Techniques for Silylation

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TECHNIQUES FOR SILYLATION

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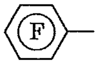
Silylation is the replacement of an active hydrogen of a protic material with a substituted silicon atom. There are two general categories of silylation. Well-defined molecular species can be modified with silyl groups for the purpose of producing blocked intermediates or producing volatile derivatives for analysis by gas chromatography. Macromolecular structures may be modified with functional silane groups to impart specific surface properties to the macromolecule, e.g. wettability, surface energy, partition parameters, orientation, covalent reactivity, and surface potential. The purpose of this presentation is to provide examples of silylation techniques.

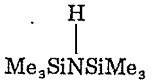
SILYLATION OF MOLECULAR SPECIES FOR DERIVATIZATION OR BLOCKED INTERMEDIATES

The most widely used silylation agents employ the trimethylsilyl group Me_3Si-. The hydrodimethylsilyl group Me_2HSi- may be used for increased volatility but is less stable and more susceptible to hydrolysis. Increased hydrolytic stability is available with bulkier silyl groups such as phenyldimethylsilyl,  Me_2Si-, t-butyldimethylsilyl, t-$BuMe_2Si$- and triisopropyl, iPr_3Si-groups. Sensitivity to electron capture techniques may be introduced with chlorodimethylsilyl $ClCH_2Me_2Si$- or pentafluorophenyldimethylsilyl  Me_2Si-groups. For industrial scale synthesis difunctional dimethylsilyl groups $Me_2Si<$ offer economic incentive in protecting two molecules simultaneously. Difunctional materials are also employed for silylation of vicinal hydroxyl groups.

Silylation reagents are selected by a number of factors: specificity, donor strength, byproducts, and cost. The most widely used are the trimethylsilyl reagents.

Me_3SiCl

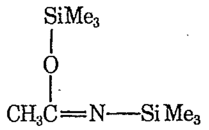
T2950 TRIMETHYLCHLOROSILANE, TMCS


$Me_3Si\overset{H}{N}SiMe_3$

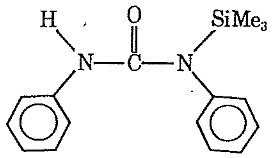
H7300 HEXAMETHYLDISILAZANE HMDS

Me_3SiNMe_2

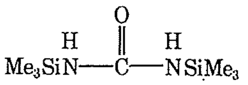
D5400 DIMETHYLAMINOTRIMETHYLSILANE TMSDMA



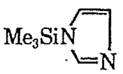
B2500 BIS(TRIMETHYLSILYL)ACETAMIDE BSA



T3500 TRIMETHYLSILYLDIPHENYLUREA TDPU


$Me_3Si\overset{H}{N}-\overset{O}{\overset{\|}{C}}-\overset{H}{N}SiMe_3$

B2595 BIS(TRIMETHYLSILYL)UREA BSU



T3600 TRIMETHYLSILYLIMIDAZOLE TMSI

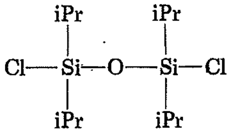
A number of other trimethylsilyl donor reagents are available, but their utility is not as generally recognized. The range of donor reagents for other silyl groups is generally more limited, but analogous to trimethylsilyl reagents.

Difunctional blocking agents include the following materials

Me_2SiCl_2
D5550

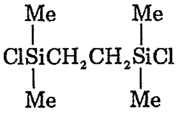
$Me_2Si(OMe)Cl$
D5635.5

$t\,Bu_2SiCl_2$
D4165



$$Cl-\underset{iPr}{\overset{iPr}{Si}}-O-\underset{iPr}{\overset{iPr}{Si}}-Cl$$

T4368



$$Cl\underset{Me}{\overset{Me}{Si}}CH_2CH_2\underset{Me}{\overset{Me}{Si}}Cl$$

T2015

With the exception of basic proton acceptors, solvents used for silylation reactions must be aprotic. If used in analysis or microchemical reactions they should be dried before use. In most cases allowing the solvent to stand over 3A molecular sieves is adequate. Typical solvents are dimethylformamide, hexane, acetonitrile, tetrahydrofuran, and toluene. When basic proton acceptor solvents are desired, pyridine and triethylamine are preferred.

CHLOROSILANES/BASE. Silylation of most protic compounds can be effected by dissolving the compound in an appropriate solvent with a 20% molar excess of base. Preferred bases are triethylamine, pyridine, and tributylamine. If the reaction is to be run with t-butyldimethylchlorosilane (B2790) instead of trimethylchlorosilane, imidazole is the preferred base. Trimethylchlorosilane is then added at a moderate rate, again in 20% molar excess. In most instances exotherm is minimal, but care should be taken with initial reactions to observe heating during addition. Most reactions are completed at room temperature, but a two hour reflux may be necessary. Amides and enol ethers may be silylated by this method, but the base is employed as the solvent in a minimum of 4–5 times mole ratio followed by a 6–8 hour reflux. While a good general technique, disadvantages of this method are the corrosive chlorosilane and filtration required, and possible difficulties in purification.

HEXAMETHYLDISILAZANE (HMDS) may be used directly with alcohols, phenols, amines and carboxylic acids. It is added to the compound to be derivatized as a 0.6 molar equivalent and utilized neat or with an appropriate solvent. The reaction proceeds at room temperature with most primary and secondary alcohols. Other compounds may require refluxing for up to 8 hours. Completion can be judged by halt of ammonia evolution. Silylation of less reactive groups may be facilitated by the addition of a few drops of H_2SO_4, 2–3% ammonium sulfate or better, 10% trimethylchlorosilane.

SILYLAMINES are used for silylation of alcohols, amines, amino acids, amides and ureas. Dimethylaminotrimethylsilane is particularly useful for aminoacid hydrochlorides, converting them directly to silylated amino acids with dimethylamine hydrochloride byproduct. Trimethylsilylimidazole is extremely active in silylation of carbohydrate hydroxyl groups. TMSI reactivity can be considered analogous to the amides. The general procedure for the silylamines is to react 0.1 M excess of the silylation reagent in a solvent at 60–70° for 15 minutes. While most of the silylamines yield volatile byproducts, imidazole is precipitated in TMSI reactions.

SILYLAMIDES are the most powerful silylation reagents employed in derivatization for analysis. They include BSA, BSU, and TDPU. BSA is an excellent solvent and may be used neat for many reactions. In general a slight molar excess of the silylamide is dissolved in 3–4 fold volume of solvent. Reactions are generally complete in 5 minutes at 65–70°. Most reactions will proceed in 20–30 mins at room temperature. Progress can usually be followed by dissolution of the material to be derivatized followed by precipitation of free amide. Potentiation of the silylamides with 10% trimethylchlorosilane results in systems strong enough to convert ketones to silyl ethers.

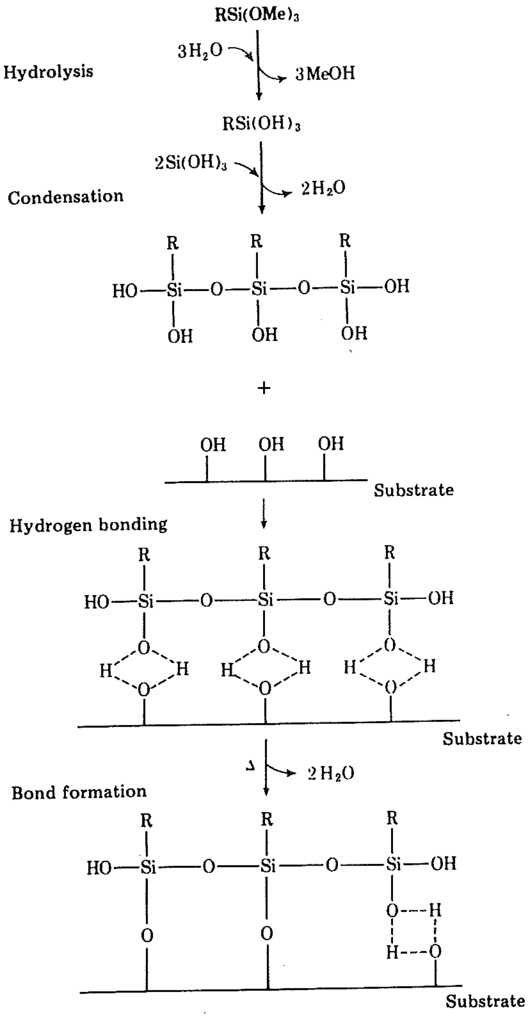
TRIMETHYLSILYLTRIFLUOROMETHYLSULFONATE (T3795) is the strongest silylation reagent available. Its primary use is for the formation of silyl enol ethers from ketones. Use in ordinary derivatization is limited due to side reactions such as ether and ester cleavage. Under ordinary conditions reactions are run neat at room temperature. Reaction time is 1–2 hours.

SILYLATION OF MACROMOLECULAR STRUCTURES FOR FUNCTIONAL MODIFICATION

The general formula of an organosilane shows the two classes of functionality one encounters.

$$R_nSiX_{(4-n)}$$

X is a hydrolyzable group typically halogen, alkoxy, acyloxy, or amine. While halo and amino silanes can react directly with substrates, in most cases the silane is subjected to hydrolysis.



Following hydrolysis, a reactive silanol group is formed, which can condense with other silanol groups, for example, those on the surface of siliceous fillers, to form siloxane linkages. Stable condensation products are also formed with other oxides such as those of aluminum, zirconium, tin, titanium, and nickel. Less stable bonds are formed with oxides of boron, iron, and carbon. Alkali metal oxides and carbonates do not form stable bonds with Si—O—.

The R group is a nonhydrolyzable organic radical that may posses a functionality that imparts desired characteristics.

Water for hydrolysis may come from several sources. It may be added, it may be present on the substrate surface, or it may come from the atmosphere. Water for hydrolysis may also be generated *in situ* by dissolving chlorosilanes in excess alcohol. Reaction with alcohol yields alkoxysilanes with HCl, which can react with additional alcohol to form alkylhalide and water.

Most of the widely used organosilanes have one organic substituent. Reaction of these silanes involves four steps. Initially, hydrolysis of the three labile groups occurs. Condensation to oligomers follows. The oligomers then hydrogen bond with OH groups of the substrate. Finally during drying or curing, a covalent linkage is formed with the substrate with concomitant loss of water. At the interface, there is usually only one bond from each silicon of the organosilane to the substrate surface. The two remaining silanol groups are present either in condensed or free form.

The number of reactive sites on a surface, the available surface area and the type of silane deposition sought, i.e. monolayer, multilayer or bulk are all factors which can be used in calculating the amount of silane necessary to silylate a surface. In order to provide monolayer coverage, the concentration of reactive sites (silanols) should be determined. Most siliceous substrates have 4–12 silanols per $m\mu^2$. Thus, one mole of evenly distributed silane should cover an average of $7500m^2$. The oligomerization of silanes with multiple hydrolyzable groups thwarts the capability of computing stoichiometries, but order of magnitude computations are successful. Silanes with one hydrolyzable group can be utilized to produce surfaces with monolayers of consistent stoichiometry. These materials are more expensive and produce surfaces with less hydrolytic stability. The number of silanols on a surface is varied by thermal history. In one example, a siliceous surface having 5.3 silanols per $m\mu^2$ had only 2.6 after exposure to 400°C and less than one after exposure to 850°C. Higher concentrations of silanol groups may be produced by treating materials with warm hydrochloric acid. Silanol anions may be produced by treating the surfaces with alkaline detergent or, more radically, by treatment with methanolic potassium hydroxide. Optimum deposition of silanes with more than one hydrolyzable group is often defined as the amount necessary to produce a surface of uniform energy. A value defined as the wetting surface (ws) describe the area in m^2 one gram of a silane deposited from solution will cover. In combination with data on the surface area of a siliceous substrate in m^2/g the amount of silane required for deposition may be calculated. Most composite, adhesive, and coating formulations do not follow any stoichiometry, but simply define optimal concentration by operational success. For most fillers a treatment level of 0.02–1.00% is used.

Deposition from aqueous alcohol solutions is the most facile method for preparing silylated surfaces. A 95% ethanol—5% water solution is adjusted to pH 4.5–5.5 with acetic acid. Silane is stirred to yield a 2% final concentration. Five minutes should be allowed for hydrolysis and silanol formation. Large objects, e.g. glass plates, are dipped into the solution, agitated gently, and removed after 1–2 minutes. They are rinsed free of excess materials by dipping briefly in ethanol. Particles, e.g. fillers and supports, are silylated by stirring them in solution for 2–3 minutes and then decanting the solution. The particles are usually rinsed twice briefly with ethanol. Cure of the silane layer is for 5–10 mins at 110°C or for 24 hours at room temperature (<60% relative humidity).

For aminosilanes this procedure is modified by omitting the addition of acetic acid. The procedure is not acceptable for chlorosilanes as bulk polymerization often occurs. Silane concentration of 2% is a starting point. It usually results in deposition of trialkoxysilanes is 3–8 molecular layers. Monoalkoxysilanes are always deposited in monolayers or incomplete monolayers. Caution must be exercised if oven curing. Exhausted, explosion-proof ovens should always be used.

Deposition from aqueous solution is employed for most commercial fiberglass systems. Alkoxysilane is dissolved at 0.5–2.0% concentration in water. For less soluble silanes, 0.1% of a non-ionic surfactant is added prior to the silane and an emulsion rather than a solution is prepared. If the silane does not contain an amine group the solution is adjusted to pH 5.5 with acetic acid. The solution is either sprayed onto the substrate or employed as a dip bath. Cure is at 110–120° for 20–30 minutes.

Stability of aqueous silane solutions varies from hours for the simple alkyl silanes to weeks for the aminosilanes. Poor solubility parameters limit the use of long chain alkyl and aromatic silanes by this method.

Bulk deposition onto powders, e.g. filler treatment, is usually accomplished by a spray-on method. It assumes that the total amount of silane necessary is known and that sufficient adsorbed moisture is present on the filler to cause hydrolysis of the silane. The silane is prepared as a 25% solution in alcohol. The powder is placed in a high intensity solid mixer, e.g. twin cone mixer with intensifier. The solution is pumped into the agitated powder as a fine spray. In general this operation is completed within 20 minutes. Dynamic drying methods are most effective. If the filler is dried in trays, care must be taken to avoid wicking or skinning of the top layer of treated material by adjusting heat and air flow.

Deposition as a primer is employed where a bulk phase is required as a transition between a substrate and a final coating. The silane is dissolved at 50% concentration in alcohol. One to three molar equivalents of water are added. The mixture is allowed to equilibrate for 15–20 mins and then diluted to 10% concentration with a higher boiling polar solvent. Materials to be coated with the primer are dipped or sprayed and then cured at 110–120° for 30–45 mirs.

Chlorosilanes may be deposited from alcohol solution. Anhydrous alcohols, particularly ethanol or isopropanol are preferred. The chlorosilane is added to the alcohol to yield a 2–5% solution. The chlorosilane reacts with the alcohol producing an alkoxysilane and HCl. Progress of the reaction is observed by halt of HCl evolution. Mild warming of the solution (30–40°) promotes completion of the reaction. Part of the HCl reacts with the alcohol to produce small quantities of alkyl halide and water. The water causes formation of silanols from alkoxy silanes. The silanols condense with those on the substrate. Treated substrates are cured for 5–10 mins at 110° or allowed to stand 24 hours at room temperature.

Chlorosilanes and Silylamines may also be employed to treat substrates under aprotic conditions. Toluene or THF solutions are prepared containing 5% silane. The mixture is refluxed for 24 hours with the substrate to be treated. It is rinsed briefly with toluene. No further cure is necessary. This reaction is a direct nucleophilic displacement by the surface silanol of the silane chlorine. If monolayer deposition is desired, substrates should be predried at 150° for 4 hours. Bulk deposition results if adsorbed water is present on the substrate. This method is cumbersome for large scale preparations and rigorous controls must be established to enable reproducible results. More reproducible results are obtained with monochlorosilanes.

COUPLING AGENTS FOR PLASTICS

Resin	Class	Product Code
THERMOSETS		
diallyl phthalate	amine	A0698 A0700 A0710
	styryl	S1588 S1580
epoxy	amine	A0700 A0750 T2910
	epoxy	G6720 B6250
	chloroalkyl	G3300 C3292
	mercapto	M8490 M8500
imide	chloromethylaromatic	T2902
	amine	A0698 A0700 A0725 A0750 T2910
melamine	amine	A0700 A0750 T2910
	epoxy	G6720 E6250
	alkanolamine	B2408
phenolic	amine	A0700 A0750 T2910
	chloroalkyl	C3292 C3300
	epoxy	G6720 E6250
	mercapto	M8490 M8500
photoresist, negative	silazane	H7300 D6208
	vinyl	D6208 V4800 V4900
	aromatic	P0320
photoresist, positive	silazane	H7300
	aromatic	P0320
polyester	amine	A0700 A0750 T2910
	methacrylate	M8500 M8540
	styryl	S1590
	vinyl	V4917 V4800 V4910
urethane	amine	A0700 A0750 T2910
	alkanolamine	B2408
	epoxy	G6720 E6250
	isocyanate	17840
THERMOPLASTICS		
polyacetal	thiouronium	T2921
polyacrylate	methacrylate	A0380 M8500 M8540
	ureido	T2507
polyamide (nylon)	amine	A0700 A0750 T2910
	ureido	T2507
polyamide-imide	chloromethylaromatic	T2902
polybutylene terephthalate	amine	A0698 A0750
polycarbonate	amine	A0700 A0750 T2910
polyethylene-vinyl acetate copolymer	ureido	T2507
polyethylene	amine	A0700 A0742 A0750
	azido	T2905
	vinyl	V4910 V4917
	vinyl-peroxy	V4950
	styryl	S1590
polyphenylene oxide	alkyl	09835
	amine	A0700 A0750 T2910
polyphenylene sulfide	amine	A0698 A0700 A0750 T2910
	mercapto	M8490 M8500 B2492
polypropylene	azido	T2905
	vinyl-peroxy	V4950
polystyrene	styryl	S1590
	azido	T2905
	aromatic	P0320
	vinyl	V1910 V4917
	styryl	S1588
polysulfone	amine	A0700 A0750 T2910
polyvinyl chloride	amine	A0700 A0710 A0750 T2910

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