



**Science of
Synthesis**

Knowledge Updates 2018/4

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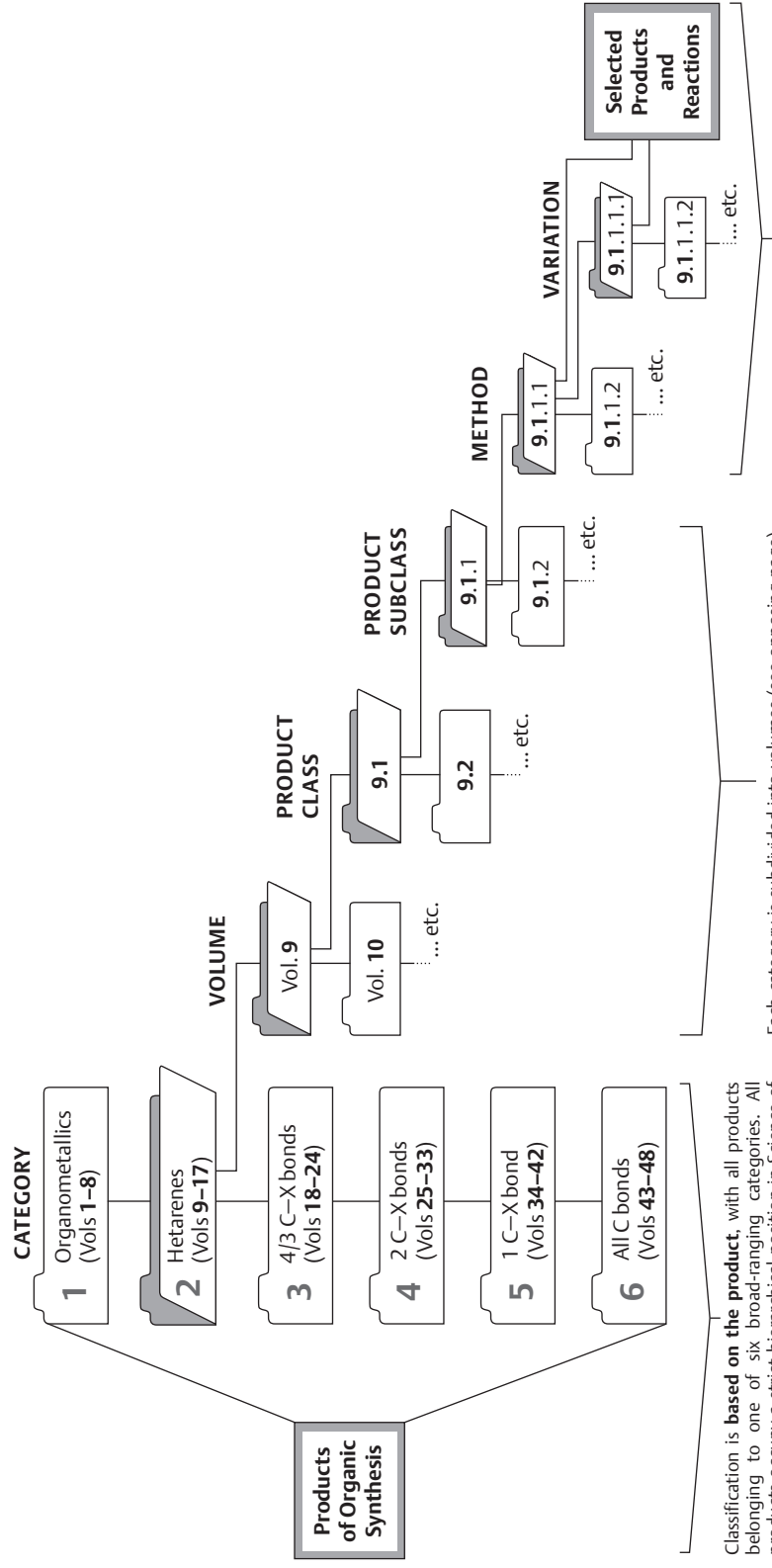
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Organizational Structure of Science of Synthesis*



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.

* 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 Heterarenes (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
5 1 C–X bond (Vols 34–42)	34	35	36	37	38	39	40a	40b	41
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

18 Four Carbon–Heteroatom Bonds: X–C≡X, X=C=X, X₂C=X, CX₄

33 Ene–X Compounds (X = S, Se, Te, N, P)

37 Ethers

* 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



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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

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Abstracts

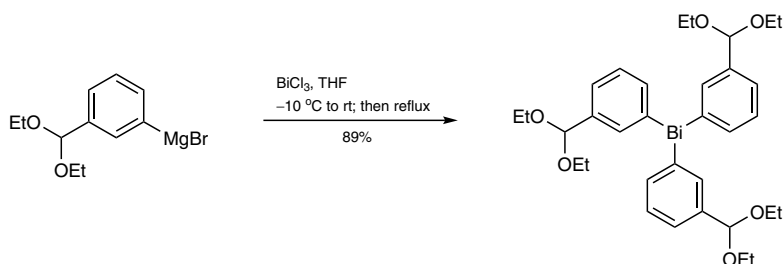
2018

p 1

4.3.15 Bismuth Compounds

A. Gagnon, E. Benoit, and A. Le Roch

This chapter is an update to the earlier *Science of Synthesis* contribution describing methods for the synthesis of organobismuth compounds and their use in organic synthesis. Organobismuth compounds are organometallic species that contain a carbon–bismuth bond. These species have been used as catalysts and reagents in various reactions that lead to the formation of carbon–carbon, carbon–nitrogen, carbon–oxygen, carbon–sulfur, and carbon–selenium bonds.



Keywords: arylation · bismuth compounds · carbon–metal bonds · copper catalysts · cross-coupling reactions · heterocycles · organometallic reagents · palladium catalysts · transition metals

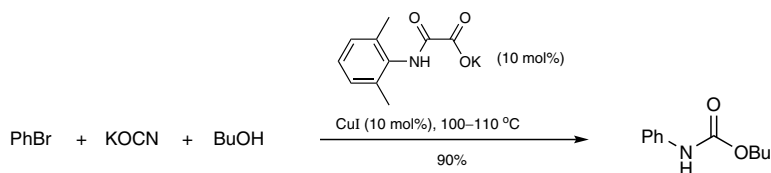
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18.6.12 Acyclic and Cyclic Carbamic Acids and Esters, and Their Sulfur, Selenium, Tellurium, and Phosphorus Analogues

J. Podlech

This chapter is an update to the earlier *Science of Synthesis* contribution on the preparation of acyclic and cyclic carbamates, thiocarbamates, selenocarbamates, tellurocarbamates, and phosphinecarboxylates, as well on their applications in organic synthesis. It focuses on the literature published in the period 2013–2017.



Keywords: carbamates · isocyanates · isothiocyanates · oxazinones · oxazolidinones · phosphorus compounds · selenium compounds · tellurium compounds · thiazines · thiazolidines · thiocarbamates

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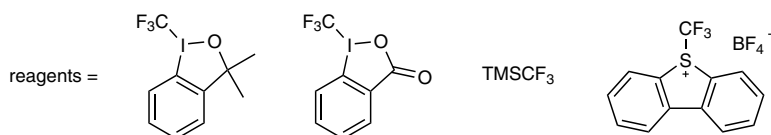
18.15.8 **Tetraheterosubstituted Methanes with a Carbon–Halogen Bond**

M. Kleoff, K. Omoregbee, and R. Zimmer

In this chapter, recent methods for the preparation and elaboration of various substituted halomethanes are summarized. In addition to updates on classical methods, recently developed procedures employing new fluorinating agents, such as Togni's reagents, are also presented. These methods are also put in the context of the synthesis of biologically active compounds.



X = O, S, Se, Te, N, P



Keywords: trifluoromethylation · trifluoromethylsulfanylation · Togni's reagents · Selectfluor · tetrahalomethanes · Umemoto's reagent · Ruppert–Prakash reagent · PhenoFluor · trifluoromethylselenylation

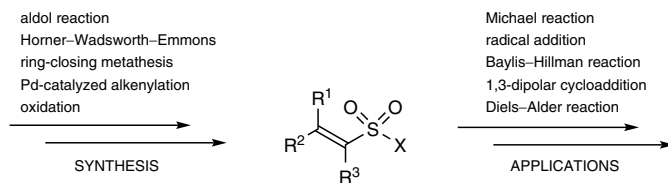
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33.1.1.2 **Alk-1-enesulfonic Acids and Derivatives**

R. Kawęcki

This chapter is an update to the earlier *Science of Synthesis* contribution describing methods for the preparation of alk-1-enesulfonic acids and derivatives and their application in synthesis. This update focuses on methods published since 2004.

X = OR⁴, NR⁴₂, halogen

Keywords: sulfonic esters · sulfonates · sulfonic acid amides · sulfonamides · sulfonic acid chlorides · sulfonyl chlorides · vinyl compounds

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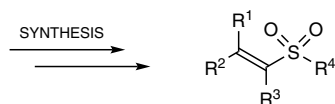
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33.1.2.2 **Alk-1-enyl Sulfones**

R. Kawęcki

This chapter is an update to the earlier *Science of Synthesis* contribution describing methods for the preparation of alk-1-enyl sulfones. This update focuses on methods published since 2004.



Keywords: sulfones · sulfonyl compounds · allenyl compounds · vinyl compounds · sulfonylation · sulfonyl carbanions · oxidation

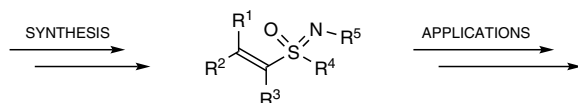
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33.1.3.2 **S-Alk-1-enylsulfoximides**

R. Kawęcki

This chapter is an update to the earlier *Science of Synthesis* contribution describing methods for the preparation of alk-1-enylsulfoximides. This update focuses on methods published since 2004. It also covers the application of alk-1-enylsulfoximides in organic synthesis.



Keywords: sulfoximides · vinyl compounds · imination · Michael addition · furans

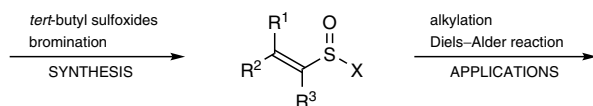
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33.1.4.2 **Alk-1-enesulfinic Acids and Derivatives**

R. Kawęcki

This chapter is an update to the earlier *Science of Synthesis* contribution describing methods for the preparation of alk-1-enesulfonates and alk-1-enesulfinamides and their applications in organic synthesis. This update focuses on methods published since 2004.

X = OR⁴, NR⁴₂

Keywords: sulfonates · sulfinic acid amides · sulfinamides · sulfinyl compounds · vinyl compounds · sulfoxides · sulfones

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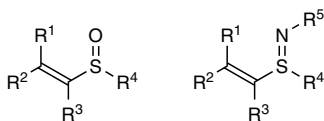
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33.1.5.2 **Alk-1-enyl Sulfoxides, Sulfimides, and Related Compounds**

R. Kawęcki

This chapter is an update to the earlier *Science of Synthesis* contribution describing methods for preparation of alk-1-enyl sulfoxides and sulfimides. It focuses on methods published since 2004.



Keywords: sulfoxides · sulfimides · vinyl compounds · sulfonylation · Heck reaction · kinetic resolution · asymmetric synthesis · oxidation

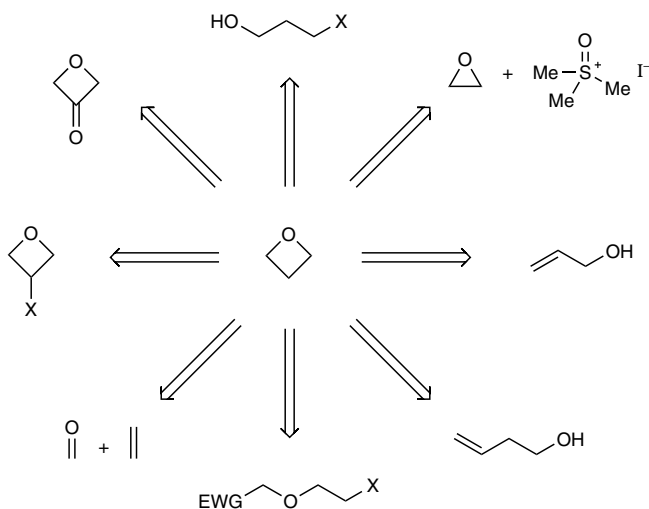
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37.3 **Oxetanes and Oxetan-3-ones**

R. A. Croft and J. A. Bull

This is a completely revised chapter on the synthesis of oxetanes and oxetan-3-ones, covering the literature up to early 2018. The last 10 years has seen many new approaches to the synthesis of oxetanes, prompted by increased interest in the use of oxetane derivatives in medicinal chemistry. Developments include cyclization methods for ring formation, as well as functionalization of oxetane-containing building blocks.



Keywords: oxetanes · oxetanones · oxygen heterocycles · cyclization · Williamson ether synthesis · Paternò-Büchi photocycloaddition · carbon–oxygen bonds · four-membered rings · carbon–oxygen bond formation · carbon–carbon bond formation

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Volume 18:
**Four Carbon—Heteroatom Bonds: $X-C\equiv X$, $X=C=X$,
 $X_2C=X$, CX_4**

18.6	Product Class 6: Acyclic and Cyclic Carbamic Acids and Esters, and Their Sulfur, Selenium, Tellurium, and Phosphorus Analogues	
18.6.12	Acyclic and Cyclic Carbamic Acids and Esters, and Their Sulfur, Selenium, Tellurium, and Phosphorus Analogues	2018
	J. Podlech	
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33.1 Product Class 1: Alk-1-enyl Sulfur Compounds

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