The reagent provides almost quantitative yields of reduced products, i.e., ketones, in the case of both aliphatic as well as aromatic alicyclic α-halo ketones in very short times (Table IV). In the case of cyclic α-halo ketones, however, the reaction is rather slow, and much higher temperature is required (**16e**, Table IV). It appears, therefore, that trichloromethylsilane/sodium iodide is selective for the reductive dehalogenation of alicyclic α-halo ketones only as compared to chlorotrimethylsilane/sodium iodide, which can be used for both alicyclic as well as cyclic α-halo ketones.[16]

Deoxygenation of Sulfoxides. The deoxygenation of sulfoxides **18** to the corresponding sulfides **19** was conveniently carried out at ambient temperature by using trichloromethylsilane/sodium iodide in acetonitrile solution (Table V). The reaction was almost instantaneous and was evident by liberation of iodine. The probable mechanism for this reaction can be shown as in Scheme IX.

According to Scheme IX 2 equiv of the silyl reagent is required for each equivalent of the sulfoxide. However, a control experiment using *p*-chlorophenylsulfoxide indi-

Table V. Deoxygenation of Sulfoxide to Sulfides



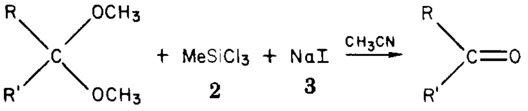
$$\overset{O}{\overset{\|}{RSR'}} + MeSiCl_3 + NaI \xrightarrow[\text{room temp}]{CH_3CN} RSR'$$

18 2 3 19

18	R	R'	time,[a] min	yield,[b] %	mp/bp, °C (torr)	lit.[19,20] mp/bp, °C (torr)
a	CH_3	CH_3	10	95[c]	154.5	158[d]
b	n-C_3H_7	n-C_3H_7	20	94	139-140 (760)	142 (760)
c	n-C_4H_9	n-C_4H_9	20	80	182 (760)	185 (760)
d	C_6H_5	C_6H_5	20	99	100-102 (0.1)	297 (760)
e	$C_6H_5CH_2$	$C_6H_5CH_2$	10	85	49-50	48-49
f	p-ClC_6H_4	p-ClC_6H_4	20	85	95	95
g	p-$CH_3C_6H_4$	p-$CH_3C_6H_4$	20	95	57	57.3

[a] The reactions were carried out at room temperature. [b] Yield of isolated product. [c] Yield based on $HgCl_2$ complex. [d] The melting point of the $HgCl_2$ complex.

Table VI. Conversion of Acetals to Carbonyl Compounds

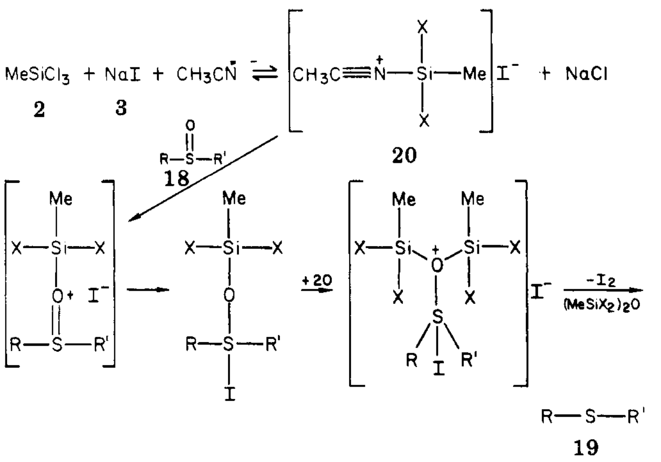


21 22

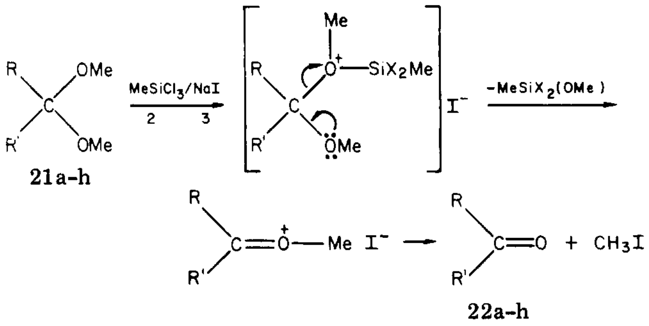
21	R	R'	time,[a] h	yield, %	mp/bp, °C (torr)	lit.[19,20] mp/bp, °C (torr)
a	CH_3	H	0.5	90[b]	167[c]	165-166[c]
b	C_6H_5	H	6	70	178 (760)	178 (760)
c	C_6H_5	C_6H_5	12	94	48.6	48-49
d	C_6H_5	CH_3	1	96	235.5	237
e	$C_6H_5CH_2$	CH_3	1	95	243	244-246
f	-$(CH_2)_5$-		1	85	128-130 (760)	130-131 (760)
g	-$(CH_2)_6$-		0.5	95	150 (760)	152 (760)

[a] The reactions were carried out at room temperature. [b] Yield is based on formation of 2,4-dinitrophenylhydrazone derivatives. [c] The melting point of the 2,4-dinitrophenylhydrazone derivative.

Scheme IX



Scheme X



cates that 1 equiv of trichloromethylsilane and 2 equiv of sodium iodide per equiv of sulfoxide are sufficient to complete the reaction. Attempts to use only $^2/_3$ equiv of trichloromethylsilane gave only about 66% conversion. These observations suggest that out of three chlorine atoms in trichloromethylsilane, only two are capable of carrying out the transformation of sulfoxide to sulfide. Once the silicon atom is attached to two oxygen atoms, its electrophilicity is decreased to a level where it is no more reactive with the sulfoxide.

An apparent advantage of the trichloromethylsilane/sodium iodide reagent system over iodotrimethylsilane or bromotrimethylsilane can be seen in the clean conversion of benzyl sulfoxide **18e** to benzyl sulfide. The latter two reagents gave mixtures of products probably arising from the halogenations of dibenzyl sulfide.

Deprotection of Acetals. All the dimethyl acetals **21** reacted rapidly with the trichloromethylsilane/sodium iodide reagent in acetonitrile solution at ambient temperature, giving excellent yields of the carbonyl compounds (Table VI). The probable mechanism for this reaction is given in Scheme X.

These results show that trichloromethylsilane/sodium iodide is a new, mild, and selective reagent system for a number of important synthetic transformations. This reagent is generally very active even at ambient temperature as in the case of cleavage of ethers, selective conversion of tertiary alcohols to iodides, deoxygenation of sulfoxides to sulfides, reductive dehalogenation of α-halo ketones to ketones, and deprotection of acetals of carbonyl compounds. In the case of cleavage of esters and lactones reflux temperatures are required to complete the reaction. The reagent was found to be more selective in its reactivity than iodotrimethylsilane or its in situ equivalents as chlorotrimethylsilane/sodium iodide. Trichloromethylsilane is also a very inexpensive and readily available silicon reagent. In view of these observations, trichloromethylsilane/sodium iodide reagent should have wide applicability in organic syntheses.

Experimental Section

All the boiling and melting points are uncorrected. All of the starting materials were either commercially available and used without further purifications of prepared in the laboratory by known procedures. Solvents were dried by usual methods before use. Trichloromethylsilane purchased from Petrarch Systems Inc., was redistilled before use. Sodium iodide was dried at 100 °C for 24 h before use. IR spectra were obtained on a Perkin-Elmer Model 297 spectrometer and ^{1}H NMR spectra were recorded on a Varian Model A 56/60, EM 360L, or XL200 spectrometer. Gas chromatographic analyses were performed on a Varian Associates Model 3700 gas chromatograph. All the products were identified by comparing their physical data with the authentic samples.

General Procedure for the Cleavage of Ethers. *Trichloromethylsilane (1.8 g, 12 mmol) and 1 (10 mmol) are added,* successively, with continuous stirring under a nitrogen atmosphere to a solution of NaI (1.8 g, 12 mmol) in dry acetonitrile (20 mL). The reaction is monitored by thin layer chromatography (hexane) and ^{1}H NMR, then quenched with water, and extracted with ether, and the ethereal extract washed with aqueous $Na_2S_2O_3$, water, and brine. The ethereal extract is dried over anhydrous Na_2SO_4 and the solvent evaporated to yield the crude product, which is further purified by crystallization or distillation.

General Procedure for the Cleavage of Esters. To a stirred solution of anhydrous sodium iodide (25 mmol) were added successively ester (20 mmol) and trichloromethylsilane (20 mmol), and the reaction mixture was refluxed for a specified time (Table II) to complete the reaction. In the end the reaction mixture was poured into ice water and extracted with ether. After washing with aqueous sodium thiosulfate the ether layer was treated with aqueous sodium hydroxide. The aqueous layer was separated, acidified with dilute HCl, and extracted with ether again. The ether layer washed with water and dried. Removal of the solvent gave the corresponding carboxylic acids which were identified by comparing the melting point/boiling point and spectral data with those of the authentic samples.

General Procedure for the Cleavage of Lactones. To a *stirred solution of anhydrous sodium iodide (25 mmol) in 40 mL* dry acetonitrile were added successively lactone (20 mmol) and trichloromethylsilane (20 mmol) and the reaction mixture was refluxed for a specified time (Table II) to complete the reaction. In the end the reaction mixture was poured into ice water and extracted with ether. The organic layer was washed with sodium thiosulfate solution, water, and brine and dried over anhydrous $MgSO_4$. Removal of the solvent gave the crude product, which was purified by passing through a silica gel column or by distillation and was identified by spectral data (Table II).

General Procedure for the Conversion of Alcohols to Iodides. Reactions were generally carried out with 20 mmol of alcohol. Alcohol and trichloromethylsilane were added successively to a stirred solution of anhydrous sodium iodide in 30 mL of dry acetonitrile (for amounts of reagents refer to Table III). The reaction mixture was stirred for a specified time at a specified temperature (see Table III), after which it was quenched with water and extracted with ether. The extract was washed with aqueous sodium thiosulfate, water, and brine and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave crude iodide, which was purified by column chromatography (silica gel, elution with hexane) and identified by spectral data.

General Procedure for the Reductive Dehalogenation of α-Halo Ketones to Ketones. Reactions were generally carried out with 20 mmol of α-halo ketones. Trichloromethylsilane (25 mmol) and α-halo ketone (20 mmol) were added successively to a stirred solution of anhydrous sodium iodide (40 mmol) in 30 mL of dry acetonitrile. The reaction was monitored by GLC (glass capillary column; 50 ft × 0.25 mm OV-101, 80–180 °C, 30 psi He). After completion of the reaction, the reaction mixture was quenched with water, washed with aqueous sodium thiosulfate, water, and brine, and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave crude product, which was purified by column chromatography (silica gel, eluted with hexane) or distillation and identified by comparing its physical and spectral data with the authentic sample.

General Procedure for Deoxygenation of Sulfoxide. To a stirred solution of trichloromethylsilane (3.0 g, 20 mmol) and dry sodium iodide (3.0 g, 20 mmol) in dry acetonitrile (20 mL) is slowly added the corresponding sulfoxide (10 mmol) under a nitrogen atmosphere. The progress of the reaction is monitored by TLC (hexane as eluent). The reaction mixture is then quenched with water, extracted with hexane, and washed with aqueous sodium thiosulfate, water, and brine successively. After drying over anhydrous sodium sulfate, the solvent is distilled off to yield the crude products in excellent yield. The crude product is purified by either crystallization or distillation and identified by comparing its boiling point or melting point and NMR data with those of the authentic sample.

General Procedure for Deprotection of Acetals. To a stirred solution of sodium iodide (25 mmol) in dry acetonitrile (40 mL) are added successively trichloromethylsilane (20 mmol) and acetal (10 mmol) under a dry nitrogen atmosphere. Iodine color formation appeared instantaneously. The reaction mixture is monitored by TLC (benzene:hexane 1:1 as eluent). The reaction mixture is quenched with water and extracted with dichloromethane (2 × 25 mL), and the organic layer was washed successively with aqueous sodium thiosulfate, water, and brine solution. Drying over anhydrous sodium sulfate and removal of solvent yielded crued product in excellent yields. The crude products are purified by column chromatography, and distillation, or crystallization and characterized by comparing their physical and spectral data with the authentic samples.

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Registry No. **1a**, 931-56-6; **1b**, 932-92-3; **1c**, 16224-09-2; **1d**, 20705-40-2; **1e**, 709-83-1; **1f**, 77067-56-2; **1g**, 77067-57-3; **1h**, 7289-51-2; **1i**, 16979-32-1; **ij**, 78371-01-4; **1k**, 78371-02-5; **1l**, 78371-03-6; **1m**, 78371-04-7; **1n**, 78371-05-8; **1o**, 78371-06-9; **1p**, 78371-07-0; **2**, 75-79-6; **3**, 7681-82-5; **4a**, 108-93-0; **4f**, 589-62-8; **4h**, 143-08-8; **4j**, 112-42-5; **4l**, 4448-75-3; **4o**, 78419-36-0; **6i**, 4282-42-2; **6j**, 4282-44-4; **6n**, 78371-08-1; **7d**, 2206-53-3; **7l**, 620-05-3; **9a**, 547-63-7; **9b**, 103-26-4; **9c**, 4630-82-4; **9d**, 93-58-3; **9e**, 16474-43-4; **9f**, 120-51-4; **9g**, 502-44-3; **9h**, 120-92-3; **9i**, 1823-54-7; **10a**, 79-31-2; **10b**, 621-82-9; **10c**, 98-89-5; **10d**, 65-85-0; **10e**, 75-98-9; **10g**, 4224-63-9; **10h**, 7425-27-6; **10i**, 69089-22-1; **11a**, 10297-57-1; **11b**, 100-51-6; **11c**, 5240-73-3; **11d**, 768-95-6; **11e**, 10347-01-0; **11g**, 623-93-8; **11h**, 112-42-5; **11i**, 6296-84-0; **12c**, 87102-15-6; **12d**, 768-93-4; **12e**, 87102-16-7; **12f**, 626-62-0; **12g**, 59456-19-8; **12h**, 4282-44-4; **15i**, 583-60-8; **16a**, 70-11-1; **16b**, 536-38-9; **16c**, 99-73-0; **16d**, 135-73-9; **16e**, 76-29-9; **16f**, 1484-50-0; **16g**, 814-75-5; **17a**, 98-86-2; **17b**, 99-91-2; **17c**, 99-90-1; **17d**, 92-91-1; **17e**, 76-22-2; **17f**, 451-40-1; **17g**, 78-93-3; **18a**, 67-68-5; **18b**, 4253-91-2; **18c**, 2168-93-6; **18d**, 945-51-7; **18e**, 621-08-9; **18f**, 3085-42-5; **18g**, 1774-35-2; **19a**, 75-18-3; **19b**, 111-47-7; **19c**, 544-40-1; **19d**, 139-66-2; **19e**, 538-74-9; **19f**, 5181-10-2; **19g**, 620-94-0; **21a**, 534-15-6; **21b**, 1125-88-8; **21c**, 2235-01-0; **21d**, 4316-35-2; **21e**, 26163-01-9; **21f**, 933-40-4; **21g**, 25632-02-4; **22a**, 75-07-0; **22a** 2,4-DNP derivative, 1019-57-4; **22b**, 100-52-7; **22c**, 119-61-9; **22d**, 98-86-2; **22e**, 103-79-7; **22f**, 108-94-1; **22g**, 502-42-1; **23**, 87102-17-8; **24**, 87102-18-9; **25**, 87102-19-0; **26**, 87102-20-3.