

## Silicon hydrides in organic synthesis

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**Abstract** - In the past few years we have developed an array of composite reducing systems based on combinations of tin or silicon hydrides with various transition-metal homogeneous catalysts such as palladium(0), ruthenium(II) and molybdenum(0) complexes. These represent a useful family of reducing media that effect highly selective reductions of various organic functional groups, such as allylic heterosubstituents,  $\alpha,\beta$ -unsaturated carbonyl compounds and  $\alpha$ -halo ketones.

More recently, we have discovered that diiodosilane (DIS), which has never been used previously in organic synthesis, transforms a broad variety of useful functional-groups under mild conditions. This new reagent was found to exhibit properties and reactivities that are, in some cases, either superior or complementary to those of the well-known iodotrimethylsilane. In addition to its ability to cleave ethers, alcohols, ketals, acetals,  $\alpha$ -haloketones, etc., this new reagent may also serve as a unique reducing agent. As a multipurpose reagent, DIS allows sequential cleavage, reduction and iodination of oxygen functionalities, all of which are carried out by a single reagent.

### COMPOSITE REDUCING SYSTEMS

Despite the bewildering variety of reducing agents available for synthetic tasks, new, and selectivity-enhanced reductants are still being sought. Most popular of selective reducing agents are the various metal hydrides, mainly those of boron and aluminum, an abundance of which have been developed over the past four decades. However, the hydridic nature of most of these group-13 and other metal hydrides can limit their usefulness when high chemoselectivity is required.

Several years ago, we initiated a research program aimed at designing a new family of reducing systems that selectively transfer a hydride ion to various electrophilic functional groups. We anticipated that one promising approach would utilize systems comprised of at least two components, i.e. a relatively inactive source of hydride entities and a transfer agent to deliver the hydride selectively from that donor to the target functionality.

Group-14 metal hydrides, especially those of silicon and tin, represent a satisfactory choice of nonreactive hydride donors, as in the absence of a catalyst they are, generally, poor reducing agents. Moreover, transition-metal complexes are attractive transfer agents because they readily insert into Si-H or Sn-H bonds and also bind specifically to various functional groups.

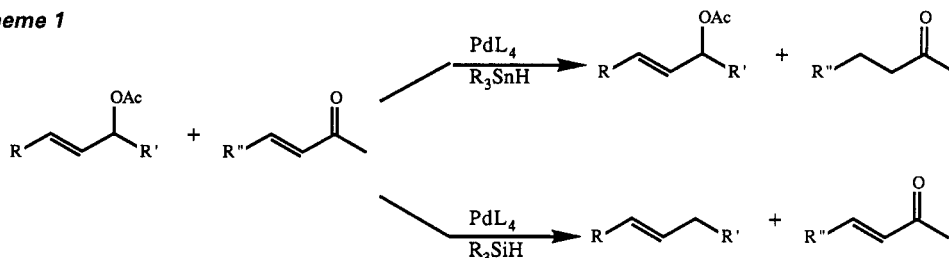
Such multiple-component reducing systems could offer high flexibility because they involve a large number of independent variables that can be tailored to various synthetic tasks, especially when compared to single-reagent metal-hydride reductions. Thus, by appropriate modification of the hydridosilane, judicious selection of a transition-metal transfer agent, and in some cases, use of a cocatalyst, opportunities arise for creating a wide variety of reducing systems that exhibit improved chemoselectivity, as well as regio- and stereocontrol.

A number of such systems were developed recently, particularly with respect to highly selective reduction of two important classes of functional groups: allylic heterosubstituents and Michael acceptors. The key details are summarized below.

**Allylic reductions.** In our initial studies we discovered that a combination of the nonnucleophilic hydride donor, tributyltin hydride, and a soluble palladium(0) catalyst produces a chemoselective reducing system that cleaves allylic heterosubstituents, even in the presence of aldehydes, benzylic acetate and benzylic chloride groups that are normally as reactive as the allylic function to standard hydride reducing agents.<sup>1</sup>

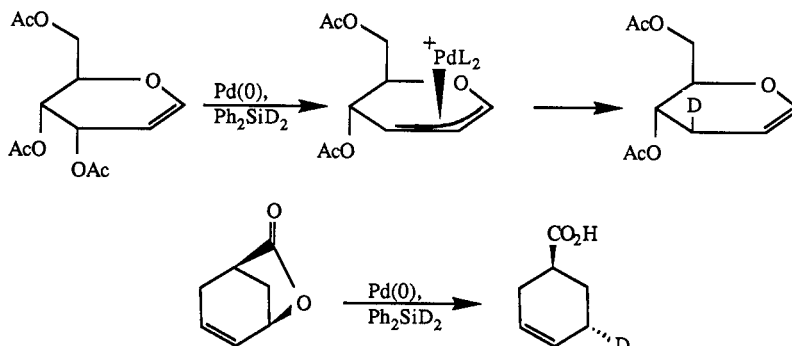
Later we found that silicon hydrides offer even greater selectivity in these reductions.<sup>2,3,4</sup> Their superiority was manifested by a) the enhanced stability of the palladium catalyst in the reaction solution and b) the absence of dienes side products, frequently formed via competing Pd-catalyzed elimination processes. Moreover, the difference in reactivities of tin and silicon hydrides could be exploited for functional-group differentiation. Tributyltin hydride, for example, was found to rapidly reduce  $\alpha,\beta$ -unsaturated ketones and aldehydes in the presence of Pd(0) catalyst (*vide infra*), while silicon hydrides were unable to do so. Thus, treatment of a mixture of an allylic acetate and an unsaturated ketone with tin hydride and Pd(0) catalyst resulted in complete conjugate reduction of the latter and an untouched allylic acetate (Scheme 1). In contrast, employment of silicon hydride provided complementary chemoselectivity: allylic reduction was completed before transformation of the Michael acceptor could be detected.

**Scheme 1**



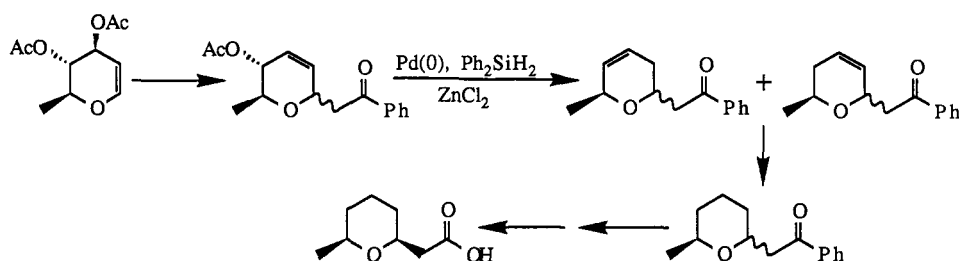
With both the tin and silicon hydride, allylic substitution occurred with absolute inversion of configuration at carbon (Scheme 2), implying that hydride is initially transferred to palladium and from there, via migratory insertion, to the allylic ligand.<sup>1,4</sup>

**Scheme 2**



A modified version of this method was applied in sugar chemistry,<sup>4</sup> and highly chemoselective reduction of allylic acetates of 1,2- and 2,3-unsaturated monosaccharides was achieved with a three-component reducing system comprised of diphenylsilane, a soluble palladium(0) catalyst and zinc chloride co-catalyst. The usefulness of the new chiral building blocks formed by this approach was demonstrated by the total synthesis of the civet constituent, (+)-(S,S)-(6-methyltetrahydropyran-2-yl)-acetic acid starting from di-O-acetylrahnal (Scheme 3).<sup>4</sup>

Scheme 3

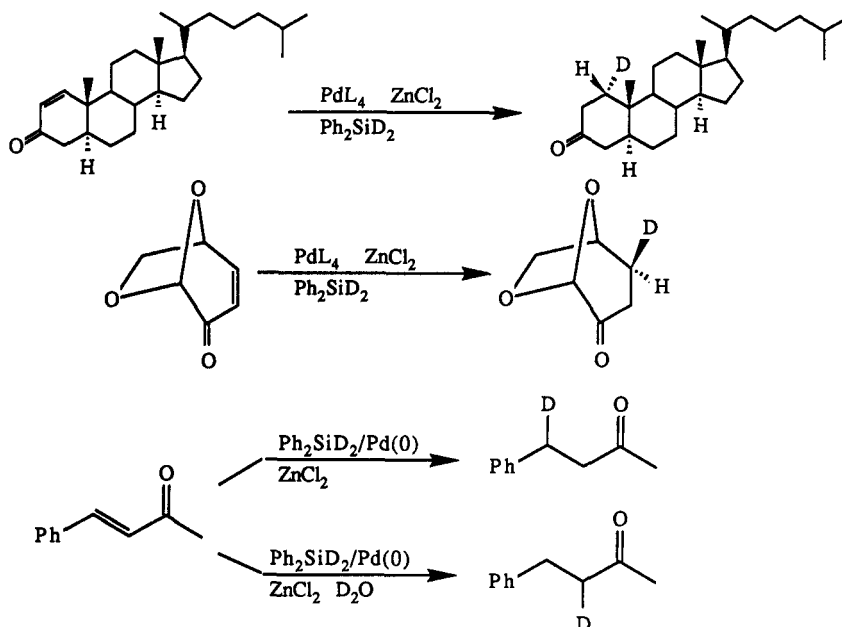


**Conjugate reduction of Michael acceptors.** The acceptor properties of  $\alpha,\beta$ -unsaturated carbonyl compounds make them excellent ligands for low-valent transition metals and, obviously, good substrates for selective reduction with group-14 hydrides. Indeed, we found that a combination of tributyltin hydride, Pd(0) catalyst and a weak acid such as ammonium chloride, forms an effective, yet very mild tool for conjugate reduction of unsaturated aldehydes and ketones,<sup>5</sup> exhibiting reaction rates that are generally higher than those of allylic reduction (Scheme 1). Additionally, conjugate reductions with this system occur with high regioselectivity, providing a useful approach for deuterium incorporation into either the  $\beta$ - or  $\alpha$ -position by using either tributyltin deuteride or D<sub>2</sub>O, respectively.

The useful flexibility of these multicomponent reducing systems is well illustrated by the silicon hydride/Pd(0) catalyst combination. As mentioned earlier, this mixture is essentially useless for reduction of electron-deficient olefins. Nevertheless, addition of catalytic amounts of zinc chloride fundamentally alters the chemistry of this system, creating a new three-component mixture that enables rapid conjugate reduction of  $\alpha,\beta$ -unsaturated ketones and aldehydes.<sup>6,7</sup> In fact, various soluble palladium complexes, regardless of the Pd oxidation state, were equally efficient catalysts, an obvious practical advantage of this method. The generality of this approach with respect to the range of substrates, its experimental simplicity, and the ease of application to large-scale work make it one of the best methods for conjugate reduction of unsaturated ketones and aldehydes.

The reaction was found to be both regio- and stereoselective. In all cases where diphenyldideuteriosilane was used to reduce unsaturated ketones, deuterium was stereoselectively introduced at the least-hindered face of the substrate and regioselectively at the  $\beta$ -position (Scheme 4). Conversely, when reductions were carried out in the presence of traces of D<sub>2</sub>O, deuterium incorporation occurred at the  $\alpha$ -position.<sup>7</sup>

Scheme 4



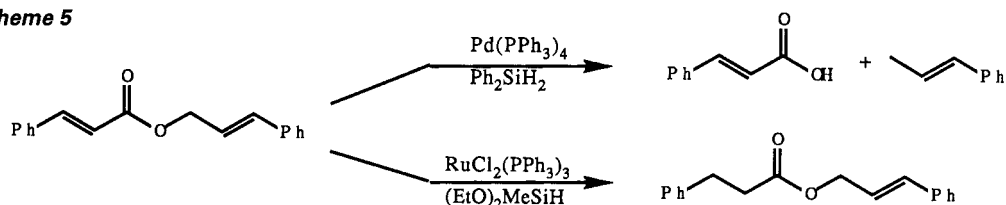
This method is highly selective for unsaturated ketones and aldehydes, because reduction of  $\alpha,\beta$ -unsaturated carboxylic acid derivatives, such as esters, amides and nitriles under these conditions was very sluggish. Thus, benzalacetone was selectively and cleanly reduced in the presence of methyl cinnamate, cinnamionitrile, or cinnamamide.

Based on deuterium incorporation experiments and  $^1\text{H}$  NMR studies, a multistep catalytic cycle was postulated<sup>7</sup> in which the first step is rapid, reversible coordination of the Pd(0)-phosphine complex to the electron-deficient olefin. Oxidative addition of silicon hydride to palladium in its olefin complex forms a hydrido-palladium olefin intermediate. Migratory insertion of hydride into the electrophilic  $\beta$ -carbon of the coordinated olefin produces an intermediate palladium enolate which, via reductive elimination of the silicon moiety and enolate ligand, completes the catalytic hydrosilation cycle and results in a silyl enol ether. The latter is prone to acid-catalyzed hydrolysis, yielding the saturated ketone.<sup>7</sup>

Switching from palladium to other transition metal catalysts enables new modes of selectivity. Combination of silicon hydrides with catalytic amounts of a ruthenium(II) complex in tetrahydrofuran, chloroform, or benzene afforded a new reducing system capable of efficient reduction of  $\alpha,\beta$ -unsaturated carboxylic acids, esters, amides, etc.<sup>8</sup> Addition of a weak proton source, such as a sterically hindered phenol, significantly increased reaction rates. The ruthenium mixture was found to exhibit the same regioselectivity observed with the systems described above.

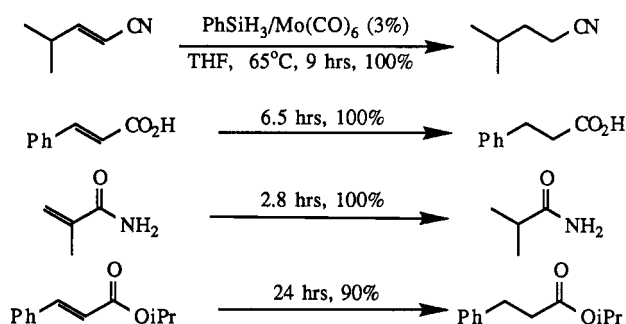
Interestingly, the order of functional group reactivity of this Ru/silane combination was found to differ greatly from that of the Pd/silane/ $\text{ZnCl}_2$  analogue. While the latter is very useful for allylic reductions and is essentially useless for unsaturated esters, the Ru-based system possesses the exact opposite reactivity. A convincing demonstration of this complementary chemoselectivity is given by the reduction of cinnamyl cinnamate (Scheme 5), a substrate containing both an allylic carboxylate and an  $\alpha,\beta$ -unsaturated ester.<sup>8</sup> Each of these can be selectively reduced by silicon hydride and the appropriate transition metal catalyst, Pd(0) in one case and Ru(II) in the other.

**Scheme 5**



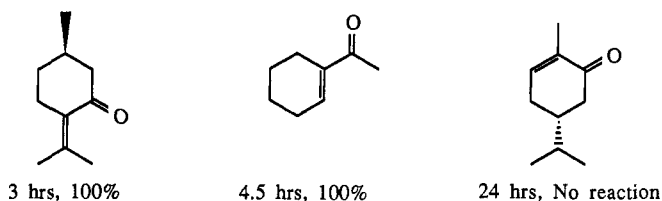
Early transition-metal complexes, including those of group-6, have been rarely used to catalyze hydrogen-transfer reactions and, in particular, little is known about hydrosilation with these catalysts. We found that under mild thermal conditions phenylsilane and catalytic amounts of  $\text{Mo}(\text{CO})_6$  engender a powerful reducing system suitable for conjugate reduction of  $\alpha,\beta$ -unsaturated ketones, carboxylic acids and esters, amides, etc.<sup>9</sup> The mixture is especially useful for conjugate reduction of unsaturated nitriles, usually difficult to reduce with other media (Scheme 6).

**Scheme 6**



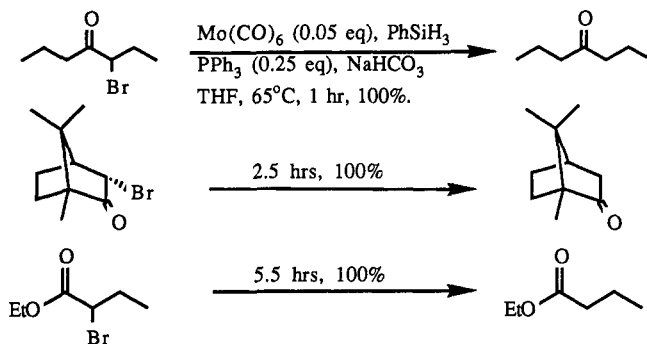
Although the reaction also takes place with mono- and dihydrosilanes, the general order of silane reactivity is:  $\text{PhSiH}_3 > \text{Ph}_2\text{SiH}_2 > \text{Me}(\text{EtO})_2\text{SiH} > \text{PMHS}, \text{PhMe}_2\text{SiH}, \text{Et}_3\text{SiH}$ . Of special interest are the relative rates of reduction of various cyclic enones, such as carvone, acetylcyclohexenone and pulegone (Scheme 7) by  $\text{PhSiH}_3/\text{Mo}(\text{CO})_6$ . While the enone system in carvone is frozen in its transoid form, in acetylcyclohexenone it is flexible and may adopt either transoid or cisoid conformation. Acetylcyclohexenone is completely reduced by this mixture, while essentially no reaction observed with carvone, demonstrating the clear preference for the cisoid form and indicating that the molybdenum atom interacts simultaneously with the olefinic bond and with the carbonyl of the enone system. Accordingly, pulegone, which is frozen in the cisoid form, is reduced much faster than the other two compounds. With  $\text{Pd}(0)$  catalyst, however, enones behave as monodentate ligands, and reductions of the above-mentioned substrates proceed at comparable rates.<sup>7</sup> These reactivity characteristics may be utilized for chemoselective differentiation between similar enones. Benzalacetone, for example, is quantitatively reduced to benzylacetone in the presence of carvone.<sup>9</sup>

Scheme 7



In addition, the  $\text{PhSiH}_3/\text{Mo}(\text{CO})_6$  system was found to be highly effective for reductive dehalogenation of  $\alpha$ -halo ketones and esters (Scheme 8). This method is even better than our palladium(0)/diphenylsilane system, producing higher yields and cleaner products.<sup>10</sup>

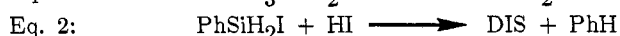
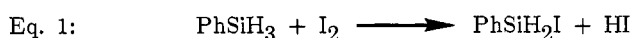
Scheme 8



### DIIDOSILANE (DIS)

Iodosilanes, particularly iodotrimethylsilane (TMSI) are useful synthetic reagents, offering a broad variety of useful functional-group transformations under mild conditions.<sup>11</sup> Their 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 the iodide ion. In our search for new modes of reactivity of yet unrecognized iodosilane reagents, we discovered that  $\text{SiH}_2\text{I}_2$  (DIS) is an extremely useful reagent, exhibiting properties and reactivities that are complementary to those of TMSI.<sup>12</sup>

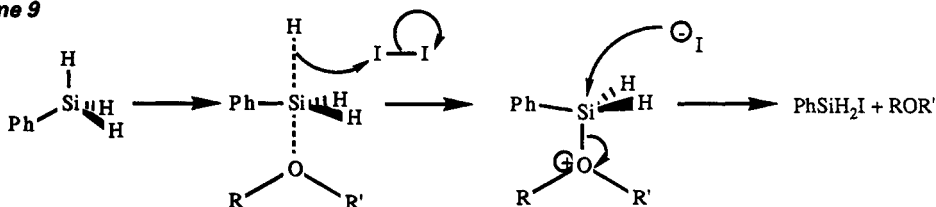
DIS is a colorless oil which boils at 150°C. It was first prepared almost 50 years ago by reaction of silane, HI and aluminum iodide.<sup>13</sup> However, apart from occasional studies on the properties of this rather exotic compound, it has never been used in organic chemistry. An improved synthesis of DIS by Fritz and Kummer in the early '60s<sup>14</sup> employs phenylsilane and iodine. Iodine reacts with phenylsilane to produce HI and phenyliodosilane, and the latter may undergo protonolysis by HI<sup>14b</sup> to produce DIS according to Equations 1 and 2. The compound may also be prepared by protonolysis of diphenylsilane with HI.<sup>14d</sup> Less expensive alternatives involve direct, inorganic syntheses of DIS from metallic silicon, HI and hydrogen, which are particularly attractive for industrial, large-scale production.



In our initial experiments we found, in agreement with earlier reports,<sup>14a,b</sup> that phenylsilane indeed reacts very sluggishly at room temperature with iodine in chloroform, in benzene or even neat. No significant enhancement of rate was observed either by heating the solution to 60-80°C or by irradiating it at 254 nm. 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 precautions must be taken when operating on large-scale. Thus, mixing iodine and phenylsilane in a 1:1 molar ratio in the presence of traces of ethyl acetate at -20°C produces one mol of DIS and one mol of benzene, a mixture which is sufficiently pure for most synthetic applications. DIS may be further purified by distillation and is stored for unlimited time under inert atmosphere.

In order to understand the catalytic role of oxygen functionalities in iodination of silanes, we reacted various silanes with I<sub>2</sub> and with HI in the presence and absence of catalytic quantities of ethyl acetate. While the reactions with HI were unaffected by presence of ethyl acetate, significant rate-enhancements (of over two orders of magnitude) were observed in the reactions involving iodine.<sup>12</sup> Since the reaction between hydrosilane 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 9), promoting nucleophilic attack of hydride at the iodine molecule and stabilizing the resultant silicenium intermediate, probably as a solvated ion-pair, that is subsequently trapped by an iodide ion.

**Scheme 9**













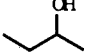



**Iodination of alcohols.** As DIS has never been used in organic synthesis, we investigated its properties as a reagent by carrying out a comparative study with HI and TMSI, the characteristics of the latter being well known. Comparison to HI is particularly important for evaluating the net activity of the reagent, as solutions of iodosilanes are generally contaminated with traces of HI 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. 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.

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<sub>N</sub>2 pathway, the latter may promote dissociative mechanisms of partial S<sub>N</sub>1 nature.

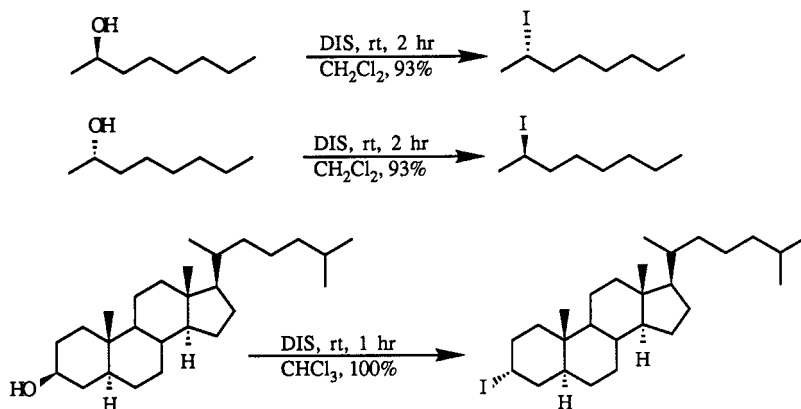
This tendency is reflected in the somewhat lower stereospecificity observed in substitution of (R)- and (S)-octan-2-ol with DIS in comparison to reactions with TMSI (Scheme 10). For example, reaction of S-(+)-octan-2-ol with TMSI produced R-(-)-2-iodooctane having approximately 82% optical purity. The same reaction carried out with DIS yielded the same product but with optical purity close to 66%. Yet, conversion of 3β-cholestanol into 3α-iodocholestanol with DIS proceeded with quantitative yield and absolute stereospecificity.

Remarkably, no epimerization of this product to the more stable  $\beta$ -iodocholestane was observed under the reaction conditions used.

Table I

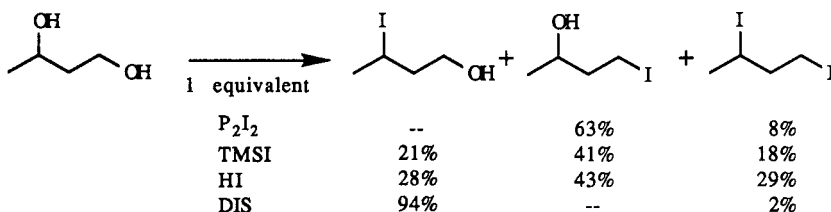
| Substrate   | Product   | Relative rates |      |      |
|---|---|----------------|------|------|
|   |   | HI             | TMSI | DIS  |
|  |  | >450           | >450 | >450 |
|  |  | >450           | >450 | >450 |
|  |  | 22.8           | 76   | 0.6  |
|  |  | 0.30           | 6.1  | 0.3  |
|  |  | 0.25           | 4.8  | 0.1  |
|  |  | 0.36           | 2.5  | 65   |
|  |  | 0.15           | 1.0  | 54   |

Scheme 10



The remarkable difference in reactivities of two closely related reagents provides new opportunities in synthesis. For example, the higher reactivity of DIS towards secondary alcohols in comparison with primary alcohols (greater than two 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 one hour at room temperature selectively iodinated the secondary position, affording pure 3-iodobutan-1-ol (Scheme 11). When using alternative reagents for this transformation, such as TMSI, HI or  $P_2I_4$ , mixtures of the starting diol, diiodobutane and the two iodoalcohols were formed, with the primary iodide dominating.



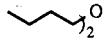
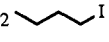
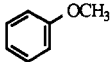
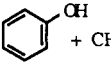
Scheme 11



**Cleavage of ethers.** Generally, solutions of iodosilanes are contaminated with traces of HI arising from partial protonolysis, which is known to cleave ethers quite effectively and may even work faster than TMSI. 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 amine.

The properties of DIS with respect to cleavage of three representative ethers were checked in comparison to 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 towards secondary alkyl ethers. The opposite selectivity was exhibited by DIS. Primary dialkyl ethers, such as di-*n*-butyl ether, are more sluggishly cleaved by both reagents, and the reaction is even slower with arylmethyl ethers, such as anisole. Interestingly, the properties of HI in these reactions fall between those of TMSI and DIS.

Table II

| Substrate   | Products  | Relative rates |  |                                       |
|---|---|----------------|--|---------------------------------------|
|   |   | HI             | TMSI (C <sub>6</sub> H <sub>10</sub> ) | DIS (C <sub>6</sub> H <sub>10</sub> ) |
|  |                      | 3.2            | 1.0 (0.75)                             | 82 (33)                               |
|  |                      | 3.0            | 1.4 (0.6)                              | 1.8 (1.5)                             |
|  |  + CH <sub>3</sub> I | 0.6            | 2.0 (0.9)                              | 0.08 (0.05)                           |

As DIS is more reactive than HI, particularly with secondary alkyl ethers, presence of HI in the reaction mixture should not significantly interfere with DIS reactivity. This assumption is confirmed by the similar rates of ether cleavage by DIS in reactions carried out both with and without cyclohexene (Table II). Reactivity of TMSI, however, is reduced in the presence of HI-scavengers. For example, methylisopropyl ether is selectively cleaved by HI to methyl iodide and isopropanol within 45 minutes. With TMSI the same product-mixture is obtained within 90 minutes. However, using TMSI along with cyclohexene results in a sluggish (19 hours), nonselective cleavage, affording methyl iodide and a 1:1 mixture of isopropanol and isopropyl iodide.

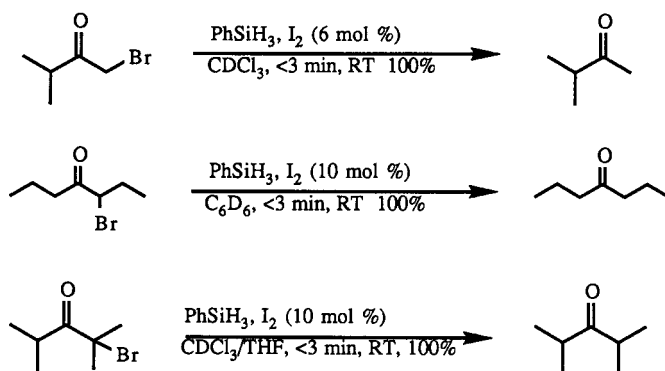
Iodination of ethers is a two-step process. The first involves cleavage of one of the C-O bonds to give iodoalkane and the silylated alcohol. The latter may react further to give a second molecule of iodoalkane. In certain cases, particularly when the two alkyl groups are significantly different from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

**Reductive dehalogenation of  $\alpha$ -halo ketones.** DIS exhibits somewhat higher reactivity than that displayed by TMSI with respect to reductive dehalogenation of  $\alpha$ -haloketones.<sup>15</sup> The same general order of substrate reactivity, primary > secondary > tertiary halides, is observed with both reagents. Most bromoketones are rapidly debrominated at room temperature, reactions being completed in less than three minutes. In some cases, particularly with primary bromides temperatures lower than 0°C are required in order to keep the reaction under control.

We found that the same transformation may be carried out with either stoichiometric quantities of DIS or with its precursor, phenylsilane, in the presence of catalytic amounts of iodine. In fact, this procedure, which can be carried out in variety of solvents, including ethers, is more convenient to perform and produces the dehalogenated carbonyl compound in higher yields (Scheme 12).

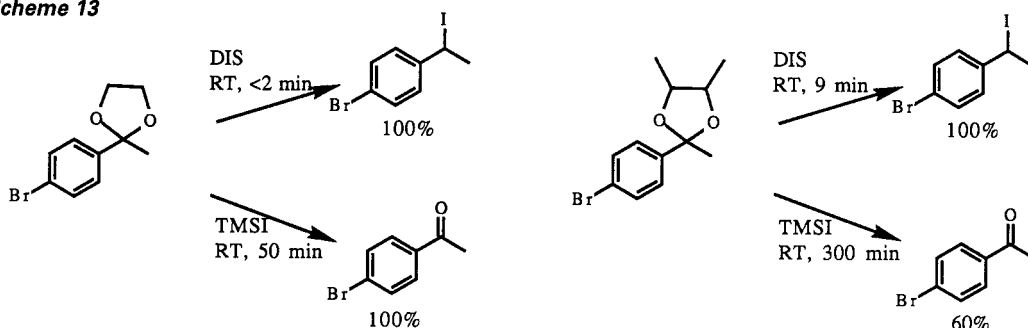


Scheme 12

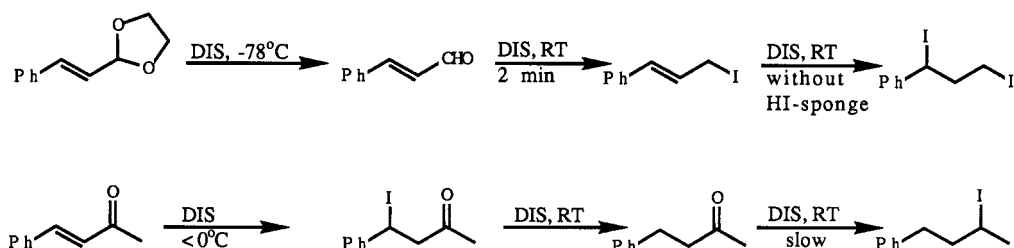


**Deketalization and reduction of carbonyl compounds.** At low temperatures, a broad variety of ketals and acetals are effectively cleaved by DIS to give the parent carbonyl compound. Again, DIS is more reactive in these reactions, particularly with sterically hindered substrates.<sup>16</sup> However, at temperatures above 0°C DIS begin to act as a reducing agent, producing the corresponding iodoalkanes (Scheme 13). Being a strong Lewis acid, a good nucleophile and, at the same time, an effective hydride donor, DIS may affect a sequence of transformations, as illustrated in the case of cinnamaldehyde and benzalacetone (Scheme 14).

Scheme 13



Scheme 14



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## REFERENCES

1. E. Keinan and N. Greenspoon, *Tetrahedron Lett.* 1982, **23**, 241.
2. E. Keinan and N. Greenspoon, *J. Org. Chem.* 1983, **48**, 3545.
3. E. Keinan and N. Greenspoon, *Israel J. Chem.* 1984, **24**, 82.
4. N. Greenspoon and E. Keinan, *J. Org. Chem.* 1988, **53**, 3723.
5. E. Keinan and P.A. Gleize, *Tetrahedron Lett.* 1982, **23**, 477.
6. E. Keinan and N. Greenspoon, *Tetrahedron Lett.* 1985, **26**, 1353.
7. E. Keinan and N. Greenspoon, *J. Am. Chem. Soc.* 1986, **108**, 7314.
8. E. Keinan N. Godinger and N. Greenspoon, unpublished results.
9. E. Keinan and D. Perez, *J. Org. Chem.* 1987, **52**, 2576.
10. D. Perez, N. Greenspoon and E. Keinan, *J. Org. Chem.* 1987, **52**, 5570.
11. a) Olah, G.A.; Narang, S.C. *Tetrahedron* 1982, **38**, 2225. b) Schmidt, A.H. *Aldrichemica Acta* 1981, **14**, 31.
12. E. Keinan and D. Perez, *J. Org. Chem.* 1978, **52**, 4846.
13. a) Maddock, A.G.; Reid, C.J.; Emeleus, H.J. *Nature* 1939, **144**, 328. b) Emeleus, H.J.; Maddock, A.G.; Reid, C. *J. Chem. Soc.* 1941, 353.
14. a) Fritz, G.; Kummer, D. *Z. Anorg. Allg. Chem.* 1960 **304**, 322. b) Fritz, G.; Kummer, D. *Z. Anorg. Allg. Chem.* 1960 **306**, 191. c) Fritz, G.; Kummer, D. *Chem. Ber.* 1961, **94**, 1143. d) Aylett, B.J.; Ellis, I.A. *J. Chem. Soc.* 1960, 3415.
15. E. Keinan and D. Perez, submitted for publication.
16. E. Keinan, D. Perez, M. Sahai and R. Shvili, submitted for publication.