Abstracts

12.4.5 Benzimidazoles
F. M. Irudayanathan and S. Lee

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 12.4) describing methods for the synthesis of benzimidazoles, which are of interest due to their biological properties. It covers various strategies and protocols, the most common of which involves the condensation of a benzene-1,2-diamine with a one-carbon unit.

![Chemical structure of benzimidazole](image)

**Keywords:** benzimidazoles · benzene-1,2-diamines · anilines · amidines · condensation reactions · transition-metal catalysis · ring closure

30.1.3 Acyclic O,N-Acetals
S. Minakata and K. Kiyokawa

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 30.1.1), which describes synthetic methods and applications of acyclic O,N-acetals in organic synthesis. This update focuses on the enantioselective synthesis of acyclic O,N-acetals via asymmetric catalysis, which has witnessed significant advances in recent years. Also, recent applications of this class of compound in asymmetric organic synthesis are described.

![Chemical structure of acyclic O,N-acetal](image)

**Keywords:** acyclic O,N-acetals · hemiaminals · hemiaminal ethers · asymmetric catalysis
30.1.3  **Cyclic O,N-Acetals**
*S. Minakata and Y. Takeda*

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 30.1.2), which describes synthetic methods and applications of cyclic O,N-acetals in organic synthesis. This update focuses on the enantioselective synthesis of cyclic O,N-acetals via asymmetric catalysis, which has witnessed significant advances in recent years. Also, recent applications of this class of compound in asymmetric organic synthesis are described.

![Chemical structure](image)

**Keywords:** cyclic O,N-acetals · hemiaminal ethers · asymmetric catalysis

30.3.11  **Deprotection of S,S-Acetals**
*K. Sugamata and T. Sasamori*

The use of S,S-acetals is increasingly popular as a strategy for the protection of carbonyl groups because, in comparison to the analogous acetals, they are chemically inert under many reaction conditions; this is due to the chemical softness of sulfur atoms. In this context, the deprotection of S,S-acetals to reveal the carbonyl group is of great importance. This update describes methods for the deprotection of S,S-acetals published between 2007 and 2017, and provides an update to Section 30.3.7.

![Chemical structure](image)

**Keywords:** S,S-acetals · carbonyl groups · aldehydes · ketones · deprotection · hydrolysis · oxidation · Lewis acids · alkylation · halogenation · electron transfer
This update to *Science of Synthesis* Section 32.4 compiles methods for the synthesis of chloro-, bromo-, and iodoalkanes reported since 2007. Starting materials include alkenylmetal compounds, alkenes, haloalkanes, carbonyl compounds, enoic acids, alkynes, haloalkynes, and allenes, among others. The advantages and limitations of the different approaches and methods are discussed, and mechanisms are described briefly in order to rationalize regio- and stereoselectivities.

**Keywords:** alkenes · alkynes · allenes · aminohalogenation · carbonyl compounds · cyclopropanes · haloacylation · haloalkanes · haloalkenes · haloalkylation · haloarylation · halocyanation · haloformylation · halogenation · Hunsdiecker reaction · hydrohalogenation · olefination · organometallic compounds · vinyl halides · vinyl chlorides · vinyl bromides · vinyl boranes · vinyl iodides · vinyl silanes · vinyl stannanes · Wittig reaction
This chapter is an update to the earlier *Science of Synthesis* contribution (Section 33.1.13) describing methods for the synthesis of 2,3-dihydrothiophenes and their derivatives. The most common routes to 2,3-dihydrothiophenes involve ring-closing reactions, ring transformations, elimination processes, and elaboration of substituents attached to the 2,3-dihydrothiophene ring. The applications of 2,3-dihydrothiophenes and derivatives in organic synthesis are also included.

**Keywords:** 2,3-dihydrothiophenes · 2,3-dihydrothiophene 1-oxides · 2,3-dihydrothiophene 1,1-dioxides · 2,5-dihydrothiophene 1,1-dioxides · rearrangement reactions · multi-component condensation · cyclization · copper-catalyzed cascade cyclization · intramolecular Diels–Alder reaction

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 33.1.14) describing methods for the synthesis of 3,4-dihydro-2H-thiopyrans and their derivatives. The most common routes to 2H-thiopyrans, 4H-thiopyrans, 3,4-dihydro-2H-thiopyrans, 4H-1-benzothiopyrans, 1H-2-benzothiopyrans, 2H-1-benzothiopyrans, and their derivatives are based on ring-closure reactions, ring transformation, elimination process, and the elaboration of substituents attached to the thiopyran ring.

**Keywords:** 2H-thiopyrans · 4H-thiopyrans · 3,4-dihydro-2H-thiopyrans · 4H-1-benzothiopyrans · 1H-2-benzothiopyrans · 2H-1-benzothiopyrans · sigmatropic rearrangement · base-induced cyclization · hetero-Diels–Alder reaction · domino Knoevenagel/hetero-Diels–Alder reaction · intramolecular cyclization · radical cyclization · hydrothiolation of alkynes
This chapter is an update to the earlier Science of Synthesis contribution (Section 37.4.1), describing the synthesis of five-, six-, seven-, eight-, and ten-membered cyclic ethers with a double-bond at C3 (namely, oxacycloalk-3-enes). This update is focused on oxacyclization (C—O bond formation) approaches developed and published in the period 2007–2018.

**Keywords:** 2,5-dihydrofurans · 3,6-dihydro-2H-pyrans · 1,3-dihydrobenzo[c]furans · 1,3-dihydroisobenzofurans · 3,4-dihydro-1H-2-benzopyrans · \( \alpha \)-allenol cycloisomerization · oxa-Diels–Alder reaction · Prins cyclization · oxa-Michael cyclization

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### Metal-Catalyzed Synthesis of Peroxides

**B. Gnanaprakasam and M. B. Chaudhari**

This chapter provides an overview of the application of metal catalysts for the peroxidation, using hydroperoxides, of unactivated hydrocarbons, alkenes, and enynes as well as activated compounds such as various carbonyl compounds.

**Keywords:** peroxides · dialkyl peroxides · peroxidation · hydroperoxides · tert-butyl hydroperoxide · addition reactions · C—H functionalization · carboxylation · carbon—heteroatom bonds · transition-metal catalysis · electron transfer · radical reactions