

Organosilicon Chemistry(有机硅化学)

Si forms stronger bonds than C to O and various halogens but weaker bonds to C and H. Listed below are some typical bond dissociation energies (KJ mol⁻¹):

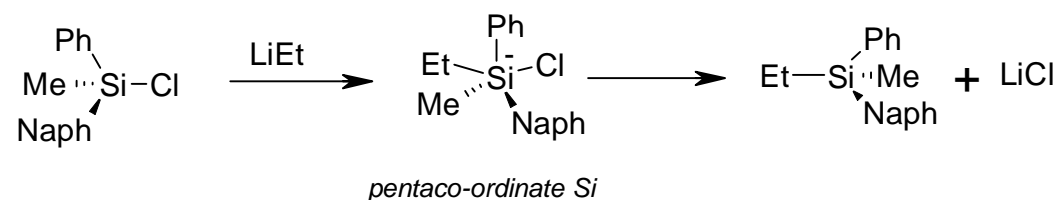
Si-O	530	C-O	340
Si-F	810*	C-F	450
Si-C	320	C-C	335

*This is one of the strongest bonds known

With the above values in mind much of the organosilicon chemistry is driven by the formation of strong Si-O or Si-F bonds at the expense of other weaker bonds.

Reactivity

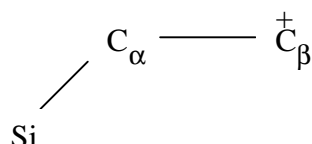
Almost all acyclic Cl, Br, and I silanes react with all nucleophiles by an SN2 type mechanism leading to an inversion of configuration at the Si atom.



In many cases the pentacovalent Si is thought to be an intermediate rather than a transition state.

Stabilization of β -carbocations

Many reactions encountered in organosilicon chemistry involve the formation of carbocations on a C atom β to a Si atom.

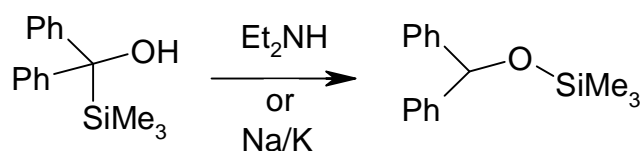


This stabilisation effect has been rationalised by the overlap between the vacant P orbital on C $_{\beta}$ and the σ orbital between the Si and the C $_{\alpha}$. Hence maximum stabilisation only occurs if the vacant P orbital and the C-Si bond are in the SAME plane .

Organosilicon chemistry is dominated by this feature.

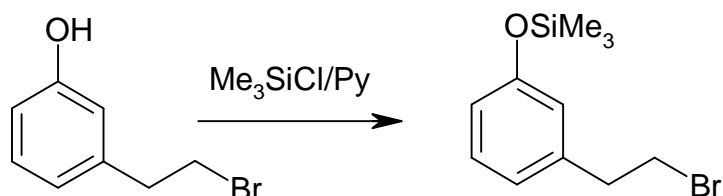
Reactions of Organosilanes*1. 1,2 rearrangements*

When silylcarbinols are treated with base or active metals the silyl group is known to migrate from the C to a neighbouring O atom e.g. Brook rearrangement

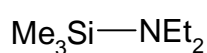


2. Protecting Groups: Silyl Ethers

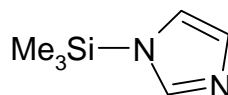
The TMS group has been extensively used for the protection of alcohols



Other reagents have been developed for the conversion of alcohols to their respective TMS ethers, either more efficiently or more selectively:



TMSDEA
N-trimethylsilyl-diethylamine



TMSI
N-trimethylsilylimidazole

Order of reactivity:

TMSI > TMSDEA > TMSCl/Py

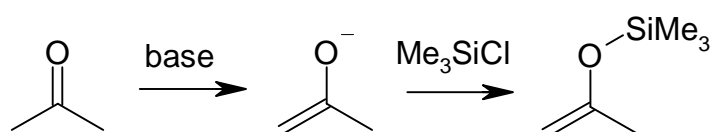
Word of warning!!!!

TMS ethers are sensitive to acidic and basic conditions and are known not to survive hydrogenolysis.

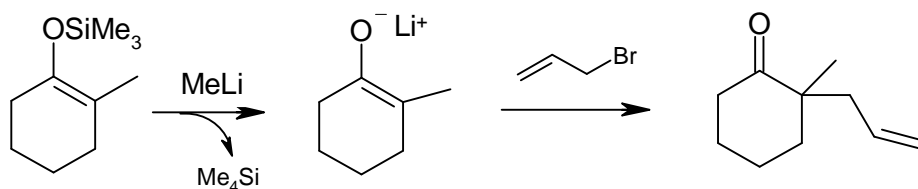
$\text{Bu}_4\text{N}^+\text{F}^-$ is extensively used for the deprotection of silyl ethers

3. Silyl Enol Ethers

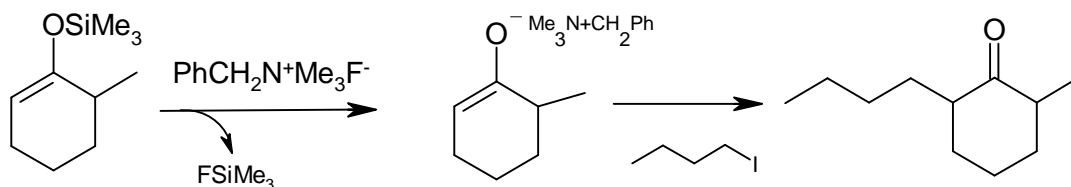
These are stable molecules which can be isolated and purified etc using standard organic procedures. They are generated by the trapping of enolate anions:



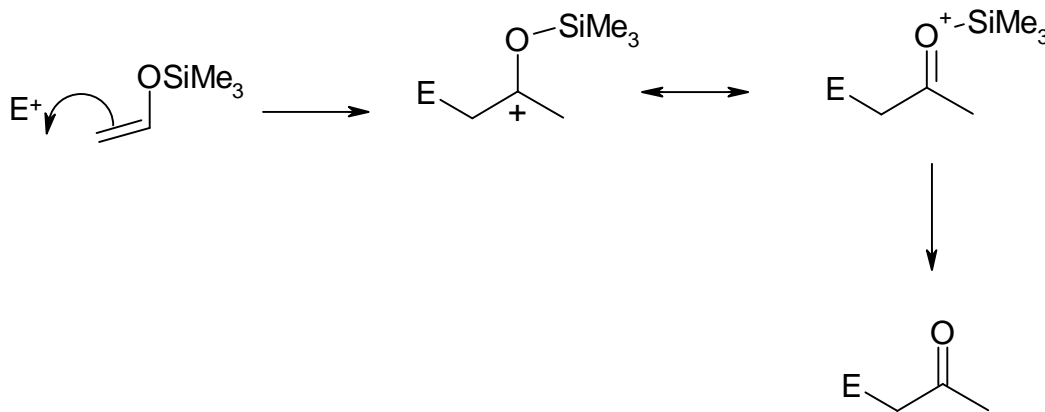
Some reactions of silyl enol ethers:



also similarly

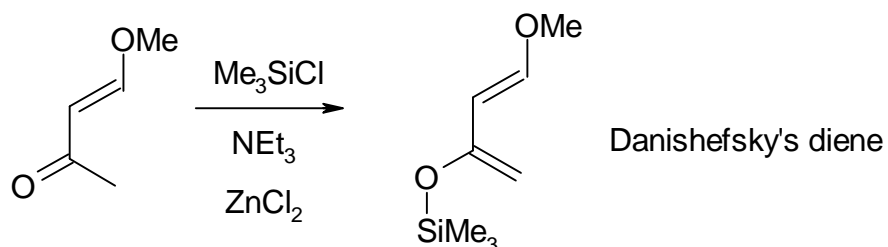
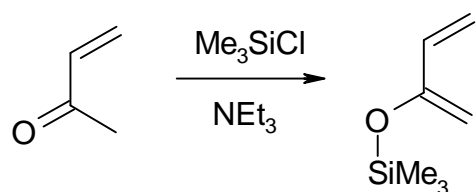


They also react very cleanly and strongly with electrophiles, especially if the electrophilicity of the alkylating agent is enhanced by the presence of a lewis acid (synthesis of Gingerol).

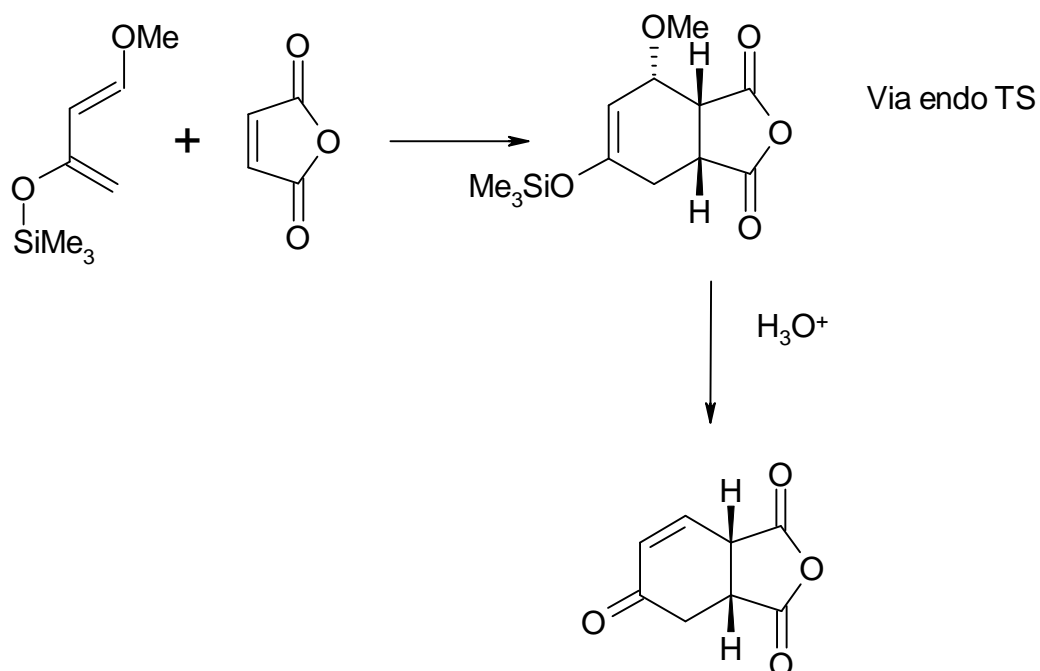


2-Trimethylsilyloxybuta-1,3-dienes

These may be used as the 4π component in Diels-Alder reactions, and are generally prepared via the following route:

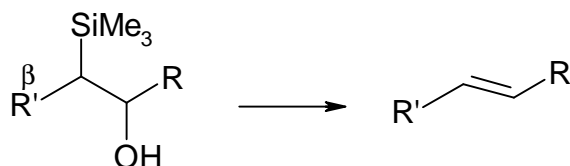


Due to their inherent polarity these 1,3-dienes undergo REGIOSPECIFIC Diels-Alder reactions.



4. Alkene Synthesis- Peterson Olefination

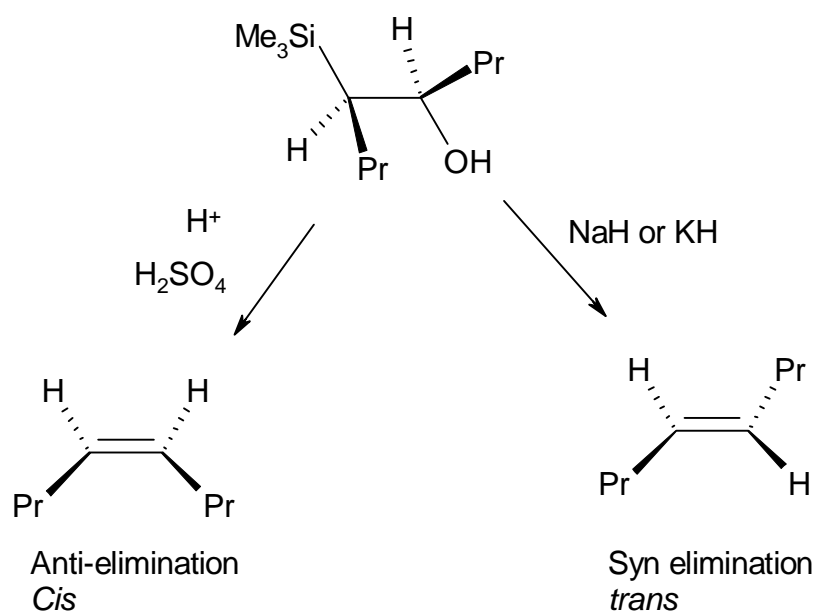
β -hydroxysilanes are key compounds in the synthesis of alkenes



The β -hydroxysilanes can be generated by the addition of

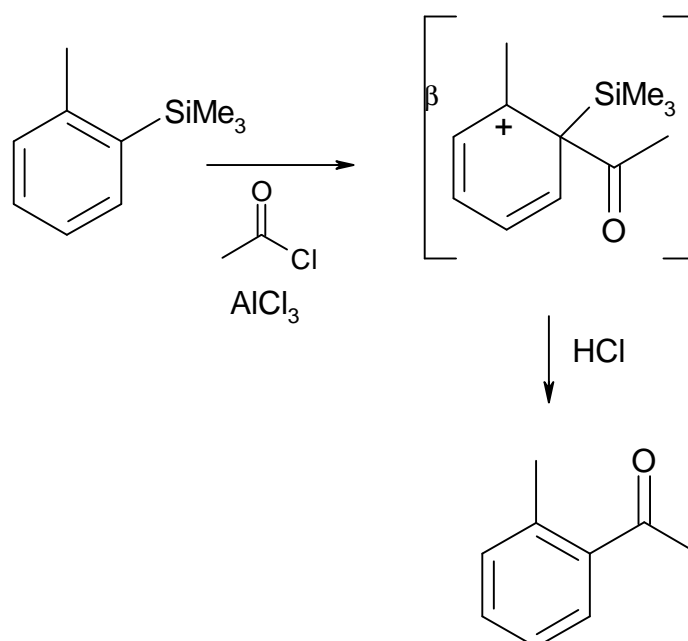
- 1 α -metalated silanes to carbonyl compounds
- 1 dialkylcuparates to α,β -epoxysilanes
- 1 hydride sources or organometallic reagents to β -ketosilanes

The generation of the alkene (Peterson Olefination) follows two distinct pathways depending on whether the elimination is done under acidic or basic conditions.



5. Arylsilanes

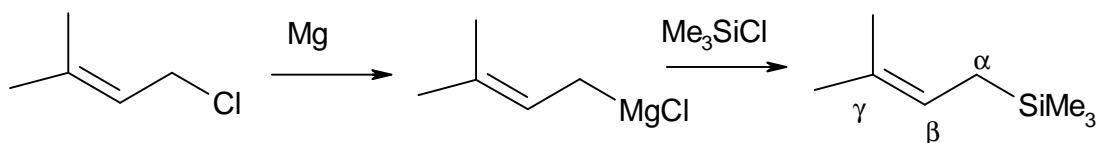
These are normally prepared by quenching an aryl-metal system with a chlorosilane. They readily undergo reactions with electrophiles known as 'ipso' desilylation. Here the incoming electrophile replaces a silyl substituent on an aromatic nucleus:



The attack at the carbon bearing the silyl group is preferred since the TS intermediate carbocation is stabilised by the Si.

6. Allylsilanes

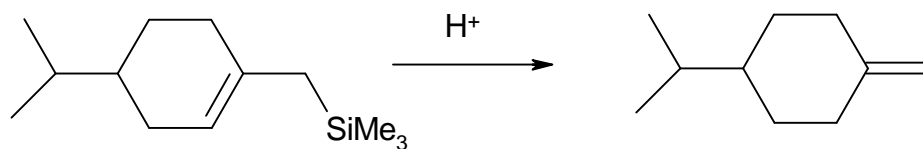
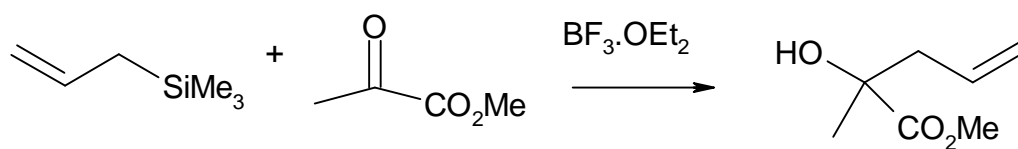
The silylation of a metal-allyl species is the direct method available for making these types of silanes.



Another route is via a Wittig type reaction.

Again these systems react very smoothly with electrophiles at their γ carbon, since the attack leads to a β carbocation.

They react with a wide range of electron deficient species:



Used in the synthesis of cyclopenten-4-ols