Abstracts

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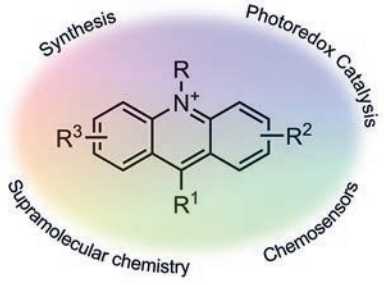
15.9.4 Synthesis and Applications of Acridinium Salts

V. Hutskalova and C. Sparr

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 15.9.3), covering selected methods for the preparation and the diverse fields of application of acridinium salts. The most important classical and recently published routes toward acridinium core construction are described and categorized according to key retrosynthetic disconnections. The utility of acridinium moieties in supramolecular chemistry is showcased by examples for various supramolecular switches containing this heterocyclic system. The application of acridinium salt derivatives as chemosensors for the detection of anionic species is also shown. Furthermore, the chapter features recent representative methods within the field of photoredox catalysis using acridinium salts as photocatalysts.



Keywords: acridinium salts · heterocycles · supramolecular chemistry · photochemistry · decarboxylation · trifluoromethylation · arynes · organometallic reagents · dehalogenation · nucleophilic aromatic substitution

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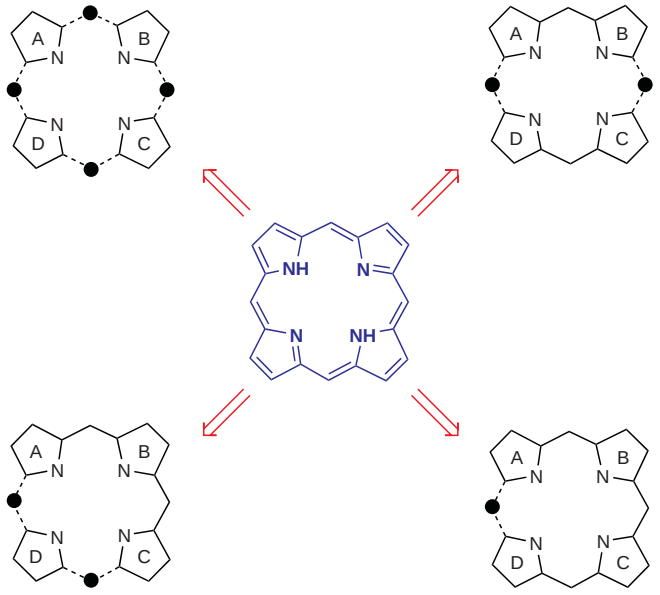
17.8.5 Porphyrins

N. Jux, F.-P. Montforts, and E. Haake

This chapter covers methods for the synthesis and transformations of porphyrins, and is an update to the earlier *Science of Synthesis* contribution Section 17.8.1. The focus is on the literature published in the period 2000–2021. The basic principles and strategies for the construction and modification of the porphyrin core are examined, with an emphasis on the most useful approaches reported in the past two decades.



Keywords: porphyrins · pyrroles · macrocycles · natural products · aldehydes · aromaticity · ring closure · total synthesis · acid catalysts · electrophilic substitution · aminoalkylation · Mannich reaction · Vilsmeier formylation

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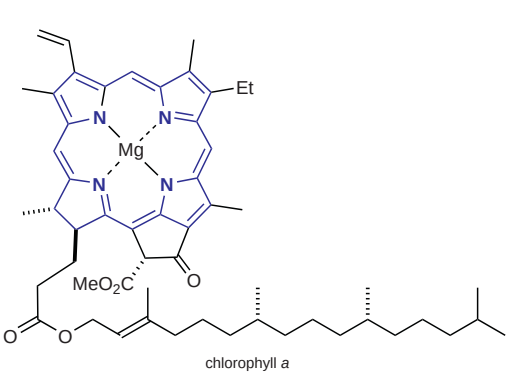
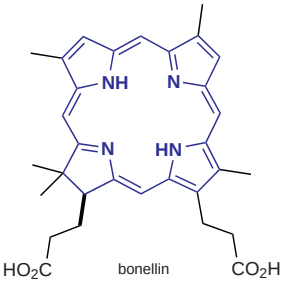
17.8.6 **Chlorins (Dihydroporphyrins)**

N. Jux, F.-P. Montforts, and E. Haake

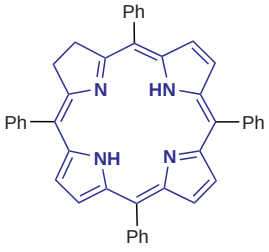
This is an update to the earlier *Science of Synthesis* contribution (Section 17.8.2.1) on chlorins, covering recent developments in reported methods for the synthesis and modifications of the chlorin core. The focus is mainly on the literature published in the period 2000–2021, and includes approaches for the synthesis of chlorins such as ring-closure reactions, oxidation or reduction of porphyrins, and cycloadditions.

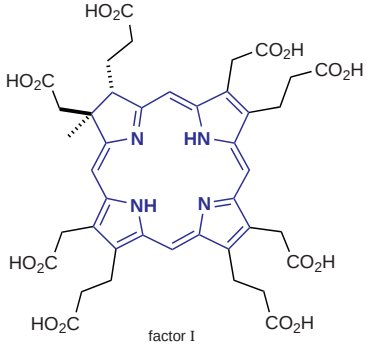


chlorophyll *a*



bonellin





factor I

Keywords: chlorins · porphyrins · pyrroles · pyrrolidines · aldimines · aromaticity · alkynylation · acylation · formylation · natural products · total synthesis · asymmetric synthesis · cross-coupling reactions · pinacol rearrangement · ring-closure reactions

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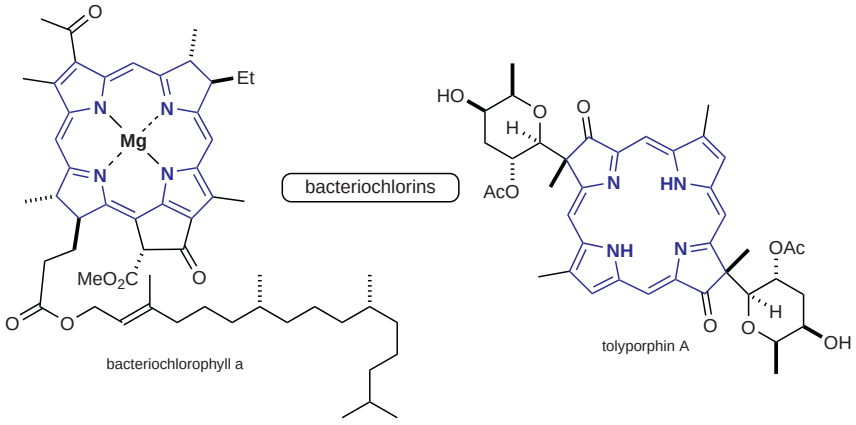
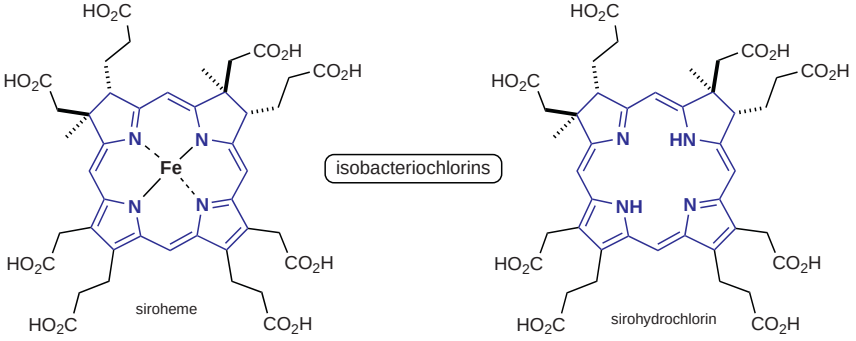
17.8.7 Bacteriochlorins and Isobacteriochlorins (Tetrahydroporphyrins), and Hexahydroporphyrins

N. Jux, F.-P. Montforts, and E. Haake

This update describes methods for the preparation and transformations of the tetrahydroporphyrin compounds bacteriochlorins and isobacteriochlorins, and also covers hexahydroporphyrin structures. The focus is mainly on the literature published in the period 2000–2021, and includes strategies such as ring-closure reactions and oxidation or reduction of porphyrins/chlorins.





Keywords: porphyrins · bacteriochlorins · isobacteriochlorins · tetrahydroporphyrins · hexahydroporphyrins · pyrroles · pyrrolidines · amidines · alkynes · nitro compounds · natural products · total synthesis · cross-coupling reactions · chirality · pinacol rearrangement · electrocyclic ring closure

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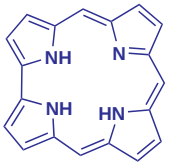
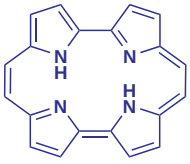
17.8.8 **Contracted, Isomeric, and Expanded Porphyrins and Carba and Hetero Analogues**

N. Jux, F.-P. Montforts, and E. Haake

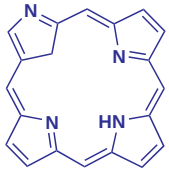
In this chapter, a range of porphyrinoid analogues and related macrocyclic structures are described and the key literature covering these types of compounds has been collated.



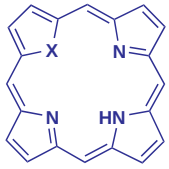
corrole



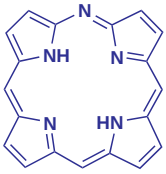
porphycene



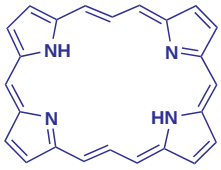
isoporphyrin
(*N*-confused porphyrin)



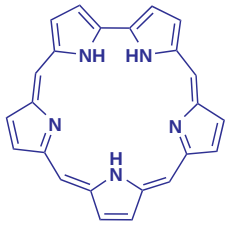
carba- and heteroporphyrins
[X = C, O, S, Se, P(Ar[1])]



meso-azaporphyrin



platyrin
[22]tetraphyrin-(3.1.3.1)



sapphyrin
[22]pentaphyrin-(1.1.1.1.0)

Keywords: porphyrins · corrins · corrole · porphycene · isoporphyrins · carbaporphyrins · heteroporphyrins · azaporphyrins · platyrin · tetraphyrins · pentaphyrins · pyrroles

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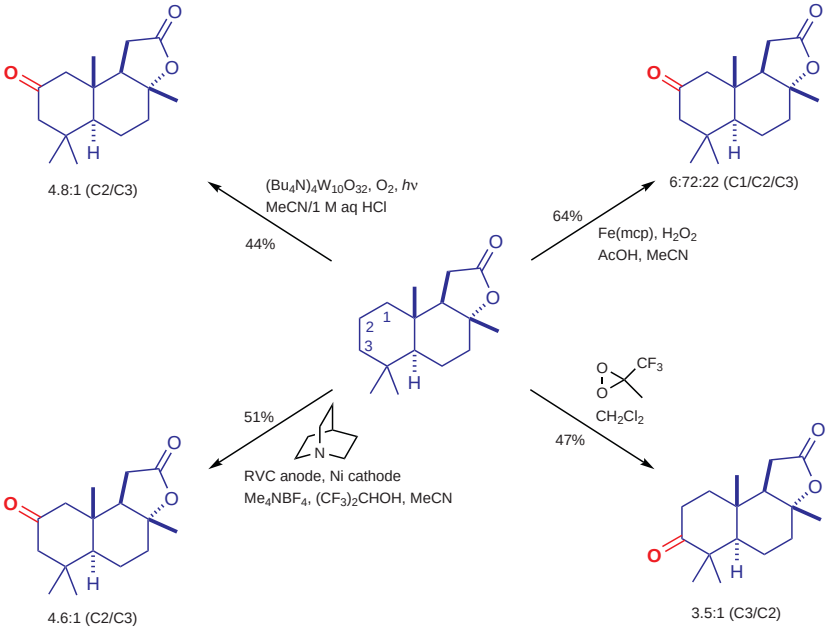
26.1.2.5 **Synthesis of Ketones by Oxidation of Alkanes**

V. C. S. Santana, L. S. Munaretto, and E. C. de Lucca, Jr.

This chapter is an update to *Science of Synthesis* Section 26.1.2, which included the synthesis of ketones by oxidation of alkanes. This contribution is focused on reports published during the period 2007–2020 that describe the synthesis of ketones by transition-metal catalysis, photochemically and electrochemically mediated methods, as well as the use of supported catalysts and metal-free oxidation of alkanes.



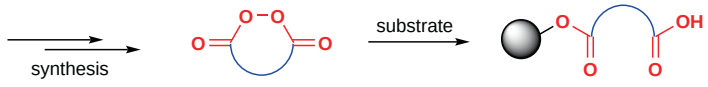
Keywords: alkanes · ketones · oxidation · transition metals · iron catalysts · manganese catalysts · homogeneous catalysis · heterogeneous catalysis · C—H activation · photooxidation · electrochemical oxidation · supported catalysis

New p 221

38.12 **Product Class 12: Cyclic Diacyl Peroxides**

Y. A. Barsegyan, V. A. Vil', N. C. O. Tomkinson, and A. O. Terent'ev

This chapter describes methods for the preparation of cyclic diacyl peroxides and their application as reagents in organic synthesis. Reaction of these peroxides with C=C and C—H compounds results in the selective formation of new C—O bonds.



Keywords: peroxides · oxidation · hydroxylation · dihydroxylation · oxyamination · acyloxylation · carbon—oxygen bonds · alkenes · arenes · carbonyl compounds

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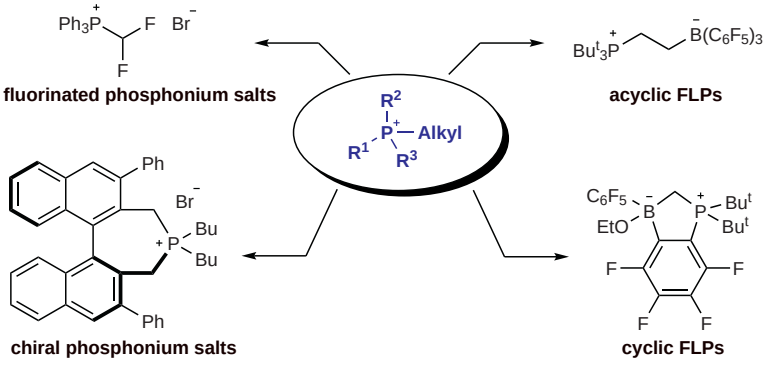
42.12.8 Alkylphosphonium Salts

T. Ayad, J.-L. Pirat, and D. Virieux

Phosphonium salts are compounds of great synthetic interest, both as reactants in numerous reactions and, more recently, as organocatalysts in enantioselective organic transformations and metal-free catalytic processes. This chapter is an update to the previously published Section 42.12 and is dedicated to the synthesis of alkylphosphonium salts, meaning that the phosphorus atom is connected to at least one alkyl substituent. The focus is on reports in the literature from 2010 to 2020. Key developments during this period that are covered include fluorinated phosphonium salts, phosphonium-based frustrated Lewis pairs (FLPs), and chiral alkylphosphonium salts. Advances in catalytic and asymmetric phase-transfer catalysis are also discussed.



Keywords: phosphonium salts · alkylation · ylides · fluorinated phosphonium salts · frustrated Lewis pairs · chiral phosphonium salts · organocatalysts · enantioselectivity · phase-transfer catalysis · P—C bond formation · electrocyclization

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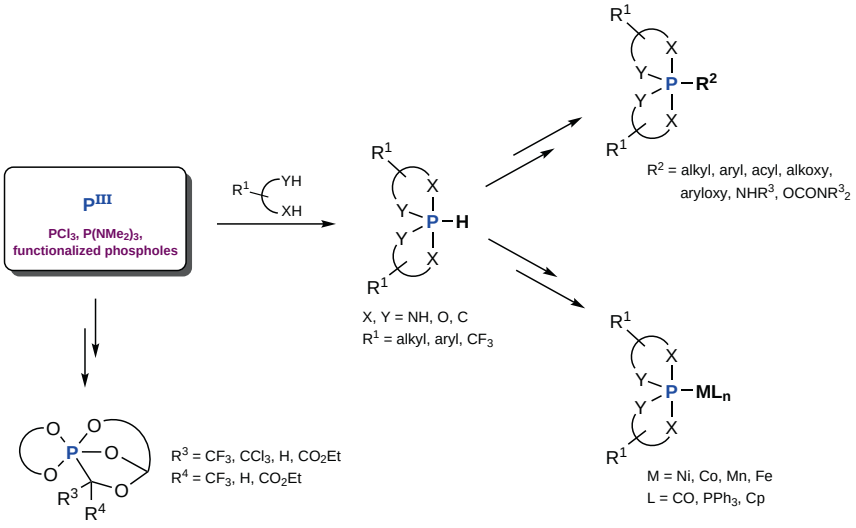
42.18.2 **Pentacoordinated Phosphoranes**

R. Pajkert and G.-V. Röschenthaler

This is an update to the previous *Science of Synthesis* chapter on pentacoordinated phosphoranes (Section 42.18), and covers methods for their synthesis and application published up to 2020. Due to the fact that the past years have seen a considerable number of papers including spirocyclic phosphoranes, reports on the synthesis have been limited to selected spirophosphoranes such as spirohydrophosphoranes, caged phosphoranes, or metallophosphoranes. In addition, some classical examples of the preparation of these types of compound are also discussed in this review.



Keywords: phosphoranes · condensation · tautomerization · bicyclic compounds · chiral compounds · Martin ligand · cascade reactions · cage phosphoranes · phosphoranides · substitution · metathesis · metallophosphoranes · apicophilicity · Atherton–Todd reaction · isomerization

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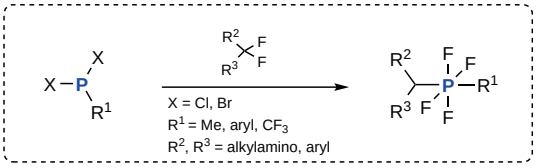
42.19.3 Hexacoordinated Phosphates

R. Pajkert and G.-V. Röschenthaler

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 42.19), and provides a survey of the chemistry of hexacoordinated phosphates published during the period 2008–2019. A noteworthy feature of the literature reviewed in this period is the considerable number of protocols describing the preparation of fluorinated phosphates. In this regard, this section focuses on a single class of these compounds, hexafluorophosphate derivatives possessing a P—C bond.



Keywords: hexafluorophosphates · fluoroalkyl phosphates · salt metathesis · carbene complexes · oxidative addition · difluoroamines · phosphorus(III) halides · fluorination · thermolytic decomposition

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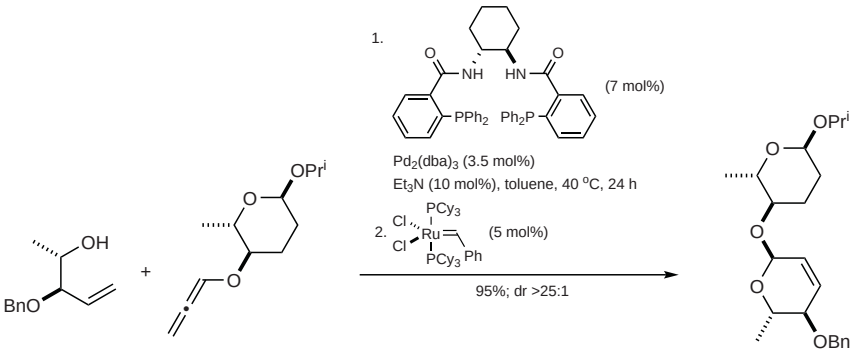
44.2.6.11 Applications of Allenes in Organic Synthesis

M. A. Tius

This chapter is an update to the earlier *Science of Synthesis* article (Section 44.2.6) that described the applications of allenes in organic synthesis. An attempt has been made to cover the literature from the end of 2005 through to approximately the end of June 2020. Allenes generally participate in the same reactions as alkenes, but their strain and the presence of the sp-hybridized carbon atom enable additional pathways. Advances in transition-metal-mediated asymmetric catalysis, especially involving gold and rhodium, have led to the development of many of the novel highly enantioselective processes that are discussed.



Keywords: allenes · allenic compounds · asymmetric catalysis · coupling reactions · cyclobutanes · gold complexes · Pauson–Khand reaction · Nazarov cyclization · rhodium catalysts