

Graphical Indices of Functional Group Transformations

How to Use the Tables¹

The tables are designed to facilitate finding specific reaction transformations in the text. In some cases, a given reaction appears at several places in the book. In these cases, the primary section and page entries, where the mechanistic or synthetic details are discussed in detail for a given compound type, are indicated in bold.

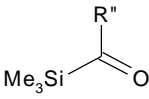
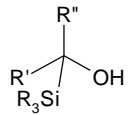
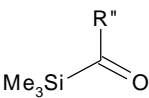
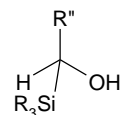
Table 1, Table 2: are collections of reactions involving the formation of organosilanes, sorted by the types of silicon-containing starting materials and products, respectively.

Table 3: lists the reactions of selected functional organosilanes in reactions leading to silicon-free products. This table is designed with synthetic organic chemists in mind.

Table 4: collects some of the reactions associated with silicon-based reactive intermediates. This table will likely be of most use to “silicon” chemists.

Table 5: is a collation of silicon-containing polymer syntheses from the book.

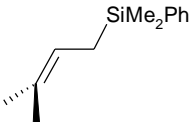
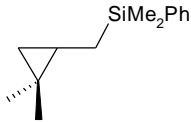

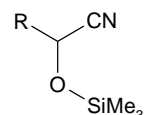
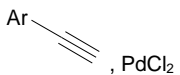
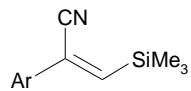
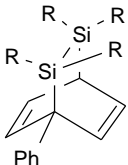
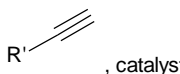
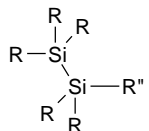
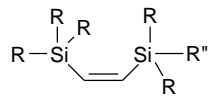
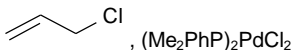
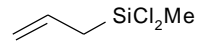
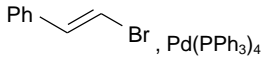
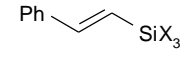
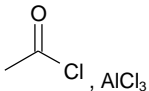
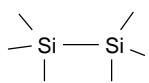
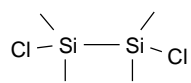
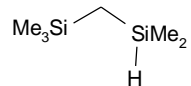
Table 1: Formation of Organosilanes (Sorted by Silicon-Containing Starting Materials)

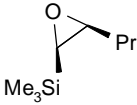
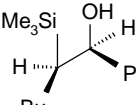
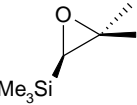
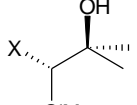
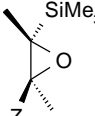
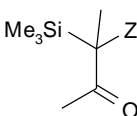
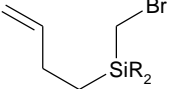
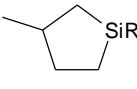

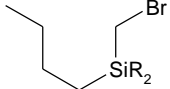
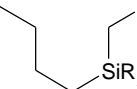
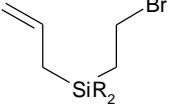
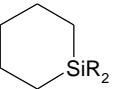
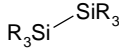

Silicon-Containing Starting Material (Organosilane)	Organic Reagent	Organosilane	Product	Reaction type	Section	Page
Acylsilanes	R'Li			Nucleophilic addition	15.7	539
	LiAlH ₄			Reduction	15.7	539

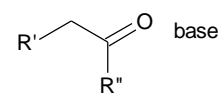
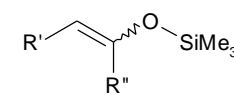
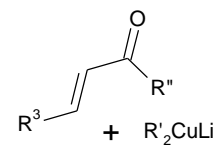
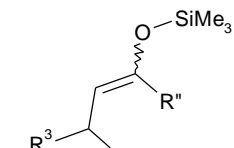
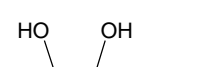
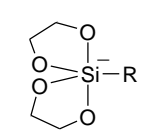
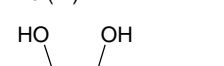
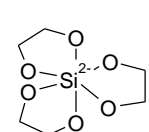
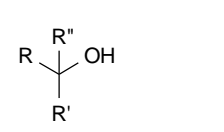
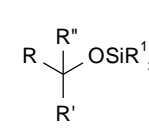
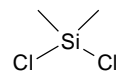
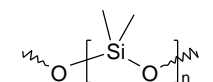
¹ These tables are available as downloadable EXCEL and WORD files from the Wiley ftp site for this book: ftp://ftp.wiley.com/public/sci_tech_med/silicon. You may also find this information on the web page starting at: <http://www.wiley.com>.

	<i>hn</i>			Rearrangement	3.5.2.1.3, 15.7	69, 541
Alkoxysilanes (silyl ethers)	 , base	RSi(OR') ₃		Nucleophilic addition, transesterification	4.2, 4.4	99, 103
	 , base	Si(OR') ₄		Nucleophilic addition, transesterification	4.5	106
	H ₂ O			Hydrolysis/condensation	9.2.2	259
	 catalyst (or silica),	R ₃ SiOR'		Hydrolysis/condensation	9.4.2, 10.2.2, 10.2.3	283, 312, 318
	RMgBr, RLi			Nucleophilic substitution	11.4.1, 12.2, 12.3	358, 385, 388
	R ₂ SiCl ₂	R ₂ Si(OR) ₂	R ₂ SiCl(OR)	Redistribution	12.10.1.4	427
	R'' ₄ NX	R ₂ Si(OR') ₂ , R ₂ SiH ₂	R ₂ Si(OR')H	Redistribution	12.10.1.3	425
	RLi			Retro-Brook rearrangement	15.1.4	518
Alkylsilanes	AlCl ₃	R ₄ Si, R' ₄ Si	R ₂ SiR' ₂	Redistribution	12.10.1.2	423


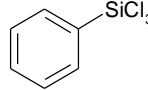
	EX			Nucleophilic substitution with silicon-containing carbanions	12.10.2, 14.2.6 , 15.1.1, 15.1.3, 16.3.3	429, 500 , 511, 513, 565
					12.10.2 , 14.2.6	429 , 500
	Base,				15.1.3	513
Alkynylsilanes				Cycloaddition	12.10.4.1	438
Allenylsilanes	Δ			Sigmatropic rearrangement	15.6.4	534
Allylsilanes	<i>m</i> CPBA			Epoxidation	12.11.2	414
	OsO ₄			Dihydroxylation	12.11.2	441
	Base, then EX				12.10.2.4 , 14.2.6, 15.1.1	432 , 500, 511

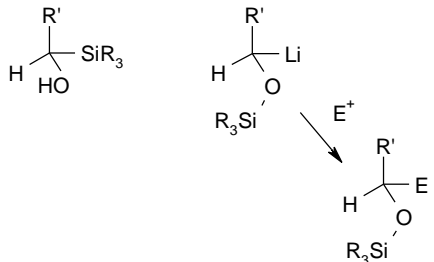

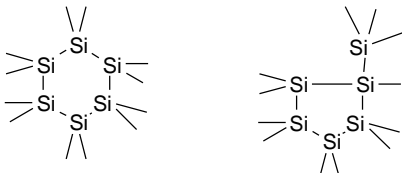
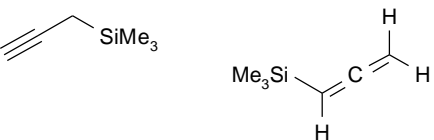
	$\text{CH}_2\text{I}_2, \text{Cu/Zn}$			Simmons-Smith	16.1, 16.4.4.3	555, 592
Cyanosilanes		R_3SiCN		Nucleophilic addition	8.1.4	196
		R_3SiCN		Nucleophilic addition	12.7	400
Disilanes (see also Polysilanes)	RLi		$(\text{R}_2\text{Si})_n$	Ring-opening polymerization	11.3.2	349
				Disilylation	11.4, 12.3.1.2, 12.6.2	358, 390, 397
		$\text{MeCl}_2\text{SiSiCl}_2\text{Me}$		Transition metal-catalyzed metathesis	12.6.1	397
		X_3SiSiX_3		Transition metal-catalyzed metathesis	12.6.1	397
				Redistribution	12.10.1.5	429
	$\Delta (\text{AlCl}_3)$	$\text{R}_3\text{Si-SiR}_3$		Rearrangement (Kumada)	15.4, 15.6.2	526, 533

Epoxy silanes	Bu ₂ CuLi			Nucleophilic substitution	15.1.3, 16.2	514, 560
	HX				15.3.2	524
	MgBr ₂			Acid-catalyzed rearrangement	15.3.2.1	525
α-Haloalkylsilanes	AIBN		 + 	Radical cyclization	8.3.2.3	211
	AIBN, HSnBu ₃			Radical reduction	14.2.5	496
β-Haloalkylsilanes	AIBN			Radical cyclization	8.3.2.4	212
Halosilanes	M (Li, Na, K)	R ₃ SiCl		Metal halogen exchange, nucleophilic attack	3.1.1.1, 11.2.2, 11.3.1	44, 345, 347
	M (Li, Na, K)		(R ₂ Si) _n	Metal halogen exchange, nucleophilic attack	3.1.1.1, 11.2.2, 11.3.1	44, 345, 347

	base	R_3SiI , R_3SiOTf		Carbonyl addition / elimination	8.1.2.2, 8.1.5, 8.5.1	191, 197, 217
	+ R'_2CuLi	Me_3SiCl		Michael addition	8.1.2.3, 8.5.1 , 16.3.3	191, 217 , 565
$Nu(F^-)$		$RSiCl_3$	$RSiNu_4^- (RSiF_4^-)$	Nucleophilic addition	4.1	98, 102- 109
	, base	$RSiCl_3$		Nucleophilic addition	4.1	99- 102, 105- 106
$Nu(F^-)$		SiF_4	$SiNu_6^- (SiF_6^{2-})$	Nucleophilic addition	4.1	98-99
	, base	SiF_4		Nucleophilic addition	4.4.2	106- 108
RNH_2		R'_3SiCl	R'_3SiNR_2	Nucleophilic substitution	8.1.3, 11.5	192, 365
		R'_3SiCl , R'_3SiOTf / Imidazole, base		Nucleophilic substitution	8.2 , 10.3	198 , 320
H_2O		R_3SiCl	$R_3SiOSiR_3$	Hydrolysis/condensation	9.2.1	258
H_2O				Hydrolysis/condensation	9.2.1	258

Silica	$R''SiCl_3$		Hydrolysis/condensation	10.4.1	324
RMgBr, RLi			Nucleophilic substitution	11.4.1, 12.2 , 12.3.1	358, 385 , 390
LiAlH ₄			Reduction	11.4.1	358
 , Li, other reducing metals	R_3SiCl		Nucleophilic substitution	12.3.1.2	390
 , Li, other reducing metals	R_3SiCl		Birch reduction / silylation	12.3.1.2	390
	R_3SiCl		Nucleophilic substitution	12.5	395
 + R_2CuLi or R_2AlH	R_3SiCl		Nucleophilic substitution	12.4	394
Hydrosilanes	$R_2Si(OR)_2, R_2SiCl_2$	$R_2SiCl(OR)$	Redistribution	12.10.1.4	427
	R_3SiH (R_3Si^*)		Radical hydrosilylation	3.3.2.1, 12.8.1 , 14.2.5	54, 401 , 500

$R'CH=CH_2$, catalyst	R_3SiH	$R'CH_2CH_2SiR_3$	Transition metal-catalyzed hydrosilylation	3.3.2.1, 11.4, 12.8.2	54, 355, 403
$R''C(=O)R'$	X_3SiH X = Cl, F, R, silaphilic catalyst	$R''C(H)(R')OSiR_3$	Reduction	4.4.1.1	103
$R''C(=O)R'$, catalyst	$HSiR_3$	$R''C(H)(R')OSiR_3$	Reduction, transition metal-catalyzed	7.4.2 , 11.3.2.2	177 , 351
R_3SiOH , catalyst	Silicone-O-Si-H	Silicone-O-Si-O-SiR ₃	Alcoholysis	9.4.1	282
Ti, Zr, Hf catalysts	$RSiH_3$	$(RHSi)_n$	Dehydrogenative polymerization	11.3.2.2.2	350
$R-C\equiv C$, radical initiator	$HSiX_3$	$R-CH=CH-SiX_3$	Radical hydrosilylation	12.8.1	401
$CH_2=CH-CH=CH_2$	$HSiR_3$	$H-CH_2-CH=CH-SiR_3$	Transition metal-catalyzed hydrosilylation	12.8.2; 12.8.3	403, 417
R''_4NX	$R_2Si(OR')_2, R_2SiH_2$	$R_2Si(OR')H$	Redistribution	12.10.1.3	425
 , BCl_3	$HSiCl_3$		Redistribution	12.10.1.5	428
$H_3Cl, PdCl_2$	Ph_3SiH	$Ph_3SiH + CH_4$	Redistribution	12.10.1.5	428

α -Hydroxysilanes	<i>t</i> -BuLi		Brook rearrangement	3.4.2, 15.1.2	59, 512
Polysilanes (see also Disilanes)	RLi		Ring-opening polymerization	11.3.2.1	350
	AlCl ₃		Redistribution	12.10.1.3	425
Propargylsilanes	Δ		Sigmatropic rearrangement	15.6.4	534
Silanols	Silicone-O-Si-H	R ₃ SiOH, catalyst	Alcoholysis	9.4.1	282
	R ₃ SiOR', catalyst	HO-Si-O-Silicone	Hydrolysis / condensation	9.4.2, 10.2.2 , 10.2.3	283, 312 , 318
Silazanes	H ₂ O	R' ₃ SiNR ₂	Nucleophilic substitution	8.1.3, 11.5	192, 365

Silyl enol ethers	$\text{R}'\text{-CH}_2\text{-C(=O)-R}'' \xrightarrow{\text{base}}$	$\text{R}_3\text{SiI, R}_3\text{SiOTf}$	$\text{R}'\text{-CH=C(R}''\text{)-O-SiMe}_3$	Carbonyl addition / elimination	8.1.2.2, 8.1.5, 8.5.1	191, 197, 217 ,
	$\text{R}^3\text{-CH=CH-C(=O)-R}'' + \text{R}'_2\text{CuLi}$	Me_3SiCl	$\text{R}^3\text{-CH}_2\text{-CH(R}'\text{)-CH=C(R}''\text{)-O-SiMe}_3$	Michael addition	8.1.2.3, 8.5.1 , 16.3.3	191, 217 , 565
Vinylsilanes	$\text{R}'\text{, R}'\text{O}'$	$\text{CH}_2=\text{CH-SiR}_3$	$\text{(R}'\text{O)R}'\text{-CH}_2\text{-CH}_2\text{-SiR}_3\cdot$	Radical addition	11.1, 14.2.5	340, 500
	CO_2Me	SiMe_3		Diels-Alder	12.10.4.2	438
	 , AlCl_3	SiX_3	$\text{Ph-CH}_2\text{-CH}_2\text{-SiCl}_3$	Friedel-Crafts addition	16.4.2.5	577
	$t\text{-BuOOH}$	$\text{HO-CH}_2\text{-CH=CH-Si}(i\text{-Pr)}_3$	$\text{HO-CH}_2\text{-CH(O)-CH}_2\text{-Si}(i\text{-Pr)}_3$	Epoxidation	12.11.1, 16.1, 16.2	440, 552-558

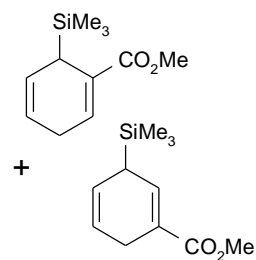
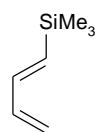
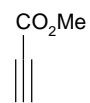
Table 2: Formation of Organosilanes (Sorted by Organosilane Product)

Organosilane Product	Organic Reagent	Organosilane	Product	Reaction type	Section	Page
Acylsilanes		R_3SiLi , Cu			12.5	396
		R_3SiCl		Nucleophilic substitution	12.5	395
Alkoxysilanes (silyl ethers)	ROH	$R'_2Si:$			3.1.2	47
	<i>t</i> -BuLi			Brook rearrangement	3.4.2, 15.1.2	59, 512
		X_3SiH , X = Cl, F, R, silaphilic catalyst		Reduction	4.4.1.1	103
	, catalyst	$HSiR_3$		Reduction, transition metal-catalyzed	7.4.2 , 11.3.2.2	177 , 351

cyanohydrins		R_3SiCN		Nucleophilic addition	8.1.4	196
organic protecting groups		R^1_3SiCl , R^1_3SiOTf / Imidazole, base		Nucleophilic substitution	8.2 , 10.3	198 , 320
	R''_4NX	$R_2Si(OR')_2$, R_2SiH_2 $R_2Si(OR)_2$, R_2SiCl_2	$R_2Si(OR')H$ $R_2SiCl(OR)$	Redistribution Redistribution	12.10.1.3 12.10.1.4	425 427
Alkylsilanes		R_3SiH (R_3Si^*)		Radical hydrosilylation	3.3.2.1, 12.8.1 , 14.2.5	54, 401 , 500
	, catalyst	R_3SiH		Transition metal-catalyzed hydrosilylation	3.3.2.1, 11.4, 12.8.2	54, 355, 403
	AIBN			Radical cyclization	8.3.2.3	211
	AIBN			Radical cyclization	8.3.2.4	212
	R', R'O			Radical addition	11.1, 14.2.5	340, 500
	RMgBr, RLi			Nucleophilic substitution	11.4.1, 12.2 , 12.3.1	358, 385 , 390
	RMgBr, RLi			Nucleophilic substitution	11.4.1, 12.2 , 12.3.1	358, 385 , 388

	$(R_3Si)_2CuLi$		Michael addition	12.4	394
$AlCl_3$	R_4Si, R'_4Si	$R_2SiR'_2$	Redistribution	12.10	423
EX				12.10.2, 14.2.6, 15.1.1, 15.1.3	430, 502, 512, 514
AIBN, $HsNBu_3$			Radical reduction	14.2.5	499
$\Delta (AlCl_3)$	$R_3Si-SiR_3$		Rearrangement (Kumada)	15.4, 15.6.2	526, 533
 $R'-CH=CH_2, AlCl_3$			Friedel-Crafts addition	16.4.2.5	577
$CH_2I_2, Cu/Zn$				16.4.4.3	593
			Simmons-Smith	16.4.4.3	592
Allenylsilanes	Δ		Sigmatropic rearrangement	15.6.4	534

Allylsilanes				Cycloaddition	3.5.2.3	71
		$R_2Si:$			3.1.1, 3.1.2.2	42, 48
	, Li, other reducing metals			Disilylation	12.3.1.2	390
	, Li, other reducing metals	R_3SiCl		Birch reduction/silylation	12.3.1.2	390
	Cl, $(Me_2PhP)_2PdCl_2$	$MeCl_2SiSiCl_2Me$		Transition metal catalyzed-metathesis	12.6.1	397
	, catalyst	$HSiR_3$		Transition metal-catalyzed hydrosilylation	12.8.2, 12.8.3	403, 417
	Cl, catalyst	$R_3Si-CH_2-CH_2-M$			12.10.2, 14.2.6	429, 500
	Base, then EX			Alkylation	12.10.2.4, 14.2.6	432, 500

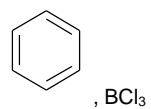


Diels-Alder

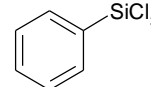
12.10.4.2

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Arylsilanes



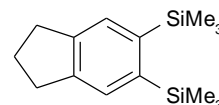
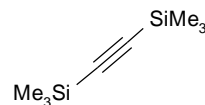
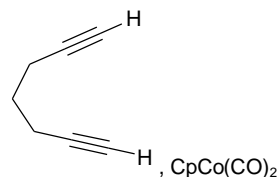
HSiCl_3



Redistribution

12.10.1.5

428



Cycloaddition

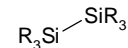
12.10.4.1

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Disilanes

M (Li, Na, K)

R_3SiCl



Metal halogen exchange,
nucleophilic substitution

3.1.1.1,
11.2.2, 11.3.1

44,
345,
347

Disiloxanes (silicones)

H_2O

$\text{R}'_3\text{SiNR}_2$



Nucleophilic substitution

8.1.3, **11.5**

192,
365

H_2O

R_3SiCl

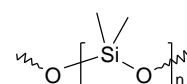
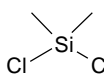


Hydrolysis/condensation

9.2.1

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H_2O

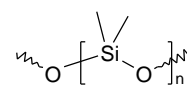
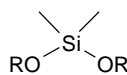


Hydrolysis/condensation

9.2.1

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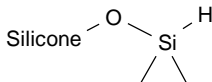
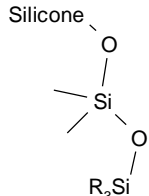
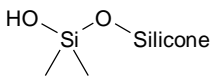
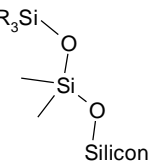
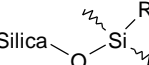
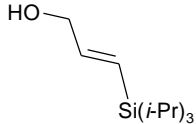
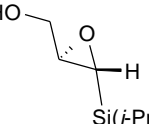
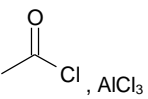
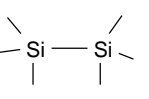
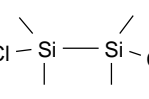
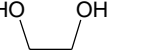
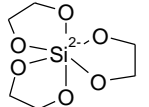
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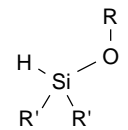
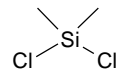
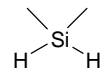
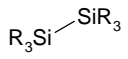
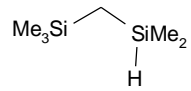
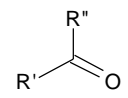
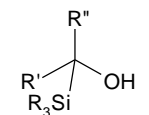
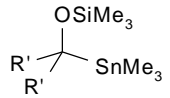
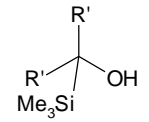
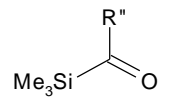
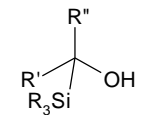
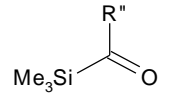
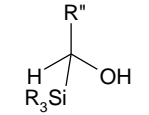
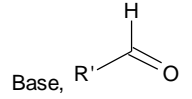
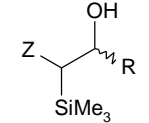
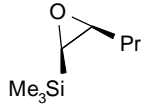
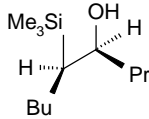


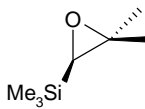
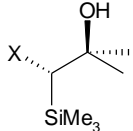
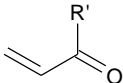
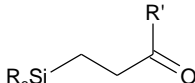
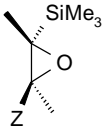
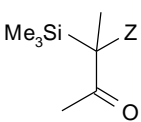

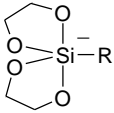
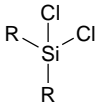
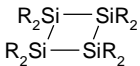
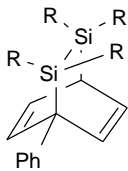
Hydrolysis/condensation

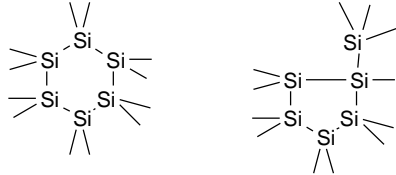
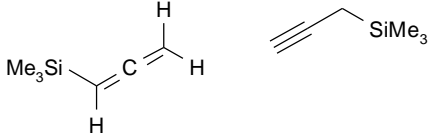
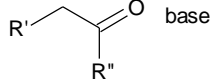
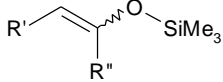
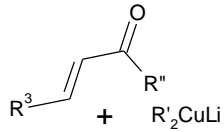
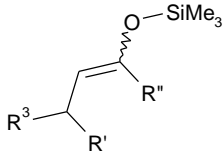
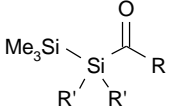
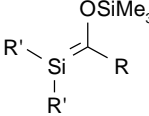
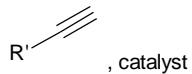
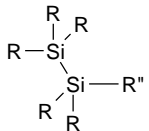
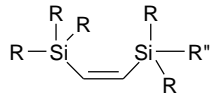
9.2.2

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	R_3SiOH , catalyst			Hydrolysis	9.4.1	282
	R_3SiOR' (or silica), catalyst			Hydrolysis/condensation	9.4.2, 10.2.2 , 10.2.3	283, 312 , 318
	Silica	$R''SiCl_3$, $R''Si(OR)_3$		Hydrolysis/condensation	10.4.1	320, 324
Epoxy silanes	<i>t</i> -BuOOH			Epoxidation	12.11.1 , 16.1, 16.2	440 , 552- 558
Halosilanes	HX (X = Cl, OR)	Si	$HSiX_3$	The Direct Process	12.1.1	382
The Direct Process	MeCl	Si	Me_2SiCl_2	The Direct Process	12.1.2	382
		$R_2Si(OR)_2$, R_2SiCl_2	$R_2SiCl(OR)$	Redistribution	12.10.1.4	427
	 , $AlCl_3$			Redistribution	12.10.1.5	429
	H_3Cl , $PdCl_2$	Ph_3SiH	$Ph_3SiH + CH_4$	Redistribution	12.10.1.5	428
Hexacoordinate silanes	$Nu(F^-)$	SiF_4	$SiNu_6^- (SiF_6^{2-})$		4.1	98-99
	 , base	SiF_4 , $Si(OR')_4$			4.4.2	106- 108

Hydrosilanes	ROH	$R'_2Si:$			3.1.2	47
	LiAlH ₄			Reduction	11.4.1	358
	R'' ₄ NX	R ₂ Si(OR') ₂ , R ₂ SiH ₂	R ₂ Si(OR')H	Redistribution	12.10.1.3	425
	Δ (AlCl ₃)			Rearrangement (Kumada)	15.4, 15.6.2	536,5 33
α-Hydroxysilanes		R ₃ Si ⁻		Nucleophilic addition	3.4.2	59
	RLi			Retro Brook rearrangement	15.1.4	518
	R'Li			Nucleophilic addition	15.7	539
	LiAlH ₄			Reduction	15.7	539
β-Hydroxysilanes	Base, 	Me ₃ Si-CH ₂ -Z			15.1.3	513
	Bu ₂ CuLi			Nucleophilic substitution	15.1.3 , 16.2	514 , 560

		HX				15.3.2	524
β -Ketosilanes			R_3Si^-		Nucleophilic addition	3.4.2, 12.4	60, 395
	MgBr ₂				Acid-catalyzed rearrangement	15.3.2.1	525
Pentacoordinate silanes	Nu (F ⁻)		RSiCl ₃	RSiNu ₄ ⁻ (RSiF ₄ ⁻)	Nucleophilic addition	4.1	98, 102- 109
		, base	RSiCl ₃ , RSi(OR) ₃		Nucleophilic addition	4.1	99- 102, 105- 106
Polysilanes	M (Li, Na, K)			(R ₂ Si) _n	Metal halogen exchange, nucleophilic substitution	3.1.1.1 , 11.2.2, 11.3.1	44 , 345, 347
	RLi			(R ₂ Si) _n	Ring-opening polymerization	11.3.2	350
	RLi			(R ₂ Si) _n	Ring-opening polymerization	11.3.2	349
	Ti, Zr, Hf catalysts		RSiH ₃	(RHSi) _n	Dehydrogenative polymerization	11.3.2.2.2	350

	AlCl_3		Redistribution	12.10.1.3	425
Propargylsilanes	Δ		Sigmatropic rearrangement	15.6.4	534
Silazanes	RNH_2	R_3SiCl	R_3SiNR_2	Nucleophilic substitution	8.1.3, 11.5 192, 365
Silyl Enol Ethers	 $\text{R}^1\text{-CH}_2\text{-C(=O)-R}''$ base	R_3SiH , R_3SiOTf		Carbonyl addition / elimination	8.1.2.2, 8.1.5, 8.5.1 191, 217
	 $\text{R}^3\text{-CH=CH-C(=O)-R}''$ + $\text{R}'_2\text{CuLi}$	Me_3SiCl		Michael addition	8.1.2.3, 8.5.1 , 16.3.3 191, 217 , 565
	<i>hn</i>			Rearrangement	15.7 542
Vinylsilanes	 $\text{R}'\text{-CH=CH}_2$, catalyst			Disilylation	11.4, 12.6.2 358, 397

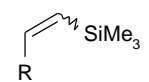
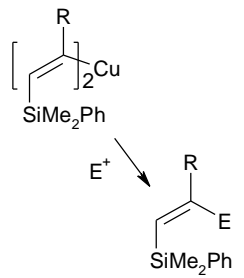
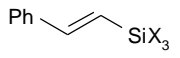
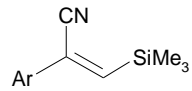
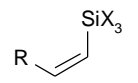
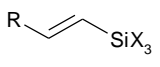
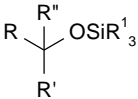
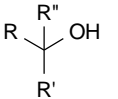
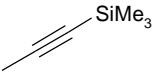
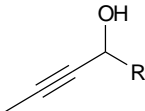
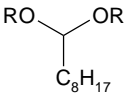
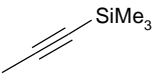
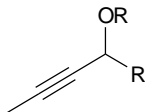
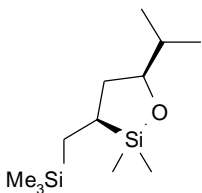
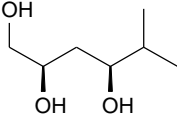
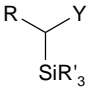
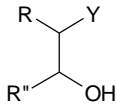
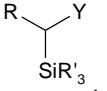

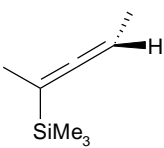
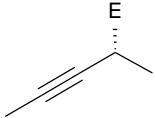

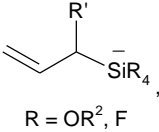
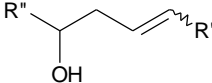
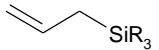
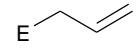
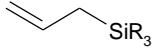
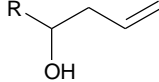
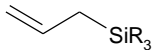
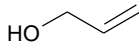
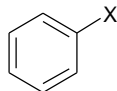
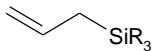
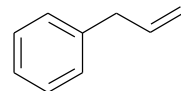
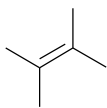
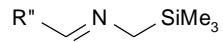
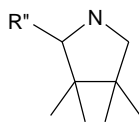
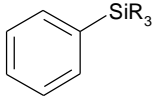
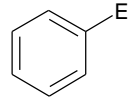
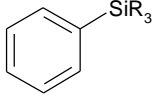
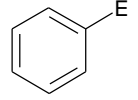
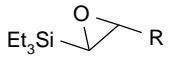
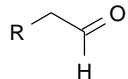
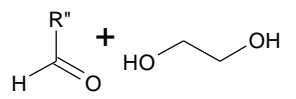
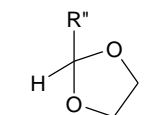
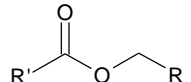
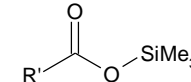
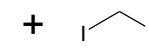
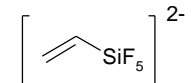
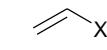
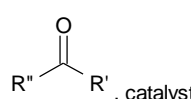
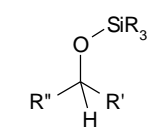
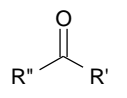
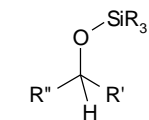
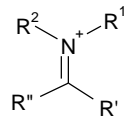

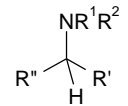
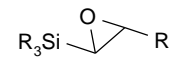
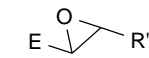
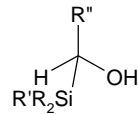
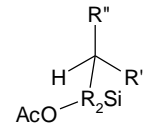
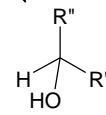
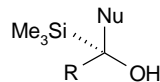
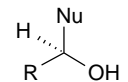
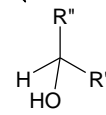
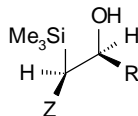
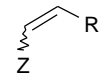
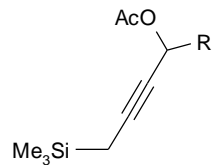
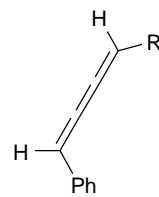
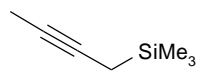
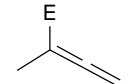
$\begin{array}{c} \text{H} \\ \text{H} \end{array} \text{C} \equiv \text{C} \text{H} + \text{R}_2\text{CuLi} \text{ or } \text{R}_2\text{AlH}$	$\text{R}'_3\text{SiCl}$			12.4, 16.4.2.4	394, 576
$\text{R} \text{C} \equiv \text{C} \text{H}$	$(\text{R}'_3\text{Si})_2\text{CuLi}$			12.4	394
$\text{Ph} \text{C} \equiv \text{C} \text{Br}, \text{Pd}(\text{PPh}_3)_4$	X_3SiX_3		Transition metal catalyzed-metathesis	12.6.1	397
$\text{Ar} \text{C} \equiv \text{C} \text{H}, \text{PdCl}_2$	R_3SiCN		Nucleophilic addition	12.7	400
$\text{R} \text{C} \equiv \text{C} \text{H}, \text{radical initiator}$	HSiX_3		Radical hydrosilylation	12.8.1	401
$\text{R} \text{C} \equiv \text{C} \text{H}, \text{transition metal catalyst}$	HSiX_3		Transition metal catalyzed-hydrosilylation	12.8.2	403

Table 3: Synthetically Useful Reactions of Organosilanes: Silicon-Free Products (Sorted by Organosilane Starting Material)

Functional Organosilane	Organic Reagent	Organosilane	Product	Reaction type	Section	Page
Alkoxysilanes, Silyl Ethers	F ⁻ (H ₂ O)			Hydrolysis	8.2, 8.2.7	198, 197
Alkynylsilanes	F ⁻ , RCHO			Nucleophile-induced desilylation	16.3.2	562
	 C ₈ H ₁₇ , Lewis acid			Electrophile-induced desilylation	16.4.3	577
Alkylsilanes	H ₂ O ₂ , F ⁻			Oxidative desilylation	5.5.1.1, 16.2	136, 558
	R''CHO, F ⁻	 Y = carbanion stabilizing group			16.3	561
	EX, F ⁻	 Y = carbanion stabilizing group			16.3	561

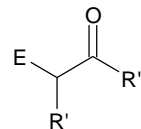
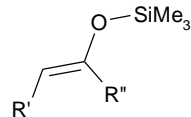
Allenylsilanes	E^+ (E = H, X, R, RR'COR", RC=O), X^-			Electrophile-induced desilylation	16.4.5	595
Allylsilanes				Allylation	4.4.2, 16.3.3	104, 564
	E^+ (E = H, X, R, RR'COR", RC=O), X^-			Electrophilic substitution	14.2.3.3, 16.4.4	491, 579
	RCHO, F^-			Nucleophile-induced desilylation	16.3.3 , 16.4.4.2	
	<i>m</i> CPBA, F^-			Oxidative desilylation	16.2	
 , Pd-catalyst			Heck-type reaction	16.3.3.1		
Allylsilanes (2-aza)	 F^-, H^+ , then			Ylid formation (dipolar cycloaddition)	16.3.5	
Arylsilanes	E^+ (E = H, X, R, RR'COR", RC=O), X^-, F^-			Nucleophile-induced desilylation	14.2.3.4, 16.2, 16.3.1	
	E^+ (E = H, X, R, RR'COR", RC=O), X^-			Electrophilic substitution	14.2.3.4, 16.2, 16.4.1	
Epoxy silanes	HX, H ₂ O				15.3.2	

Halosilanes	RCOOH, R'OH	R''_3SiCl	RCO_2R'	Esterification, Lewis acid	4.1, 8.1.1
		R''_3SiCl		Acetalization, Lewis acid	4.1, 8.1.1
		$R''_3SiI (Br)$		Ester cleavage	8.1.2.1
<i>m</i> CPBA	$R'-SiR_2R''$, R = alkyl, aryl, F, OR, R'' = X, OR		Oxidative desilylation	16.2	
Hexacoordinate silanes	X^+			Electrophilic substitution	14.2.3.3
	<i>m</i> CBPA	$RSiF_5^{2-}$	ROH	Oxidative desilylation	4.4.2
	H_2O_2, F^-	R_3SiR''	$R''OH$	Oxidative desilylation	5.5.1.1, 8.2.7.2 , 8.3.1, 8.3.2.3
Hydrosilanes	$R-Cl$, AIBN	$HSi(SiMe_3)_3$	$R-H$	Reduction	7.2.1
	 , catalyst	$HSiR_3$		Reduction (silicon lost during hydrolysis)	7.4.2
		$HSi(OR)_5^-$		Reduction (silicon lost during hydrolysis)	7.4.2, 15.7

					Reduction	7.4.2
	F ⁻ , then E ⁺				Alkyl/hydro-desilylation	16.1
α -Hydroxysilanes	Ac ₂ O, then Δ				Rearrangement, oxidative desilylation	15.7
	F ⁻				Brook rearrangement (silicon lost during hydrolysis)	15.7
β -Hydroxysilanes	KH or acid (H ⁺ or Lewis acid)				Peterson olefination	15.1.2
Propargylsilanes	F ⁻				Vinylogous Peterson olefination	16.3.4
	EX (E = H, X, R, RR'COR'', RC=O), Lewis acid catalyst				Electrophile-induced desilylation	16.4.5

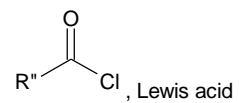
Silyl Enol Ethers

EX, Lewis acid

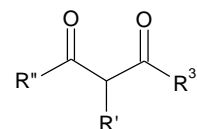
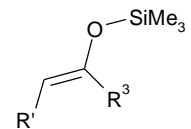


Enol alkylation

8.5.2

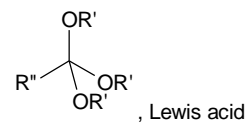


, Lewis acid

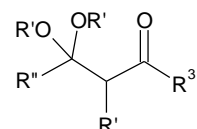
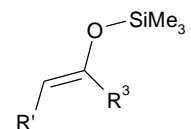


Enol acylation

8.5.2.4.2

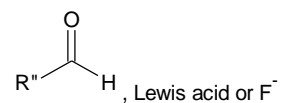
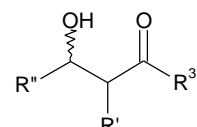
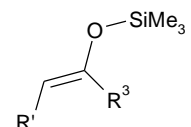


, Lewis acid

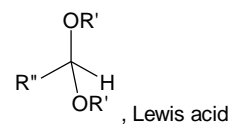


Enol acylation

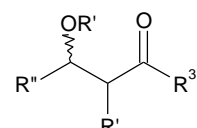
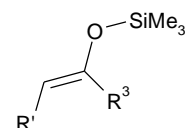
8.5.2.4.2

, Lewis acid or F⁻

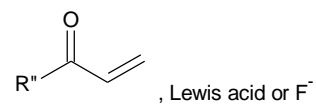
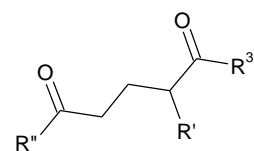
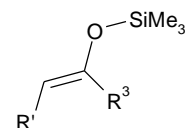
Aldol

8.5.2.4.3,
8.5.2.4.5

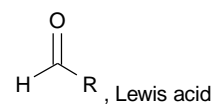
, Lewis acid



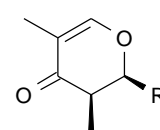
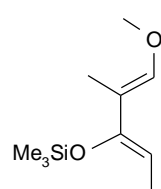
Aldol

8.5.2.4.3,
8.5.2.4.5, Lewis acid or F⁻

Michael addition

8.5.2.4.4,
8.5.2.4.5.1

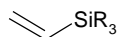
, Lewis acid



Cycloaddition [4+2], [3+3]

8.5.2.5.1,
8.5.2.5.2

Vinylsilanes

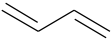
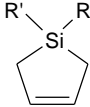


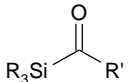
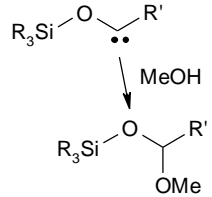
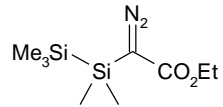
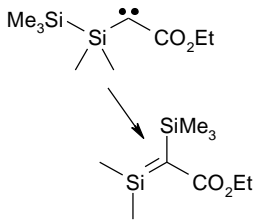
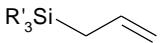
E⁺ (E = H, X, R, RR'COR'', RC=O),

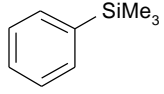
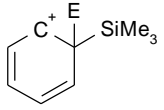
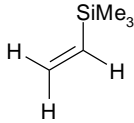
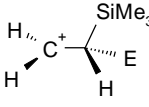
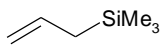
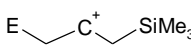
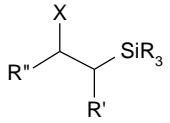
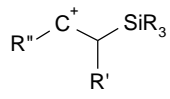
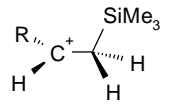
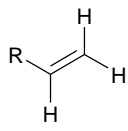
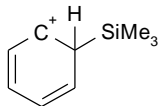
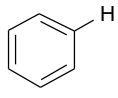
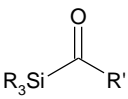
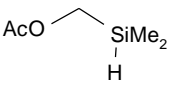
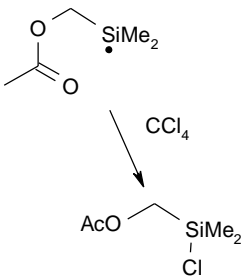
Electrophilic substitution

14.2.3.2,
14.2.3.3,

X^-				16.4.2
NaH, HMPA			Hyrodesilylation	16.1
E^+ (E = H, X, R, RR'COR'', RC=O), X^-, F^-			Nucleophile-induced desilylation	16.3.2
 , Pd catalyst, F^-			Nucleophile-induced desilylation	16.3.2

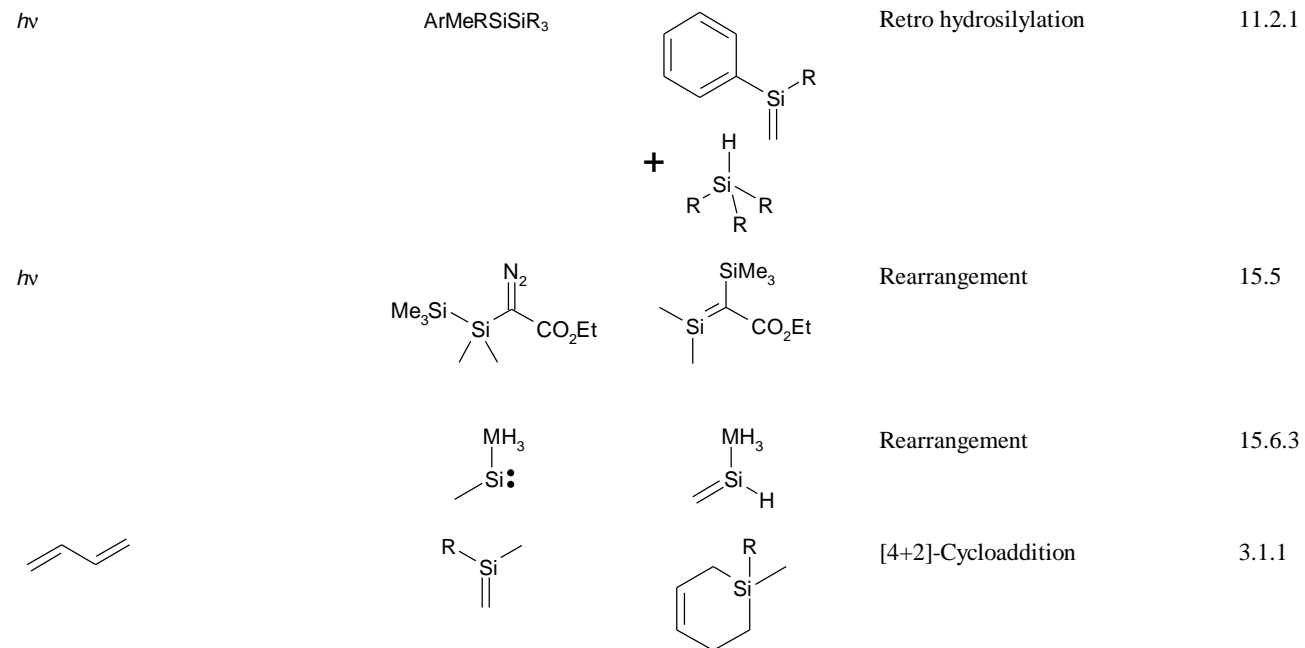
Table 4: Silicon-based and Silicon-Containing ,Carbon-based Reactive Intermediatesⁱ (sorted by number of substituents and electron count).ⁱⁱ

Silicon-based Reactive Intermediate	Organic Reagent	Organosilane	Product	Reaction type	Section	Page
Silylenes (R ₂ Si:)	<i>hν</i> 	R ₃ SiSiR' ₂ SiR ₃	R' ₂ Si:	Photolysis	11.2.1	
		R' ₂ Si:			3.1.1, 3.1.2	
				Rearrangement	15.6.3	
α-Siloxycarbenes	<i>hν</i> , or Δ			Rearrangement	14.2.1, 15.5	
α-Silylcarbenes	<i>hν</i>			Rearrangement	15.5	
Silylium Ions (silyl cations R ₃ Si ⁺)	Ar ₃ C ⁺ Y ⁻ (Y is a non-nucleophilic counterion)	R ₃ SiH	R ₃ Si ⁺ Y ⁻	Hydride abstraction	3.2	
Note that most reactions of halosilanes (above) formally go via silyl cation intermediates	R' ₃ Si ⁺ Y ⁻ (Y is a non-nucleophilic counterion)		R' ₃ Si ⁺ Y ⁻	Electrophilic substitution	3.2	

β -Silyl cations	E^+			Electrophilic addition	14.2.3.2
	E^+			Electrophilic addition	14.2.3.1, 14.2.3.3
	E^+			Electrophilic addition	14.2.3.3
	Lewis acid				15.2
	Nucleophile				14.2.3 , 15.2.1
	Nucleophile				14.2.3.4
Silyl radicals (R_3Si^\bullet)	ROOR	$HSiR'_3$	R_3Si^\bullet		3.3.1
	$h\nu$, R''_3CCl		R_3SiCl		3.3
	$h\nu$				15.4

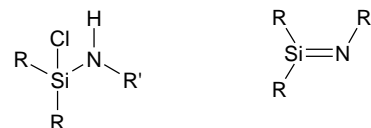
	O_2			Autoxidation	15.4
	$R'CH=CH_2$, $R''OOR''$ or other initiator	R_3SiH	$R'CH_2CH_2SiR_3$	Radical hydrosilylation	3.3.2.1, 12.8.1, 14.2.5
Silyl anions (R_3Si^-)	RM , $R = H$, alkyl, $M = Li, K$, etc.	$R'_3SiR'_3$	R_3Si^-	Reduction	3.4.1.1
	RM , $R = H$, alkyl, $M = Li, K$, etc.	R'_3SiH	R_3Si^-	Reduction	3.4.1.2
	Li, Na, K	R_3SiCl	R_3Si^-	Metal halogen exchange	11.2.1, 11.3.1.1
		R_3SiLi, Cu			12.5
		R_3SiM		Nucleophilic addition	15.7
		R_3Si^-		Nucleophilic addition	3.4.2
	$(R'_3Si)_2CuLi$		Michael addition	3.4.2, 12.4	
	$(R'_3Si)_2CuLi$			12.4	

α -Silyl anions	Base			Deprotonation	14.2.6, 15.1.1, 15.1.3
	Base			Nucleophilic addition	14.2.6
					12.10.2, 14.2.6
	Base,				15.1.2
Disilenes		$R_2Si:$		Dimerization	3.1.2, 3.5.1.2
	Li			Metal halogen exchange, salt elimination	3.5.1.1
Silenes ($R_2Si=CR_2$)				Thermolysis	3.1.1
	$R''Li$			Metal halogen exchange, salt elimination	3.5.2.2.2
		ArR_2SiSiR_3		Sigmatropic Rearrangement	11.2.1



Silanimines

R^iLi



Metal halogen exchange, salt elimination

3.5.4

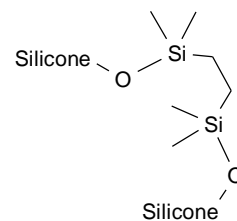
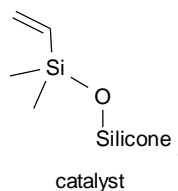
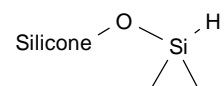
ⁱ For a definition, see Chap. 3. These reactive intermediates are silicon-containing compounds that are typically unstable at room temperature.

ⁱⁱ For each intermediate type, preparations are first listed, followed by reactions.

Table 5: Silicon-Based Polymers (sorted by product polymer type)

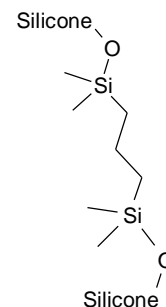
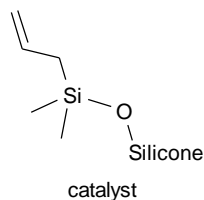
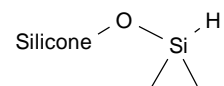
Silicon-based Product	Organic Reagent	Organosilane	Polymer Product	Reaction type	Section	Page
Polycarbosilanes, pendant -poly(vinylsilanes)	*R', R'O*			Radical addition, radical polymerization	11.1, 14.2.5	340, 500
-poly(alkynylsilanes) -polyacetylenes	WCl ₆			Transition metal Lewis acid-catalyzed polymerization	11.1	
-poly(allylsilanes) -polyacetylenes	WCl ₆			Transition metal Lewis acid-catalyzed polymerization	11.1	
Polycarbosilanes	RLi, or TM catalyst			Ring-opening polymerization	11.4	
Poly(siloxanes), silicones	H ₂ O	R ₂ SiCl ₂		Hydrolysis/condensation	9.2.1	258
	H ₂ O			Hydrolysis/condensation	9.2.2	259
	R ₃ SiOH, catalyst			Alcoholysis	9.4.1	282

Polysiloxanes (silica-reinforced, silica surface modification, coupling agents)	Silica	$\begin{array}{c} \text{RO} \quad \text{R}'' \\ \diagdown \quad / \\ \text{Si} \\ / \quad \diagdown \\ \text{RO} \quad \text{OR} \end{array},$ $\text{R}''\text{SiCl}_3$	$\text{Silica}-\text{O}-\begin{array}{c} \text{R}'' \\ \diagdown \quad / \\ \text{Si} \\ / \quad \diagdown \\ \text{---} \quad \text{---} \end{array}$	Hydrolysis/condensation	10.4.1	320, 324
Poly(siloxanes); crosslinked	R ₃ SiOR', catalyst (e.g., Ti(OR) ₄ , R ₂ SnO ₂ CR'), RTV	$\begin{array}{c} \text{HO} \quad \text{O} \\ \diagdown \quad / \\ \text{Si} \\ / \quad \diagdown \\ \text{---} \quad \text{---} \end{array} \text{Silicone}$	$\begin{array}{c} \text{R}_3\text{Si} \quad \text{O} \\ \diagdown \quad / \\ \text{Si} \\ / \quad \diagdown \\ \text{---} \quad \text{---} \end{array} \text{O} \text{---} \text{Silicone}$	Hydrolysis/condensation	9.4.2, 10.2.2, 10.2.3	283, 312, 318
	peroxide	$\begin{array}{c} \text{CH}_3 \\ \\ \text{Silicone}-\text{O}-\text{Si} \\ \\ \text{Silicone}-\text{O} \end{array}$	$\begin{array}{c} \text{Silicone} \quad \text{O} \\ \diagdown \quad / \\ \text{Si} \\ / \quad \diagdown \\ \text{---} \quad \text{---} \end{array} \text{O}-\begin{array}{c} \text{O} \\ \\ \text{---} \end{array} \text{---} \text{Silicone}$		9.4.3, 9.4.4	
		$\begin{array}{c} \text{CH}_3 \\ \\ \text{Silicone}-\text{O}-\text{Si} \\ \\ \text{Silicone}-\text{O} \end{array}, \text{ peroxide}$	$\begin{array}{c} \text{---} \quad \text{---} \\ \diagdown \quad / \\ \text{Si} \\ / \quad \diagdown \\ \text{---} \quad \text{---} \end{array} \text{O}-\text{Silicone}$	$\begin{array}{c} \text{Silicone} \quad \text{O} \\ \diagdown \quad / \\ \text{Si} \\ / \quad \diagdown \\ \text{---} \quad \text{---} \end{array} \text{O}-\begin{array}{c} \text{---} \quad \text{---} \\ \diagdown \quad / \\ \text{Si} \\ / \quad \diagdown \\ \text{---} \quad \text{---} \end{array} \text{O}-\text{Silicone}$	9.4.3, 9.4.4	
		$\begin{array}{c} \text{H} \\ \\ \text{Silicone}-\text{O}-\text{Si} \\ \\ \text{Silicone}-\text{O} \end{array}, \text{ peroxide}$	$\begin{array}{c} \text{---} \quad \text{---} \\ \diagdown \quad / \\ \text{Si} \\ / \quad \diagdown \\ \text{---} \quad \text{---} \end{array} \text{O}-\text{Silicone}$	$\begin{array}{c} \text{Silicone} \quad \text{O} \\ \diagdown \quad / \\ \text{Si} \\ / \quad \diagdown \\ \text{---} \quad \text{---} \end{array} \text{O}-\begin{array}{c} \text{---} \quad \text{---} \\ \diagdown \quad / \\ \text{Si} \\ / \quad \diagdown \\ \text{---} \quad \text{---} \end{array} \text{O}-\text{Silicone}$	Radical hydrosilylation	9.4.4, 14.2.5, for mechanism, see 12.8.1



Transition metal-catalyzed hydrosilylation

9.4.5

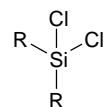


Transition metal-catalyzed hydrosilylation

3.3.2.1,
9.3.1.4, **9.3.3**,
9.3.3.1, 9.4.5
11.4.1, for
mechanism,
see 12.8.2

Poly(silanes)

M (Li, Na, K)

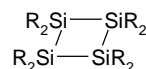


$(R_2Si)_n$

Metal halogen exchange,
nucleophilic substitution

3.1.1.1, **44**,
11.2.2, **11.3.1**
345,
347

R'Li



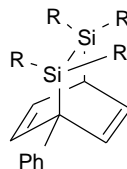
$(R_2Si)_n$

Ring-opening polymerization

11.3.2.1

350

R'Li



$(R_2Si)_n$

Ring-opening polymerization

11.3.2

349

Ti, Zr, Hf catalysts

$RSiH_3$

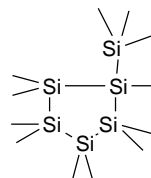
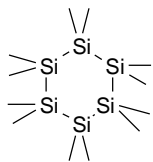
$(RHSi)_n$

Dehydrogenative polymerization

11.3.2.2.2

250

AlCl_3



Redistribution

12.10.1.3

425
