SOS Science of Synthesis

Knowledge Updates 2020/1

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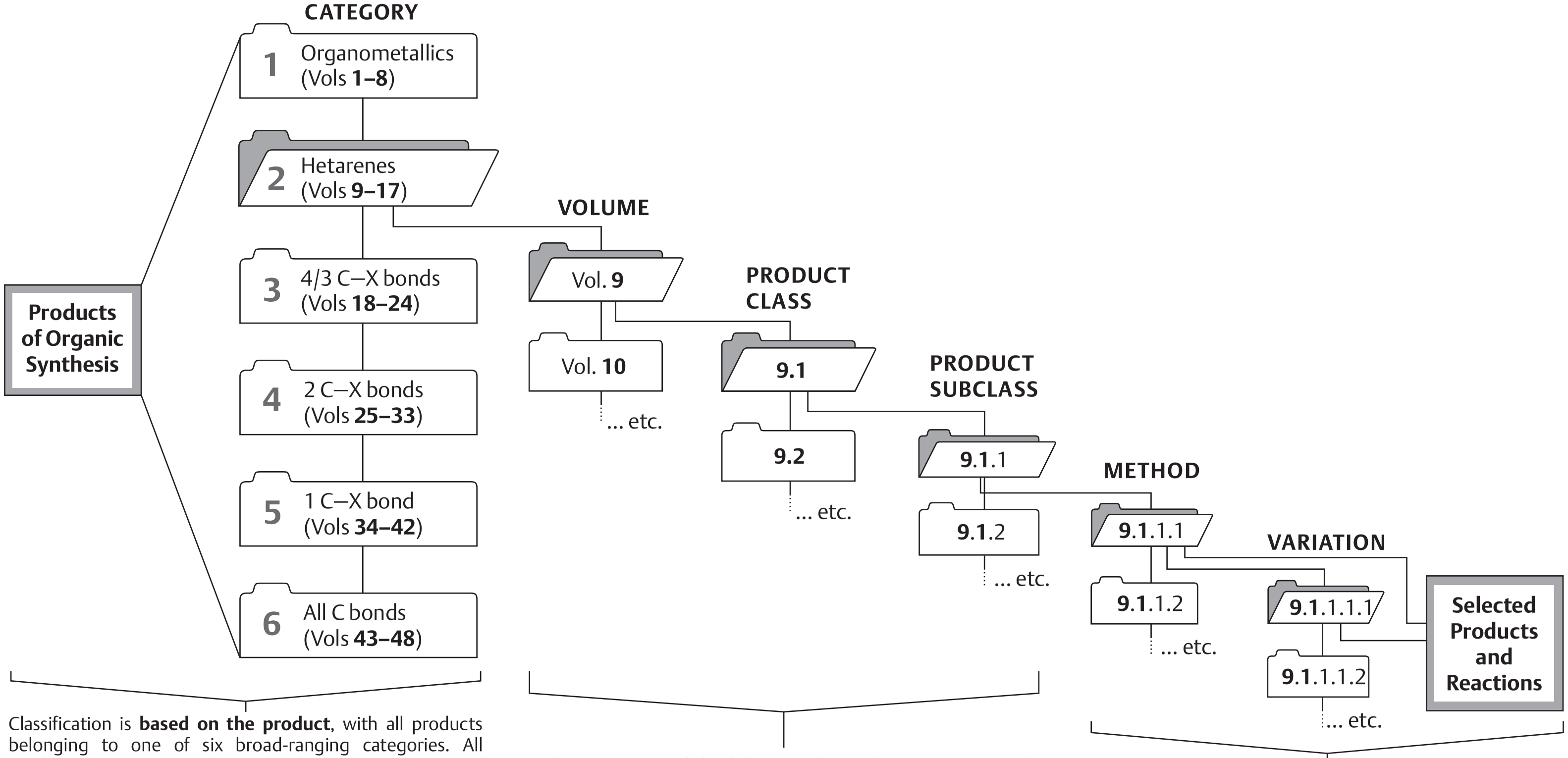
Organizational Structure of Science of Synthesis*



Classification is **based on the product**, with all products belonging to one of six broad-ranging categories. All products occupy a strict hierarchical position in Science of Synthesis, defined according to the classification principles*. Products in Categories 3–6 are organized according to oxidation state, with products containing the greatest number of carbon–heteroatom (C—X) or C—C π-bonds to a single carbon occupying the highest positions (e.g., carboxylates, enolates, and alcoholates are covered in Categories 3, 4, and 5, respectively).

Each category is subdivided into volumes (see opposing page), each of which is devoted to discrete groupings of compounds called **product classes** (e.g., “Thiophenes” is Product Class 10 of Volume 9). Product classes may be further subdivided into **product subclasses**, (e.g., “Thiophene 1,1-Dioxides” is Product Subclass 3 of Product Class 10 of Volume 9). Consequently, the relationship between heading name and heading number varies below product class level within individual volumes.

For each product class or subclass, a number of methods are described for synthesizing the general product type. Often there are variations on a method given. Both methods and variations contain experimental procedures with relevant background information and literature references. **Selected products and reactions** display the scope and limitations of the methods.

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* A complete description of the full classification principles can be found in the **Science of Synthesis Guidebook.**

CATEGORY	UPDATED VOLUMES									
1 Organometallics (Vols **1–8**)	1	2	3	4	5	6	7	8a	8b	
2 Hetarenes (Vols **9–17**)	9	10	11	12	13	14	15	16	17	
3 4/3 C—X bonds (Vols **18–24**)	18	19	20a	20b	21	22	23	24		
4 2 C—X bonds (Vols **25–33**)	25	26	27	28	29	30	31a	31b	32	33
5 1 C—X bond (Vols **34–42**)	34	35	36	37	38	39	40a	40b	41	42
6 All C bonds (Vols **43–48**)	43	44	45a	45b	46	47a	47b	48		

4	Compounds of Group 15 (As, Sb, Bi) and Silicon Compounds
14	Six-Membered Hetarenes with One Chalcogen
16	Six-Membered Hetarenes with Two Identical Heteroatoms
21	Three Carbon—Heteroatom Bonds: Amides and Derivatives; Peptides; Lactams
40a	Amines and Ammonium Salts
48	Alkanes

* Detailed listings of product classes and subclasses, methods, and variations can be found in the **Table of Contents** sections of every volume.

Science of Synthesis

Science of Synthesis is the authoritative and comprehensive reference work for the entire field of organic and organometallic synthesis.

Science of Synthesis presents the important synthetic methods for all classes of compounds and includes:

- Methods critically evaluated by leading scientists
- Background information and detailed experimental procedures
- Schemes and tables which illustrate the reaction scope

Science of Synthesis

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Preface

As the pace and breadth of research intensifies, organic synthesis is playing an increasingly central role in the discovery process within all imaginable areas of science: from pharmaceuticals, agrochemicals, and materials science to areas of biology and physics, the most impactful investigations are becoming more and more molecular. As an enabling science, synthetic organic chemistry is uniquely poised to provide access to compounds with exciting and valuable new properties. Organic molecules of extreme complexity can, given expert knowledge, be prepared with exquisite efficiency and selectivity, allowing virtually any phenomenon to be probed at levels never before imagined. With ready access to materials of remarkable structural diversity, critical studies can be conducted that reveal the intimate workings of chemical, biological, or physical processes with stunning detail.

The sheer variety of chemical structural space required for these investigations and the design elements necessary to assemble molecular targets of increasing intricacy place extraordinary demands on the individual synthetic methods used. They must be robust and provide reliably high yields on both small and large scales, have broad applicability, and exhibit high selectivity. Increasingly, synthetic approaches to organic molecules must take into account environmental sustainability. Thus, atom economy and the overall environmental impact of the transformations are taking on increased importance.

The need to provide a dependable source of information on evaluated synthetic methods in organic chemistry embracing these characteristics was first acknowledged over 100 years ago, when the highly regarded reference source **Houben–Weyl Methoden der Organischen Chemie** was first introduced. Recognizing the necessity to provide a modernized, comprehensive, and critical assessment of synthetic organic chemistry, in 2000 Thieme launched **Science of Synthesis, Houben–Weyl Methods of Molecular Transformations**. This effort, assembled by almost 1000 leading experts from both industry and academia, provides a balanced and critical analysis of the entire literature from the early 1800s until the year of publication. The accompanying online version of **Science of Synthesis** provides text, structure, substructure, and reaction searching capabilities by a powerful, yet easy-to-use, intuitive interface.

From 2010 onward, **Science of Synthesis** is being updated quarterly with high-quality content via **Science of Synthesis Knowledge Updates**. The goal of the **Science of Synthesis Knowledge Updates** is to provide a continuous review of the field of synthetic organic chemistry, with an eye toward evaluating and analyzing significant new developments in synthetic methods. A list of stringent criteria for inclusion of each synthetic transformation ensures that only the best and most reliable synthetic methods are incorporated. These efforts guarantee that **Science of Synthesis** will continue to be the most up-to-date electronic database available for the documentation of validated synthetic methods.

Also from 2010, **Science of Synthesis** includes the **Science of Synthesis Reference Library**, comprising volumes covering special topics of organic chemistry in a modular fashion, with six main classifications: (1) Classical, (2) Advances, (3) Transformations, (4) Applications, (5) Structures, and (6) Techniques. Titles will include *Stereoselective Synthesis*, *Water in Organic Synthesis*, and *Asymmetric Organocatalysis*, among others. With expert-evaluated content focusing on subjects of particular current interest, the **Science of Synthesis Reference Library** complements the **Science of Synthesis Knowledge Updates**, to make **Science of Synthesis** the complete information source for the modern synthetic chemist.

The overarching goal of the **Science of Synthesis** Editorial Board is to make the suite of **Science of Synthesis** resources the first and foremost focal point for critically evaluated information on chemical transformations for those individuals involved in the design and construction of organic molecules.

Throughout the years, the chemical community has benefited tremendously from the outstanding contribution of hundreds of highly dedicated expert authors who have devoted their energies and intellectual capital to these projects. We thank all of these individuals for the heroic efforts they have made throughout the entire publication process to make **Science of Synthesis** a reference work of the highest integrity and quality.

The Editorial Board September 2018

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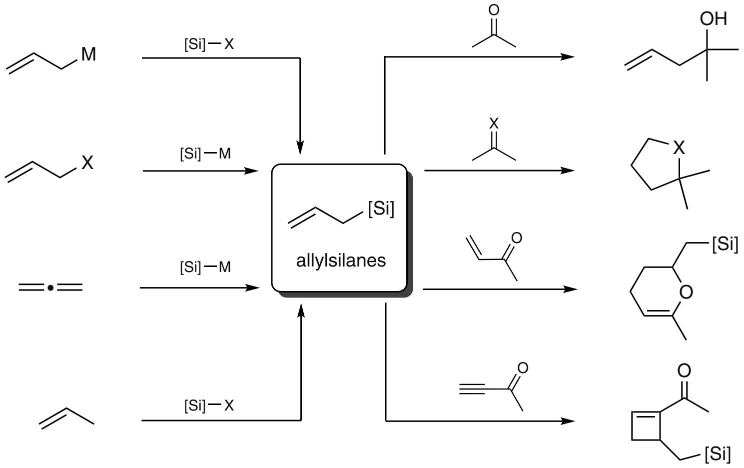
Abstracts

2020 p 1

4.4.40.72 **Allylsilanes**

K. Okamoto and K. Ohe

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 4.4.40), which describes methods for the synthesis of allylsilanes as well as their applications in organic synthesis. This update summarizes the recently reported (from 2001 to 2018) efficient synthetic methods and synthetic applications of allylsilanes involving transition-metal-catalyzed reactions.



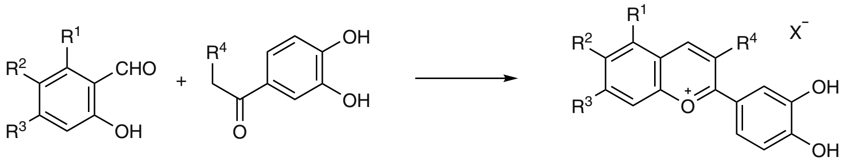
Keywords: allylsilanes · vinylsilanes · alkenes · allenes · dienes · silanes · carbonyl compounds · cycloaddition reactions · organosilicon chemistry · transition-metal catalysis

2020 p 159

14.2.5 **Benzopyrylium Salts**

F. Wu and S. Zhu

This chapter is an update to the earlier *Science of Synthesis* contribution describing methods for the synthesis of benzopyrylium salts (1-benzopyrylium salts, 2-benzopyrylium salts, and dibenzo[*b*,*e*]pyrylium salts). Classical routes to benzopyrylium salts involve intermolecular or intramolecular cyclization, aromatization, and oxidation processes, while recent developments with alternative approaches are also included.



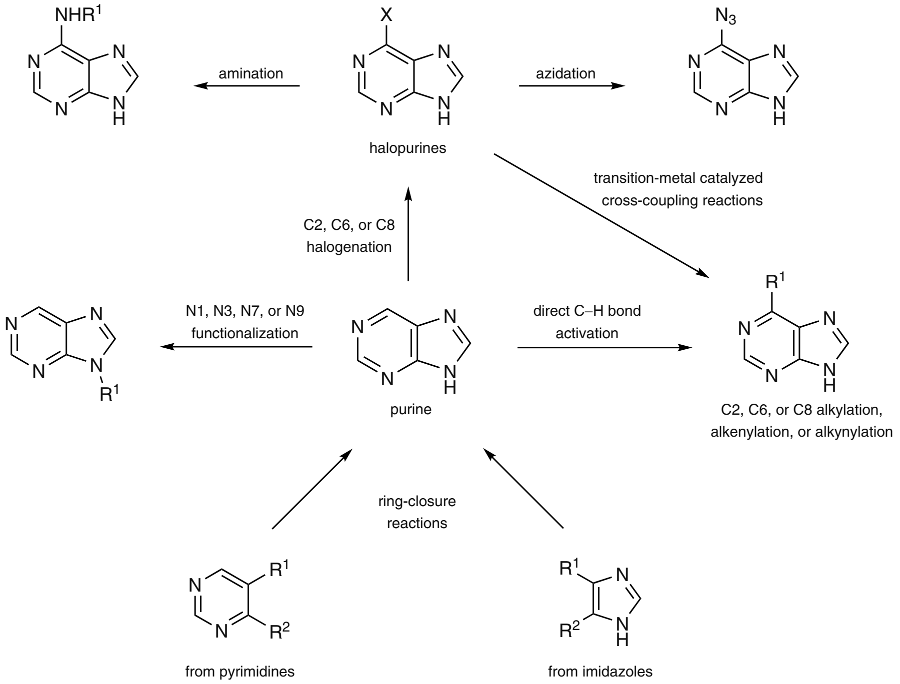
Keywords: benzopyrylium · flavylium · xanthylium · chromenium · cyclization · condensation · oxidation

2020 p 195

16.17.7 Purines

Y. Liang, Z. Wen, M. Cabrera, A. H. Howlader, and S. F. Wnuk

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 16.17) describing methods for the synthesis and chemical modification of purine and purine derivatives. It focuses on the literature published in the period 2002–2019, with a particular emphasis on regioselective direct C—H functionalization of purines, transition-metal-catalyzed cross-coupling reactions of halopurines, and synthesis of purine analogues, including azidopurines, by exchange of substituents.



Keywords: adenines · alkenylation · alkylation · alkynylation · amination · arylation · azidopurines · Buchwald–Hartwig reaction · carbon–carbon coupling · C—H bond activation · click reactions · cross-coupling reactions · cyclization · double C—H activation · fluorination · fused purines · guanines · halogen-exchange reactions · halogenation · halopurines · hypoxanthines · imidazoles · Negishi coupling · nucleosides · organometallic reagents · palladium catalysts · purines · pyrimidines · radical reactions · ring closure · Sonogashira coupling · Stille coupling · Suzuki–Miyaura coupling · transition metals

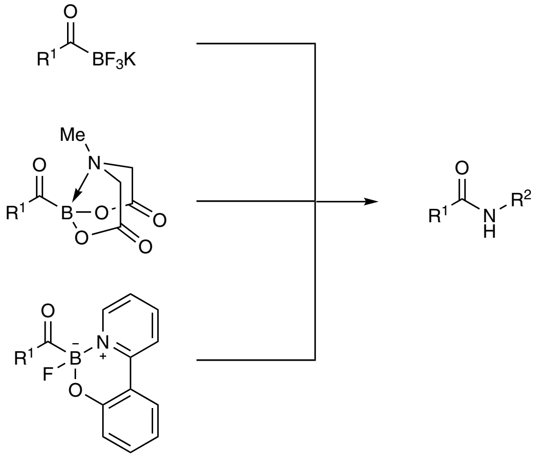
New — p 375 —

21.1.7 Synthesis of Amides from Acylboron Compounds

A. Osuna Gálvez and J. W. Bode

Recently, acylboronates have been shown to be applicable in the fast and chemoselective synthesis of amides. The methods covered in this review include the use of potassium acyltrifluoroborates (KATs), *N*-methyliminodiacetyl (MIDA) acylboronates, and monofluoro(acyl)boronates.

Acylboronates are, in general, bench-stable solids that can be easily handled in the laboratory. Among them, potassium acyltrifluoroborates stand out as remarkably stable salts that resist a variety of reaction conditions including acid, base, and heating. *N*-Methyliminodiacetyl acylboronates have the advantage of being amenable to purification by column chromatography and they exhibit high reactivity in amide ligation, but are limited by their poor stability under aqueous conditions. Monofluoro(acyl)boronates lie in between the above two classes, having acceptable half-life values in solution and improved overall reactivities compared to potassium acyltrifluoroborate reagents.



Keywords: acylboronates · amides · potassium acyltrifluoroborates (KATs) · *N*-methyliminodiacetyl acylboronates (MIDA boronates) · monofluoro(acyl)boronates · amide bond formation · azides · hydroxylamines · *N*-chloroamines

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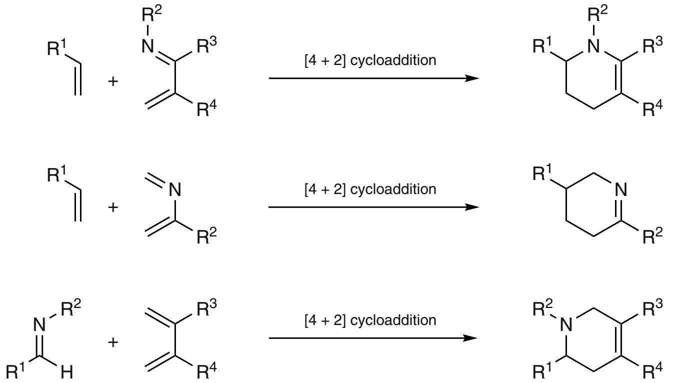
40.1.1.3.3.6 Synthesis of Amines by Pericyclic Reactions Involving C=N Units

W. Maison

The synthesis of nitrogen heterocycles, such as piperidines and tetrahydroquinolines, with high chemo-, regio-, and stereoselectivity can be achieved via cycloaddition reactions that involve imine derivatives either as dienes or dienophiles. This topic was previously covered in Section 40.1.1.3.3, to which this chapter is an update, covering the literature from 2008 to 2019. The field has seen significant advances in recent years; this is particularly true for catalytic, enantioselective variants and new hetero-Diels–Alder variants using aza-*o*-quinone methides as reactive 1-azabutadienes. Both topics are therefore a special focus of this update.



Keywords: aza-Diels–Alder reactions · imines · dienes · dienophiles · pericyclic reactions · piperidines · tetrahydroquinolines · [4 + 2] cycloaddition · Povarov reactions · Lewis acid catalysis · Brønsted acid catalysis · stereoselective synthesis

New p 425

48.1.6.4 Alkane Metathesis

G. Liu and Z. Huang

Alkane metathesis is a class of chemical reaction in which alkanes are covalently rearranged and exchange carbon atoms to form a new distribution of alkane products. The process involves both cleavage and formation of C—H and C—C bonds, and usually proceeds through a sequence containing dehydrogenation of alkanes to form alkenes, alkene (olefin) metathesis, and hydrogenation of the new alkenes. Both single-site systems and tandem dual-catalytic systems have been developed to effect this process. Alkane metathesis has been applied in the transformation of medium-weight alkanes into a mixture of longer and shorter alkanes, upgrading short-chain alkanes, and for the degradation of polyethylenes.

$$C_mH_{2m+2} + C_nH_{2n+2} \longrightarrow C_{m+x}H_{2(m+x)+2} + C_{n-x}H_{2(n-x)+2}$$

Keywords: alkanes · catalysis · dehydrogenation · iridium · metathesis

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4.4.40.72 **Allylsilanes (Update 2020)**

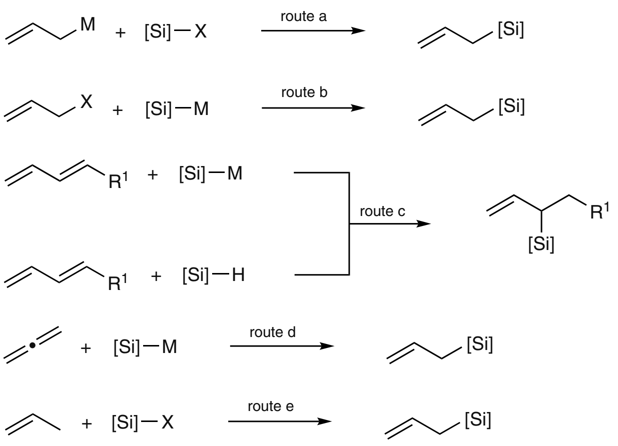
K. Okamoto and K. Ohe

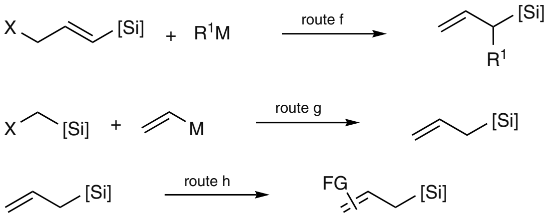
General Introduction

In synthetic organic chemistry, organosilicon compounds have been widely used for the construction of complex molecules since the discovery of useful C—C bond forming reactions such as the Sakurai–Hosomi allylation in the 1970s. Allylsilanes are recognized as one of the most important classes of organosilicon compounds and have been well studied until now.[1–16]

The synthetic methods for allylsilanes can be divided into several reaction types (Scheme 1). The simplest approaches are the silylation of allylmetal reagents and the allylation of silylmetal reagents, which are complementary to each other (routes a and b, respectively). Although these methods can provide simple allylsilanes selectively, they generally might not be suitable for the preparation of functionalized allylsilanes because of the high reactivities of allylmetal or silylmetal reagents. However, there are some exceptions that employ transition-metal-catalyzed allylic silylation using more stable silylmetal reagents such as silylboranes, which can provide wider reaction scope. Different approaches using transition-metal catalysts are based on the catalytic hydrosilylation or silylmetalation of 1,3-dienes or 1,2-dienes (allenes) to give allylsilanes (routes c and d, respectively). The regioselectivity of these reactions can be highly controlled by the skillful choice of metals and ligands. Recently, the synthesis of allylsilanes based on transition-metal-catalyzed direct silylation of simple alkenes has also been reported (route e). Vinylsilanes or (silylmethyl)metal reagents can be used as building blocks for the synthesis of allylsilanes (routes f and g, respectively). Transformation of simple allylsilanes by direct functionalization has also emerged as a preparative method for more complicated allylsilanes (route h). Skeletal rearrangements of the alkenic structures bearing silyl moieties are also used for the synthesis of allylsilanes.

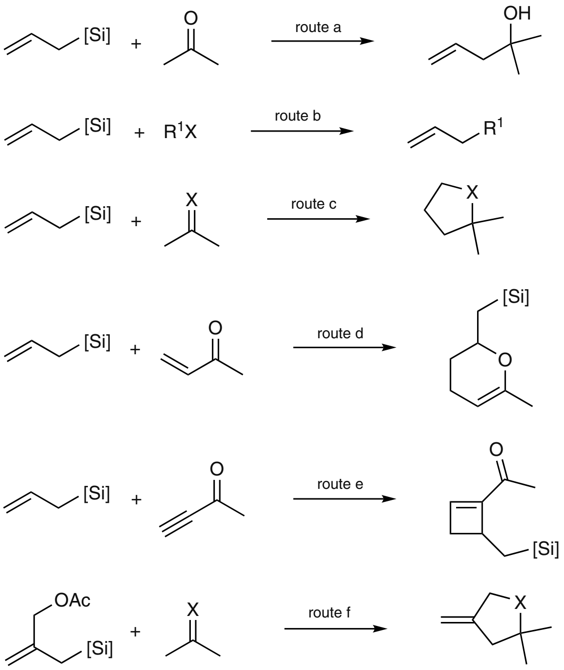
Scheme 1 Synthesis of Allylsilanes





The most representative reaction of allylsilanes is the allylation of carbonyl compounds (Scheme 2; route a). Sakurai–Hosomi allylation reactions represent this method. Allyl–alkyl coupling using allylsilanes as allylmetal reagents is also known as a tool for the synthesis of terminal alkenes (route b). Allylation of carbonyl compounds usually leads to loss of the silicon moieties in the reaction products because the reaction cleaves the C—Si bond and forms an O—Si bond. Recent efforts have enabled cycloaddition reactions with installation of silicon moieties from allylsilanes remaining in the products (routes d and e). This type of cycloaddition reaction is highly atom-efficient and more useful because the organosilicon moieties can be employed for further transformations such as Tamao–Fleming oxidation to make complex molecules. The other type of cycloaddition, palladium-catalyzed trimethylenemethane cycloaddition using β-acetoxymethyl allylsilanes as precursors, is also a useful type of reaction, giving five- or six-membered cyclic compounds (route f). Overall, recent progress based on catalyst designs and reaction designs involving allylsilanes has increasingly achieved unprecedented high stereoselectivity and product selectivity.

Scheme 2 Reactions of Allylsilanes



In this update, recent progress (from 2001 to 2018) regarding synthetic methods of allylsilanes and their synthetically useful applications are summarized. For the previous *Science of Synthesis* review of allylsilanes, see Section 4.4.40.