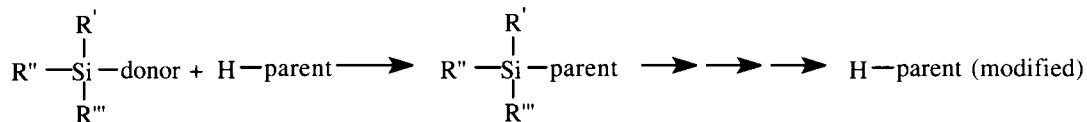


Silane Blocking Agents

Silane blocking agents are employed to derivatize and protect various substrates during synthetic sequences. In a typical application, a silane blocking group replaces an active hydrogen in a parent compound, a series of chemical transformations are performed on the modified parent compound, and finally the blocking agent is removed.



The optimum blocking agent is one that derivatizes the parent readily, withstands the transforming reactions, is readily deblocked, and has reasonable economics.

Two tables are provided for selecting and comparing the most common silylation reagents. Table 1 provides a basis for selecting a blocking group depending on the transformations the derivatized intermediate will undergo. Times given are the half-times for reaction at room temperature. Table 2 provides a basis for selecting the reagent when the blocking group is known and the main consideration is donor strength and byproduct chemistry.

Resistance of Silylated Compounds to Chemical Transformations

Table 1 $t^{1/2}$ for Si-OR bond scission at room temperature









Blocking group	Substrate	HCl THF	KF methanol	CH ₃ MgBr in ether	n-Butyl lithium	LAH- THF	Pryridinium Chlorochromate
	n-butanol	<15 min	2 min	48 hr	2 hr	30 min	<30 min
	cyclohexanol	<15 min	2 min	>48 hr	3 hr	1hr	<30 min
	1-butanol	<15 min	24 hr	>48 hr	50 hr	24 hr	<30 min
	n-butanol	<15 min	2 hr	no reaction	24 hr	1 hr	<30 min
	cyclohexanol	<15 min	20 min	no reaction	>48 hr	2 hr	<30 min
	1-butanol	<15 min	no reaction	no reaction	no reaction	no reaction	1 hr
	cyclohexanol	<15 min	10 hr	no reaction	36 hr	2 hr	<30 min
	cyclohexanol	<15 min	10 hr	no reaction	36 hr	2 hr	<30 min
	n-butanol	<3 hr	no reaction	no reaction	no reaction	25 hr	10 hr
	cyclohexanol	<3 hr	no reaction	no reaction	no reaction	>50 hr	>20 hr
	1-butanol	no reaction	no reaction	no reaction	no reaction	no reaction	>20 hr
	n-butanol	16 hr	no reaction	no reaction	no reaction	>30 hr	22 hr
	cyclohexanol	30 hr	no reaction	no reaction	no reaction	no reaction	50 hr
	1-butanol	no reaction	no reaction	no reaction	no reaction	no reaction	no reaction
	cyclohexanol	no reaction	no reaction	no reaction	no reaction	no reaction	>72 hr
	n-butanol	no reaction	100 hr	no reaction	no reaction	no reaction	no reaction
	cyclohexanol	no reaction	no reaction	no reaction	no reaction	no reaction	no reaction
	1-butanol	no reaction	no reaction	no reaction	no reaction	no reaction	no reaction



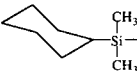
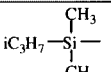
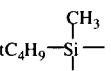
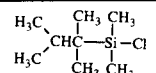
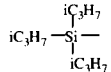

Table 1 data are derived or extrapolated from two primary references:

G. Larson, R. Chawla, J. Steinmetz, Xth International Silicon Symposium, Poznan, Poland, O-24, 72, 1993.

L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, 1965, p. 127.

Table 2

Blocking Agent Product Selector

Blocking group	Acidic Byproducts			Basic Byproducts			Neutral Byproducts		
	leaving group	product name	product code	leaving group	product name	product code	leaving group	product name	product code
	HCl	trimethylbromosilane	SIT8510.1	NH ₃	hexamethyldisilazane	SIH6110.1	acetamide	bis(trimethylsilyl)-acetamide	SIB1846.0
	HBr	trimethylbromosilane	SIT8430.0	HNMe ₂	dimethylamino-trimethylsilane	SID3605.0	trifluoroacetamide	bis(trimethylsilyl)-trifluoroacetamide	SIB1846.0
	HOSO ₂ CF ₃	trimethylsilyltrifluoromethanesulfonate	SIT8620.0	HNEt ₂	diethylamino-trimethylsilane	SIT3398.0	urea	bis(trimethylsilyl)-urea	SIB1878.0
				imidazole	trimethylsilyl-imidazole	SIT8590.0			
	HCl	triethylchlorosilane	SIT8250.0	HNMe ₂	dimethylamino-trimethylsilane	SID3603.0			
	HOSO ₂ CF ₃	trimethylsilyltrifluoromethanesulfonate	SIT8335.0						
	HCl	cyclohexyldimethylchlorosilane	SIC2465.0						
	HCl	isopropyldimethylchlorosilane	SI16462.0						
	HCl	t-butyl dimethylchlorosilane	SIB1935.0	HONH ₂	O-(t-butyl dimethylsilyl)hydroxylamine	SIB1961.0	N-methyl-trifluoroacetamide	N-(t-butyl dimethylsilyl)-N-methyl-trifluoroacetamide	SIB1966.0
	HOSO ₂ CF ₃	t-butyl dimethylsilyl-trifluoromethanesulfonate	SIB1967.0						
	HCl	t-hexyl dimethylchlorosilane	SIB7906.0						
	HCl	triisopropyltrifluorosilane	SIT8384.0						
	HOSO ₂ CF ₃	triisopropyltrifluoromethanesulfonate	SIT8387.0						
	HCl	t-butyl diphenylchlorosilane	SIB1968.0						
Difunctional Blocking Groups									
-Me ₂ Si-	HCl	dimethyldichlorosilane	SID4120.1	NH ₃	hexamethylcyclotrisilazane	SIH6102.0	C ₂ H ₅ OH	dimethyldiethoxysilane	SID4121.0
-Me ₂ SiCH ₂ CH ₂ SiMe ₂ -	HCl	bis(chlorodimethylsilyl)ethane	SIB1042.0	NH ₃	tetramethyl-2,5-disilazacyclopentane	SIT7536.0			
-iPr ₂ SiOSiPr ₂ -	HCl	tetraisopropyl dichloro-disiloxane	SIT7273.0						