$C(O)Cl$, 20448-91-3; $CH_3C(O)CH{=}CHC(O)Cl$, 110295-11-9; $MeOC(O)CH{=}CHC(O)Cl$, 78140-66-6; $MeOC(CH_3){=}CHC(O)Cl$, 110295-12-0; $ClCH{=}CHC(O)Cl$, 54358-89-3; $PhSCH{=}CHC(O)Cl$, 1077-15-2; (E)-$CH_2{=}CHCH{=}CHOSiMe_3$, 63383-46-0; m-$Me_2NC_6H_4OCH_2CH{=}CH_2$, 110295-46-0; pyruvaldehyde ethylene dithioketal, 26419-66-9; 2-[2-(ethoxycarbonyl)ethenyl]-2-methyl-1,3-dithiolane, 110295-09-5; 2-(2-carboxyethenyl)-2-methyl-1,3-dithiolane, 110295-10-8; 5-bromo-2-furancarbonyl chloride, 26726-16-9; 4-(1-methylethenyl)-1-cyclohexene-1-carbonyl chloride, 90554-83-9; 2-(3-chloro-3-oxo-1-propen-1-yl)-2-methyl-1,3-dithiane, 110295-13-1; 2-(3-chloro-3-oxo-1-propen-1-yl)-2-methyl-1,3-dithiolane, 110295-14-2; 2-acetyl-4-[(2-propen-1-yl)oxy]phenol, 40815-75-6; 1-methoxy-1,3-cyclohexadiene, 2161-90-2; 1,4-bis[(trimethylsilyl)oxy]-1,3-cyclohexadiene, 59733-55-0; 3-(2-methyl-1,3-dithiolan-2-yl)-5,8,9-trihydroxy-3,4,5,8-tetrahydroanthracen-1(2H)-one, 110313-46-7; sorboyl chloride, 2614-88-2.

Diiodosilane. 1. A Novel Reagent for Deoxygenation of Alcohols and Ethers

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Diiodosilane (DIS), which has never been used previously in organic synthesis, has been shown to exhibit properties and reactivities that are complementary to those of iodotrimethylsilane. This new reagent was used to cleave and deoxygenate ethers and alcohols with high selectivity for secondary oxygen functions. Synthesis of DIS is easily and rapidly carried out by reacting phenylsilane with iodine.

Introduction

Use of organosilicon reagents in organic synthesis has expanded bewilderingly over the past decade. Iodotrimethylsilane (TMSI) is one of the most important such reagents, offering a broad variety of useful functional group transformations under mild conditions.[1] Its unique properties and high reactivity arise from a combination of the relatively high Lewis acidity of silicon (with a specific affinity to oxygen functionalities) and the strong nucleophilicity of iodide ion. These properties of TMSI make it a versatile and selective reagent for cleavage of carbon–oxygen bonds.

Therefore, it is quite surprising that despite the many reports on synthetic applications of TMSI, very little effort was devoted to attempts to modify the reactivity of the Si–I bond and thereby to obtain new reagents with novel chemical properties. There were, however, some investigations devoted to altering the steric demands of the reagent, designing iodotrialkylsilanes with bulkier alkyl groups, such as t-$BuMe_2SiI$ or t-$BuPh_2SiI$.[2] These modifications, however, did not affect the basic properties and selectivities of the reagent, e.g., its preference for cleaving methyl ethers rather than primary and secondary alkyl ethers. Moreover, the reactivity pattern of Cl_3SiI (prepared in situ from tetrachlorosilane and sodium iodide)[3] was also similar to that of TMSI, as was a combination of trichloromethylsilane and sodium iodide, despite its reduced reactivity.[4] Nevertheless, modifications of either the Lewis acidity or nucleophilicity of this family of reagents could lead to modified reactivity profiles and, in particular, alternative chemoselectivities. In fact, during attempts to generate TMSI in situ from various organosilicon precursors,[1] including TMSCl and NaI,[5] hexamethyldisilane and iodine,[6] allyltrimethylsilane and iodine,[7] $PhSiMe_3$ and iodine,[8] etc., it was noticed that the combination of reagents exhibited properties that differed from those of preformed TMSI. The latter combination, for example, exhibited enhanced efficiency in cleaving alkyl aryl ethers.[8,9] The altered behavior of these systems seems to be associated with the precursors whose characteristics differ from those of TMSI (e.g., acidity and nucleophilicity).

In our search for new modes of reactivity of yet unrecognized iodosilane reagents, we discovered that diiodosilane (DIS) is an extremely useful reagent, exhibiting properties and reactivities that are complementary to those of TMSI. In this paper, we present an easy and rapid synthesis of DIS and demonstrate this reagent's application to cleavage and deoxygenation of alcohols and ethers with chemoselectivities that are complementary to those of the iodotrialkylsilanes.

Results and Discussion

Preparation of DIS. DIS[10] was first prepared almost 50 years ago by reaction of silane, HI, and aluminum iodide.[11] However, apart from occasional studies on the properties of this rather exotic compound, it has never

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† Incumbent of the Joseph and Madeleine Nash Career Development Chair established by Fondacion Madelon, Zurich, Switzerland.

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(10) DIS (or Dite in the Italian diction) is the Latin name of Hell in Dante's Divine Comedy (*Inferno*, VIII, 67–69).

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been used in organic chemistry. The improved method of Fritz and Kummer of the early 1960s[12] employs phenylsilane and iodine. It has been shown[12a] that iodine reacts with phenylsilane to produce monoiodosilanes according to eq 1 and 2.

$$PhSiH_3 + I_2 \rightarrow PhSiH_2I + HI \qquad (1)$$

$$PhSiH_3 + HI \rightarrow SiH_3I + PhH \qquad (2)$$

Phenyliodosilane may further react with excess HI[12b] to produce DIS according to eq 3. Similarly, DIS may be prepared by protonolysis of diphenylsilane with HI.[12d] Less expensive alternatives involve direct, inorganic syntheses of DIS[13] that are particularly attractive for an industrial, large-scale production.

$$PhSiH_2I + HI \rightarrow DIS + PhH \qquad (3)$$

In our initial experiments we found, in agreement with earlier reports,[12a,b] that phenylsilane indeed reacts very sluggishly at room temperature with iodine in chloroform, in benzene, or even without solvent. No significant enhancement of rate was observed upon either heating the solution to 60–80 °C or irradiating it at 254 nm. Nor did employment of BrI instead of I_2 have any effect on the reaction.

To our surprise, we discovered that trace quantities of almost any organic compound containing an oxygen functionality, such as ketones, ethers, esters, etc., have a tremendous catalytic effect on this reaction. In fact, the reaction becomes so rapid and exothermic that cooling is required; particular precaution should be taken when operating on large scale. According to eq 1–3, mixing iodine and phenylsilane in a 1:1 molar ratio in the presence of traces of ethyl acetate at −20 °C produces 1 mol of DIS and 1 mol of benzene. This approach (see the Experimental Section) represents a rapid and convenient preparation, affording crude DIS, which is sufficiently pure for most synthetic applications. The volatile byproducts—benzene, minor amounts of HI, SiH_3I, and traces of EtI—are easily removed under reduced pressure.

In order to understand the catalytic role of oxygen functionalities in iodination of silanes, we carried out four reactions in the presence and absence of catalytic quantities of ethyl acetate. In two of these experiments iodine was reacted with $PhSiH_3$ and with SiH_3I to give $PhSiH_2I$ and SiH_2I_2, respectively. In the other two experiments, HI was reacted with $PhSiH_3$ and $PhSiH_2I$, affording SiH_3I and SiH_2I_2, respectively. While the reactions with HI were unaffected by the presence of ethyl acetate, significant rate enhancements (of over 2 orders of magnitude) were observed in the reactions involving iodine.

According to eq 1 and 3, conversion of phenylsilane into DIS involves at least two steps: (a) reaction with iodine that results in hydride–iodide exchange, accompanied by HI formation; (b) reaction with HI that causes protonolysis of a phenyl–silicon bond. From our results, it is apparent that in reactions carried out in chloroform only the first step is catalyzed by ethyl acetate, with protonolysis functioning as the rate-determining step. (Reactions carried out without solvent behave similarly to those performed in chloroform, although they are generally faster.) It is also clear that formation of monoiodosilane is generally faster than formation of diiodosilane, a trend that may explain the absence of triiodosilanes in our mixtures.

Scheme I

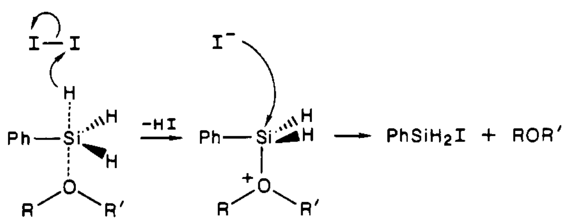

Table I. Relative Rates of Conversion of Alcohols to Iodoalkanes[a]

entry	alcohol	conversion rates with HI	with TMSI	with DIS
1	*tert*-butyl	>450	>450	>450
2	benzyl	>450	>450	>450
3	methyl	22.8	76	0.6
4	ethyl	0.30	6.1	0.3
5	*n*-butyl	0.25	4.8	0.1
6	*sec*-butyl	0.36	2.5	65
7	isopropyl	0.15	1	54

[a] All reactions were carried out by addition of the appropriate alcohol (0.2 mmol) to a solution of either DIS (0.3 mmol) or TMSI (0.6 mmol) in $CDCl_3$ (0.5 mL) at room temperature. Reaction progress was followed by NMR. Relative rates were calculated from the time required to achieve 50% conversion. The rate of isopropyl alcohol iodination with TMSI is defined as unity (iodination of isopropyl alcohol under these conditions was completed within 30 h).

Since the reaction between hydridosilane and iodine may be visualized as a nucleophile–electrophile interaction, it is plausible that oxygen functions could increase the nucleophilicity of the silicon–hydrogen bond (Scheme I), promoting nucleophilic attack of hydride at the iodine molecule and stabilizing the resultant silicenium intermediate,[14] probably as a solvated ion pair that is subsequently trapped by an iodide ion.

Iodination of Alcohols. As DIS has never been used in organic synthesis, we investigated its properties as a reagent by carrying out a comparative study with HI and TMSI, the characteristics of the latter being well-known. Comparison with HI is particularly important for evaluating the net activity of the reagent, as solutions of iodosilanes are generally contaminated with traces of HI[8,15] arising from partial protonolysis. We started this investigation by examining the conversion of alcohols into their corresponding iodides (Table I). Although all reactions could be driven to completion, striking differences were noticed in the order of reactivity of the various substrates examined. Expectedly, substitution of the highly reactive varieties—tertiary and benzylic alcohols—proceeded very rapidly with all three reagents (entries 1 and 2). However, in contrast to the known orders of reactivity of TMSI and HI toward alcohols, i.e., methanol > primary > secondary, a strikingly different order was exhibited by DIS: secondary ≫ methanol > primary (entries 3–7).

These observations imply that in contrast to TMSI, which is a moderate Lewis acid and strong nucleophile, DIS is a much stronger acid and, perhaps weaker nucleophile. Thus, while the former appears to operate via an S_N2 pathway, the latter may promote dissociative mech-

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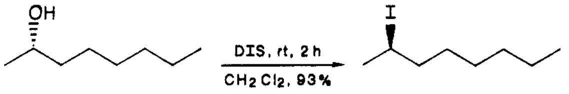
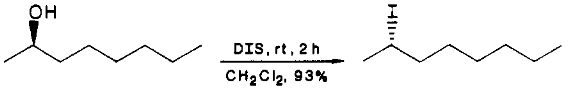
anisms of partial S_N1 nature.

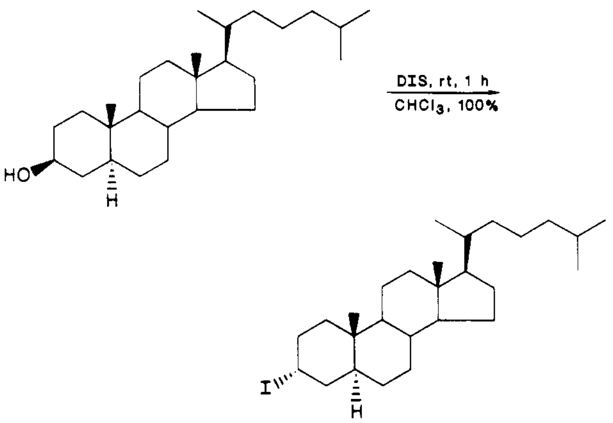
This tendency is reflected in the somewhat lower stereospecificity observed in substitution of (*R*)- and (*S*)-octan-2-ol with DIS in comparison with reactions with TMSI (eq 4 and 5). For example, reaction of (*S*)-(+)-octan-2-ol with TMSI produced (*R*)-(−)-2-iodooctane, having approximately 82% optical purity. The same reaction carried out with DIS yielded the same product but with optical purity close to 66%. Yet, conversion of 3β-cholestanol into 3α-iodocholestane with DIS proceeded with quantitative yield and absolute stereospecificity (eq 6). Remarkably, no epimerization of this product to the more stable β-iodocholestane[16,27] was observed under the reaction conditions used.



(4)



(5)



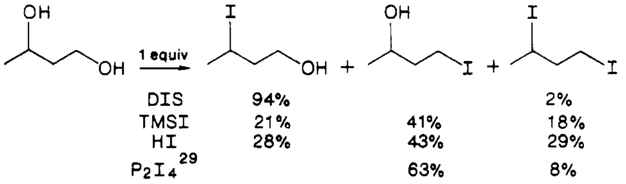
(6)

The remarkable difference in reactivities of two closely related reagents provides new opportunities in synthesis. For example, the higher reactivity of DIS toward secondary alcohols in comparison with primary alcohols (greater than 2 orders of magnitude) allows essentially quantitative differentiation between the two alcohols when present in the same molecule. Thus, treatment of 1,3-dihydroxybutane with excess DIS for 1 h at room temperature selectively iodinated the secondary position, affording pure 3-iodobutan-1-ol (eq 7). When alternative reagents were used for this transformation, such as TMSI, HI, or P_2I_4, mixtures of the starting diol, diiodobutane, and the two iodo alcohols were formed, with the primary iodide dominating.

Table II. Relative Rates of Ether Cleavage with TMSI, HI, and DIS[a]

entry	reagent	cleavage rates *i*-Pr_2O	 *n*-Bu_2O	 anisole[b]
1	TMSI	1	1.4	2
2	TMSI + C_6H_{10}	0.75	0.6	0.9
3	TMSI + *i*-Pr_2NH	0.65	0.56	0.7
4	TMSI + I_2	27.4	11.8	0.5
5	TMSI + *i*-Pr_2NH + I_2	15	6.9	0.6
6	HI	3.2[c]	3[d]	0.6
7	DIS	82	1.8	0.08
8	DIS + C_6H_{10}	33	1.5	0.05
9	DIS + *i*-Pr_2NH	1.5	0.45	<0.01
10	DIS + I_2	270	15.5	3.7
11	DIS + *i*-Pr_2NH + I_2	67.5	2.3	0.2

[a] Detailed procedures are given in the Experimental Section. Relative rates were calculated from the time required to achieve 50% conversion of 1 mol of substrate into 2 mol of iodoalkane. The rate of cleavage of diisopropyl ether with TMSI is defined as unity (iodination of isopropyl alcohol under these conditions was completed within 90 h). [b] The only products obtained from cleavage of anisole were phenol and methyl iodide. Accordingly, relative rates of this reaction refer to 50% conversion of anisole to these products. [c] The first step of the reaction, i.e., formation of 1 mol of iodoalkane and 1 mol of alcohol, proceeded with a relative rate of 56. [d] The first step of the reaction proceeded with a relative rate of 30.



(7)

Cleavage of Ethers. Generally, solutions of iodosilanes are contaminated with traces of HI,[8,15] which arise either from partial protonolysis or from decomposition caused by minor impurities. Solutions of HI in organic solvents cleave ethers quite effectively[17] and may even work faster than TMSI.[18] Therefore, in order to study the net effect of the iodosilanes, we scavenged HI from the reaction mixture by addition of either an olefin or an amine. Although either of these reagents is useful, they do have limits. Olefins do not remove HI efficiently enough when the latter is formed rapidly. Amines are much more effective scavengers, but they interact directly with the iodosilane reagent,[19] reducing its Lewis acidity. In agreement with previous reports on TMSI,[1,9] we found that addition of excess iodine to the mixture regenerates the original reactivity of the silane without interfering with the ability of the amine to remove HI.

The properties of DIS with respect to cleavage of three representative ethers were checked in comparison with TMSI and HI (Table II), and their general orders of reactivity were found to parallel the above-described observations with alcohols, namely, selective cleavage of methyl ethers with TMSI and lower reactivity toward secondary alkyl ethers. The opposite selectivity was exhibited by DIS. Primary dialkyl ethers, such a di-*n*-butyl ether, are more sluggishly cleaved by both reagents, and the reaction is even slower with aryl methyl ethers, such as anisole. Interestingly, the properties of HI in these

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(20) Monoiodosilanes, such as $PhSiH_2I$, SiH_3I, and $C_{18}H_{37}SiH_2I$, exhibit reactivity patterns similar to those of TMSI. Diiodosilanes, including $PhSiHI_2$ and $C_{18}H_{37}SiHI_2$, show reactivity that is reminiscent of our observations with DIS. For example, they convert diisopropyl ether into 2 mol of 2-iodopropane almost as efficiently as DIS. Conversely, tetraiodosilane reacted very sluggishly with alcohols and ethers in comparison with both mono- and diiodosilanes: D. Perez, unpublished results in these laboratories.

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Table III. Cleavage of Ethers (ROR′) with DIS[a]

	substrate		product, %				
entry	R	R′	ROH	RI	R′OH	R′I	time, h
1	benzyl	benzyl	0	100	0	100	<0.03[b]
2	*t*-Bu	Me	0	100	90	10	<0.03[b]
3	*t*-Bu	Me	0	100	0	100	2[b]
4	THF	THF	0	100	100	0	<0.03
5	THF	THF	0	100	0	100	18
6	*i*-Pr	*i*-Pr	0	100	0	100	5[b]
7	*s*-Bu	Me	0	100	0	100	2, 3.5[c]
8	*i*-Pr	Me	0	100	0	100	4, 3.5[c]
9	*i*-Pr	*n*-Bu	0	100	0	100	3
10	*i*-Pr	*n*-Bu	5	95	87	13	5[c]
11	*n*-Bu	Me	60	40	0	100	2.5
12	*n*-Bu	Me	100	0	0	100	2[c]
13	*n*-Bu	Me	60	40	0	100	46[c]
14	*n*-Bu	Me	0	100	0	100	25
15	Et	Et	0	100	0	100	60, 30[c]
16	*n*-Bu	*n*-Bu	0	100	0	100	100, 50[c]
17	*n*-Hex	*n*-Hex	0	100	0	100	70
18	β-naphthyl	Me	100	0	0	100	190
19	Ph	Me	10	0	10	0	91
20	Ph	Et	0	0	0	0	90

[a] Detailed procedures are given in the Experimental Section. Yields were determined by GC with internal standards. [b] Identical results were obtained when the reaction was carried out in the presence of cyclohexene. [c] Time of reaction carried out in the presence of cyclohexene.

reactions fall between those of TMSI and DIS.

As reactivity of TMSI is reduced in the presence of HI scavengers and because HI is more reactive than TMSI toward aliphatic ethers (entry 6), we suspected that cleavage of ethers (in particular, of the first C–O bond) might actually be carried out by the HI. This was found to be the case with cleavage of methyl ethers. For example, employing the conditions described in Table II, we selectively cleaved methyl isopropyl ether to methyl iodide and isopropyl alcohol within 1.5 h. However, with HI instead of TMSI, we obtained the same mixture in less than 45 min. Moreover, using TMSI along with cyclohexene resulted in a sluggish (19 h), nonselective cleavage, affording methyl iodide and a 1:1 mixture of isopropyl alcohol and isopropyl iodide.

The results given in Table II indicate that DIS is more reactive than HI, particularly with secondary alkyl ethers. The presence of HI in the reaction mixture, therfore, does not significantly interfere with the reaction of DIS. These findings are confirmed by the data in Table III, indicating similar rates of ether cleavage by DIS in reactions carried out both with and without cyclohexene.

Iodination of ethers is a two-step process. The first involves cleavage of one of the C–O bonds to give iodoalkane and the silylated alcohol. The latter may react further to give a second molecule of iodoalkane. In certain cases, particularly when the two alkyl groups are significantly different from one another, it is possible to quench the reaction after the first step (vide supra). For example, *tert*-butyl methyl ether may be selectively cleaved to *tert*-butyl iodide and either methanol or methyl iodide, depending on reaction time (Table III, entries 2 and 3). Similarly, the cleavage of isopropyl butyl ether could be stopped at the first step under appropriate conditions (entries 9 and 10), and THF was selectively cleaved to either 4-iodobutan-1-ol or 1,4-diiodobutane (entries 4 and 5).

Similar to our observations with alcohols, tertiary and benzylic ethers are highly reactive toward both DIS and TMSI (entries 1–3). Yet, because DIS may facilitate S_N1-type mechanisms, it would be expected that these substrates will react faster with DIS than with TMSI. Indeed, at 0 °C dibenzyl ether was quantitatively converted into benzyl iodide in less than 5 min, while no reaction was observed with TMSI under identical conditions. Similarly, methyl *tert*-butyl ether is cleaved by DIS at −78 °C into *tert*-butyl iodide and silylated methanol in less than 30 min, whereas no reaction took place with TMSI. THF, however, is cleaved to 4-iodobutan-1-ol equally well by both reagents at 0 °C, with the reaction going to completion within 5 min.

Conclusion

In this paper we have presented the first application of DIS in organic synthesis. The reagent exhibits properties and reactivities that are complementary to those of iodotrimethylsilane.[20] Synthesis of DIS is easily and rapidly carried out via the reaction of phenylsilane with iodine. With regard to large-scale synthesis of DIS, it may be less expensively prepared from metallic silicon, HI, and H_2. In addition to the use of DIS in cleavage and deoxygenation of alcohols and ethers presented here, we are currently investigating its reactivity with respect to other functional groups.

Experimental Section

Infrared spectra were measured on the neat compounds with an FT infrared Nicolet MX-1 spectrometer. ^{1}H NMR spectra were measured in deuteriochloroform on a Varian FT-80A or Bruker WH-270 NMR spectrometer. GC–MS analyses were carried out on a Finnigan 4500 spectrometer. Thin-layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck, Kieselgel 60, F-254, Art. 5549). Column chromatography separations were performed on silica gel (Merck, Kieselgel 60, 230–400 mesh, Art. 9385) under pressure of 0.4 atm (flash chromatography). GC analyses were performed on either a Varian 3300 or a Spectra Physics 7100 (FI detector) gas chromatograph equipped with a 0.125 in. × 4 ft column packed with 5% OV-101 on Chromosorb W. Preparative GC separations were carried out with a Varian Aerograph 90P (TC detector) equipped with either a $^1/_2$ in. × 20 ft column packed with 10% Carbowax 20M on Chromosorb W or a $^3/_8$ in. × 20 ft column packed with 10% SE-30 on Chromosorb W. Distillations were usually performed with a Buchi Kugelrohr apparatus, and the temperatures given are pot temperatures. Tetrahydrofuran, diglyme, benzene, and toluene were distilled over sodium benzophenone ketyl. Phenylsilane was prepared by reduction of trichlorophenylsilane with $LiAlH_4$ in dry ether.[21] Hexamethyldisilane was prepared according to a literature procedure,[22] slightly modified, from trimethylchlorosilane, in a week-long reaction, with small pieces of lithium, activated at the beginning with a small amount of octylbromide. TMSI was prepared neat, according to the literature.[6b,23]

Substrates. All compounds, except *s*-BuOMe, *i*-PrOMe, *n*-BuOMe, and *i*-PrO-*n*-Bu, were purchased from Aldrich. The latter ethers were prepared by reaction of the appropriate sodium alkoxide with either methyl or butyl iodide at room temperature. The mixture was washed with water, dried over $MgSO_4$, and distilled (twice) over sodium metal. Products were found to be pure by GC, NMR, and boiling points.

The Catalytic Effect of Ethyl Acetate in Iodination of Silanes. A. $PhSiH_3 + I_2 \rightarrow PhSiH_2I + HI$. Phenylsilane (0.1 mmol) and iodine (0.08 mmol) were dissolved in 0.5 mL of $CDCl_3$ in an NMR tube at 20 °C, and the reaction was monitored by ^1H NMR. Very slow conversion of $PhSiH_3$ (4.20 ppm) into $PhSiH_2I$ (4.60 ppm)[24] was observed. After 12 h, 0.4 mmol of the latter was formed, accompanied by 0.5 mmol of SiH_3I (3.44 ppm).[25]

An experiment similar to that described above was carried out with the exception that ethyl acetate (0.02 mmol) was added to the mixture. Within 6 min the red iodine color disappeared, and most of the phenylsilane was converted into $PhSiH_2I$ and SiH_3I in a 5:1 ratio, respectively.

B. $PhSiH_3 + HI \rightarrow SiH_3I + PhH$. Phenylsilane (0.1 mmol) was dissolved in $CDCl_3$ in an NMR tube at 20 °C. A solution of HI was added (0.25 mmol), and the reaction was followed by NMR. Conversion of phenylsilane into SiH_3I proceeded cleanly with 50% reaction within 0.5 h and 100% in 4 h.

The same reaction was repeated with 0.02 mmol of ethyl acetate, leading to the almost identical results (50% conversion in 26 min and 100% in 3.9 h).

C. $PhSiH_2I + HI \rightarrow DIS + PhH$. Phenyliodosilane (0.1 mmol) was dissolved in $CDCl_3$ in an NMR tube at 20 °C. ($PhSiH_2I$ was prepared by mixing $PhSiH_3$ (0.4 mmol) with iodine (0.2 mmol) and 0.0015 mL of ether for 5 min and subsequently removing all volatile components under reduced pressure.) A solution of HI was added (0.25 mmol), and the reaction was followed by NMR. Formation of SiH_2I_2 (DIS) proceeded very slowly (15% conversion within 24 h).

The same reaction was repeated with 0.02 mmol of ethyl acetate, leading to identical results.

D. $SiH_3I + I_2 \rightarrow DIS + HI$. Iodosilane (0.1 mmol) and iodine (0.08 mmol) were dissolved in $CDCl_3$ (0.5 mL) in an NMR tube at 20 °C, and the reaction was monitored by ^1H NMR. Slow conversion to DIS (15% in 17 h) was observed. When the same reaction was carried out in the presence of ethyl acetate (0.02 mmol), the reaction rate was significantly enhanced (50% conversion in 2 h).

Preparation of DIS. A. Iodine (1.05 g, 4.13 mmol) was placed in a dry flask equipped with a stirring bar, under argon, and cooled to −78 °C. Phenylsilane (0.5 mL, 4.02 mmol) was added, and the mixture was allowed to freeze. Ethyl acetate (0.01 mL) was then added, the dry ice bath was replaced by an ice–salt bath (−20 °C), and the solution was vigorously stirred. After 10 min at −20 °C, the mixture was slowly warmed to room temperature and stirred at that temperature for 3–5 h until the red color of iodine disappeared (indicating complete conversion). Most of the volatile side products (benzene and traces of HI, SiH_3I, and EtI) were removed under reduced pressure (20–30 mm) at room temperature, resulting in diiodosilane (DIS) in the form of a clear, colorless oil (85% yield). This crude reagent is satisfactorily pure and may be used directly for all of the reactions described in this paper. The actual concentration of DIS in solution was determined by ^1H NMR (from the singlet at 4.02 ppm).

B. In order to obtain further purified DIS, the above-described procedure was repeated on a larger scale using a 50-mL flask and 4 mL of phenylsilane. The crude product was transferred to a 10-mL flask and subjected to fractional distillation under atmospheric pressure. The fraction collected at 148–155 °C (4.8 g, 65%) contained essentially pure DIS.

C. Small amounts of DIS of slightly lower quality, which is still acceptable for most purposes, may be quickly prepared in the following way: Finely powdered iodine (0.1–0.2 g) is placed in a 2–4-mL vial under argon, and then, without cooling, phenylsilane (1 equiv) containing 5 mol % ethyl acetate is added to the vigorously stirred iodine. The exothermic reaction is generally completed in less than 20 s. After volatile side products are removed under reduced pressure (30 mm), a reagent is obtained (70% yield), which is contaminated with approximately 10% of $PhSiH_2I$. Yet, the lower reactivity of the latter, compared with that of DIS, makes it a tolerable contaminant.

General Procedure for Cleavage of Alcohols and Ethers with DIS. DIS (0.3 mmol) was dissolved in $CDCl_3$ (0.5 mL) under argon in an NMR tube. The appropriate substrate (0.25 mmol) was added and mixed well with the solution in the closed tube. The tube was kept at room temperature, and reaction progress was followed by NMR. Upon completion, the solution was treated with saturated aqueous $NaHCO_3$ (0.1 mL), and the organic layer was analyzed by NMR and/or GC (with internal standard) or GC–MS.

General Procedure for Ether Cleavage with TMSI. The same procedure as the one described above was carried out except that TMSI (0.6 mmol) was used instead of DIS.

General Procedure for Ether Cleavage with HI. An experiment similar to that described above was carried out except that a solution of HI (0.8 mmol) in $CDCl_3$ (0.8 mL) was employed instead of DIS.

General Procedure for Reactions in the Presence of Various Additives. Experiments similar to the above described were carried out employing either DIS or TMSI. However, one or more of the following additives was introduced prior to addition of substrate: cyclohexene (0.15 mmol), diisopropylamine (0.15 mmol), and iodine (0.12 mmol). Reactions in the presence of *i*-Pr_2NH were carried out in a larger volume of chloroform (1.25 mL).

Reaction of Butane-1,3-diol with DIS. Butane-1,3-diol (117 mg, 1.3 mmol) was added to a stirred solution of DIS (2.6 mmol) in chloroform (3 mL) under argon, and the solution was stirred at room temperature for 75 min. An aqueous solution of K_2CO_3 (20%, 2 mL) was added, the mixture was stirred for 5 min, ether (15 mL) was added, the aqueous layer was extracted with additional ether (10 mL), and the combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure, affording essentially pure 3-iodobutan-1-ol (244 mg, 94%) contaminated with 1,3-diiodobutane (2%, by GC and NMR).

Reaction of 5α,3β-Cholestanol with DIS. 5α,3β-Cholestanol [Fluka, 190 mg, 0.49 mmol, $[\alpha]_D$ +24° (chloroform, *c* 1)] was added to a stirred solution of DIS (1.25 mmol) in chloroform (3 mL). The solution was stirred for 1 h and then quenched with 1 mL of aqueous K_2CO_3 (20%). The aqueous phase was separated and extracted with 2 × 1 mL of chloroform, the combined organic phases were filtered through a short (2-cm) silica gel column, and the solvent was removed under reduced pressure, affording 243 mg (100%) of 3α-iodocholestane. The product was found to be pure by GC and NMR [a one-proton signal at 4.96 ppm and no absorption at 4.16 ppm (lit.[26] 3α-iodocholestane 4.94 ppm, 3β-iodocholestane 4.16 ppm)]; $[\alpha]_D$ +30.5° (chloroform, *c* 3.1) [lit.[27] +32.3° (chloroform)].

An α-configuration for this product was further supported by converting it to the more stable β-isomer under equilibration conditions.[16,27]. α-Iodocholestane (15 mg) and NaI (20 mg) were mixed with 2-pentanone, and the resultant mixture was heated in a sealed tube (90 °C) for 2 h. Solvent was removed under reduced pressure, and the solid residue was extracted with $CDCl_3$. NMR integration showed the presence of α-iodocholestane (4.94 ppm) and β-iodocholestane (4.16 ppm) in a 1:5 ratio, respectively.

Conversion of (*R*)- and (*S*)-Octan-2-ol into 2-Iodooctane. A. With DIS. (*S*)-(+)-Octan-2-ol [183 mg, 1.41 mmol, Fluka; $[\alpha]_D$ +10.5° (EtOH, *c* 1.31)], was added to a stirred solution of DIS (2 mmol) in CH_2Cl_2 (3 mL) at 17 °C, progress of the reaction being monitored by GC. Upon completion (12 h), the reaction mixture was quenched with 2 mL of aqueous K_2CO_3 (20%) and worked up as described in previous experiments. The crude product was purified by filtration through a short (5-cm) silica gel column using CH_2Cl_2, affording (*R*)-(−)-2-iodooctane (314 mg, 93%), pure by GC and NMR; $[\alpha]_D$ −40.02° (ethanol, *c* 1.56). This figure corresponds to approximately 66% optical purity on the basis of earlier data;[28] $[\alpha]_D$ −60.2° (neat).

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A similar experiment was carried out with (*R*)-(–)-octan-2-ol [182 mg, 1.40 mmol, Fluka; $[\alpha]_D$ –10.9° (EtOH, *c* 1.10)] and a solution of DIS (2 mmol) in CH_2Cl_2 (3 mL). This reaction was completed within 2 h at 27 °C, affording, after the usual workup, (*S*)-(+)-2-iodooctane (315 mg, 93%), $[\alpha]_D$ +34.0° (ethanol, *c* 1.52) (approximately 57% optical purity).

The above experiment with (*R*)-(–)-octan-2-ol and DIS was repeated as described (2 h at 27 °C). After completion, the reaction mixture was stirred at 17 °C for 3 days. The usual workup afforded (*S*)-(+)-2-iodooctane (315 mg, 93%), $[\alpha]_D$ +30.8° (ethanol, *c* 1.98) (approximately 51% optical purity).

B. With TMSI. A similar experiment was carried out with (*S*)-(+)-octan-2-ol (182 mg, 1.40 mmol) with TMSI (4 mmol) instead of DIS. The reaction was completed within 3 days at 17 °C, affording (*R*)-(–)-2-iodooctane (283 mg, 85%),[28b] $[\alpha]_D$ –49.4° (ethanol, *c* 1.44) (approximately 82% optical purity).

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Registry No. $PhSiH_3$, 694-53-1; $PhSiH_2I$, 18139-86-1; SiH_3I, 13598-42-0; SiH_2I_2, 13760-02-6; *t*-BuOH, 75-65-0; $PhCH_2OH$, 100-51-6; EtOH, 64-17-5; *sec*-BuOH, 78-92-2; *i*-PrOH, 67-63-0; $PhCH_2OCH_2Ph$, 103-50-4; *t*-BuOMe, 1634-04-4; $(i\text{-Pr})_2O$, 108-20-3; *sec*-BuOMe, 6795-87-5; *i*-PrOMe, 598-53-8; *i*-PrOBu-*n*, 1860-27-1; *n*-BuOMe, 628-28-4; $(Et)_2O$, 60-29-7; $(n\text{-Bu})_2O$, 142-96-1; $(n\text{-Hex})_2O$, 112-58-3; PhOMe, 100-66-3; PhOEt, 103-73-1; $PhCH_2I$, 620-05-3; *t*-BuI, 558-17-8; MeOH, 67-56-1; MeI, 74-88-4; $I(CH_2)_4OH$, 3210-08-0; $I(CH_2)_4I$, 628-21-7; *i*-PrI, 75-30-9; *sec*-BuI, 513-48-4; *n*-BuI, 542-69-8; *n*-BuOH, 71-36-3; EtI, 75-03-6; *n*-HexI, 638-45-9; β-naphthylOMe, 93-04-9; ethyl acetate, 141-78-6; butane-1,3-diol, 107-88-0; 3-iodobutan-1-ol, 6089-13-0; 5α,3β-cholestanol, 80-97-7; 3α-iodocholestane, 29108-97-2; 3β-iodocholestane, 82863-87-4; (*R*)-octan-2-ol, 5978-70-1; (*S*)-octan-2-ol, 6169-06-8; (*R*)-2-iodooctane, 29117-48-4; (*S*)-2-iodooctane, 1809-04-7; β-naphthyl alcohol, 135-19-3; phenol, 108-95-2; TMSI, 16029-98-4; THF, 109-99-9.

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Oxidation of Vicinal Diols to α-Dicarbonyl Compounds by Trifluoroacetic Anhydride "Activated" Dimethyl Sulfoxide

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Trifluoroacetic anhydride "activated" dimethyl sulfoxide is an effective oxidant for the conversion of vicinal diols into the corresponding α-dicarbonyl compounds or products derived therefrom. Unlike the Swern oxidant, the title reagent system gives good yields of products derived from halogenated substrates. The method has permitted syntheses of previously inaccessible compounds including tropolones, a σ-homo-*o*-benzoquinone, and a "hyperreactive" α-keto aldehyde.

In connection with the development of a new route to tropolones, we observed[2] that the trifluoroacetic anhydride (TFAA)/dimethyl sulfoxide/triethylamine (Et_3N) reagent system[3] efficiently (≥73% yield) converts various 7-halobicyclo[4.1.0]heptane-2,3- and -3,4-diols into the corresponding α-diketones. In contrast, the use[2] of other oxidizing agents, many of which have been previously employed for converting vicinal diols into α-hydroxy ketones[4,5] or α-diketones,[6–9] led to decomposition of the bicyclic diols [with $(Ph_3P)_3RuCl_2$, benzalacetone, tetrahydrofuran (THF), 195 °C, 10 h[8]], low yields (≤25%) of the desired products (oxalyl chloride, dimethyl sulfoxide, Et_3N[9]), or no reaction (*N*-chlorosuccinimide, dimethyl sulfide, Et_3N;[4] acetic anhydride, dimethyl sulfoxide;[6] pyridine, SO_3, dimethyl sulfoxide;[5,7] dicyclohexylcarbodiimide, dimethyl sulfoxide, H^+[10]).[11] Other workers have noted[13,16] the inability of the last group of reagents to oxidize certain vicinal diols. In view of these results, and because no systematic assessment has been made of the ability of the TFAA "activated" dimethyl sulfoxide oxidant[17] to effect the synthetically valuable vicinal diol to α-dicarbonyl conversion,[18] a more extensive investigation of this reagent

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