Enabling Synthetic Organic Transformations
Organosilicon Based and Metal-Organic Synthetic Reagents

Offering Selective and Versatile Reagents for:

- Reductions
- Functional Group Protection
- Synthetic Organic Transformations
- Cross-Coupling C-C Bond Formation

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Organosilane Reducing Agents

Organosilane reductions are very commonplace in synthetic organic chemistry with the Si-H bond, being weakly polarized such that the hydrogen is hydridic in nature. Because the Si-H bond is only weakly hydridic, the silanes have the potential to be highly selective reducing agents, reducing a number of functionalities with excellent tolerance for other reducible functionalities. Organosilanes have further advantages in terms of low toxicity, ease of handling, and ease of final product purification. In addition, a number of enantioselective organosilane reductions have been reported. Ionic and organometallic-catalyzed organosilane reductions have been extensively reviewed. 1, 2

The extensive electronic and steric diversity of organosilanes offers a large range of selectivities in reactivity. For example, the homopolymeric methylhydrogensiloxane, HMS-992, and related homopolymers represent a high molecular weight silane reducing agent that can offer significant product isolation advantages. 3 Diphenylsilane, SID4559.0, has been shown to selectively reduce amides to aldehydes. 4 Triisopropylsilane, SIT8385.0, has been shown to offer a steric advantage leading to a higher degree of the β-aryl glucoside from the hemiketal precursor. 5

Tetramethyldisiloxane, TMDS, SIT7546.0, has recently been shown to be highly useful in the reduction of hemiketals to the corresponding ether. This has been applied to successful syntheses of the pharmaceutically important gliflozin family of diabetes 2 Specific Glucose Transport 2 (SGLT2) inhibitor drugs, such as canagliflozin, (Invokana) and dapagliflozin (Farxiga) among others. 6 TMDS has also been shown to very effectively reduce nitroaryls to anilines and is an improvement over triethyilsilane in the reduction of a ketone to a methylene in the production of a key intermediate in the preparation of ziprasidone. 8

References:
**Other Gelest Synthetic Reagents**

Gelest offers a number of other organosilane reagents that are of high use in the organic synthetic area. These include, among others, trimethyldichlorosilane, trimethylbromosilane, trimethylsilyl triflate, cyanotrimethylsilane, a number of silyl enol ethers and silyl ketene acetals, in addition to an extensive variety of organosilanes that are attached to inorganic surfaces for the purpose of final purification of desired products. Gelest also offers several non-silicon-based synthetic reagents that complement and, oftentimes, assist in the reactions of the silicon-based reagents. These include a number of Lewis acid catalysts such as tin tetrachloride, tetraisopropyltitanate, tris(pentafluorophenyl)boron, and a variety of metal diketonates. In addition Gelest offers several metal-organic reagents for various synthetic transformations.
Cross-coupling reactions are usually associated with the metals of boron (Suzuki-Miyaura), zinc (Negishi), tin (Stille), and copper (Sonogashira) along with magnesium (Kumada). As a viable alternative to these metals the Hiyama-Denmark cross-coupling reactions involve organosilicon reagents as the nucleophilic partner in C-C bond forming cross-coupling protocols. The organosilanes have several advantages, including being readily prepared by a variety of approaches, excellent storage stability, ease of removal or recycling of the organosilane by-products, good functional group tolerance, and low to non-toxicity profiles. The organosilane cross-coupling chemistry has been thoroughly reviewed. The use of sodium and potassium silanolates as the nucleophilic partner in the silicon-based cross-coupling transformations has been shown to be of practical utility.

![Organosilane Cross-Coupling Reagents](image)

References:
Organosilane Protecting Groups

It is very common that in a multi-step synthetic sequence the protection of one or more functional groups will be required. The most common groups that fall into this class are alcohols, amines, thiols, acids, and carboxyls, in particular ketones and aldehydes. For the protection of functional groups with active hydrogens, such as alcohols and amines, organosilanes have proven to be among the best and most favored alternatives.¹ The reasons for this are that the silyl groups can be both introduced and removed in high-yield, facile processes. In addition, the organosilanes have the ability to be modified both sterically and electronically, thus giving them excellent selectivity and versatility in their reactivity, stability, and ease of deprotection. Indeed, in many of the more complicated and lengthy synthetic sequences it is common to have a requirement to remove one organosilyl-protected group in the presence of other similar groups. A thorough presentation on the selective deprotection of one organosilyl-protected group in the present of another has been compiled.² Gelest offers an extensive range of organosilanes designed for the protection of various functional groups including alcohols, diols, amines, thiols, carboxylic acids and terminal alkynes. Of particular note is the use of the trimethylsilylenol ether of acetone, SII6264.0, for the protection of diols as their acetonides in a very fast and high-yield reaction.³ Gelest is proud to offer the E. J. Corey BIBS reagent for the protection of alcohols, amines, and carboxylic acids and the formation of highly stable enol silyl ethers.⁴

References:
Gelest, Inc.
The core manufacturing technology of Gelest is silanes, silicones and metal-organics with the capability to handle flammable, corrosive and air sensitive liquids, gases and solids. Headquartered in Morrisville, PA, Gelest is recognized worldwide as an innovator, manufacturer and supplier of commercial and research quantities serving advanced technology markets through a materials science driven approach. The company provides focused technical development and application support for: semiconductors, optical materials, pharmaceutical synthesis, diagnostics and separation science, and specialty polymeric materials.

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