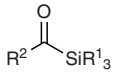
Abstracts

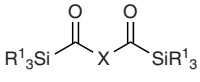
2012 p 1

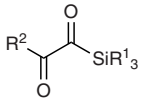
4.4.25.11 **Acylsilanes**

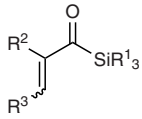
M. Nahm Garrett and J. S. Johnson

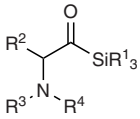
This chapter is an update to the previous *Science of Synthesis* contribution on the synthesis and applications of acylsilanes. It covers syntheses and applications reported since 2000. Synthetic methods described herein are divided according to five target product subtypes: simple acylsilanes, bis(acylsilanes), α-oxo acylsilanes, α,β-unsaturated acylsilanes, and α-amino acylsilanes. The largest of those sections, simple acylsilanes, is further divided according to the main strategies used for their synthesis: hydrolysis of acetals, oxidation of organocuprates, and acyl substitution of carboxylic amides. The major applications of the various types of acylsilanes are also described.











Keywords: acylsilanes · dithianes · hydrolysis · cuprates · oxidation · amides · substitution · bis(acylsilanes) · nucleophilic addition · Brook rearrangement · acyl anion equivalent

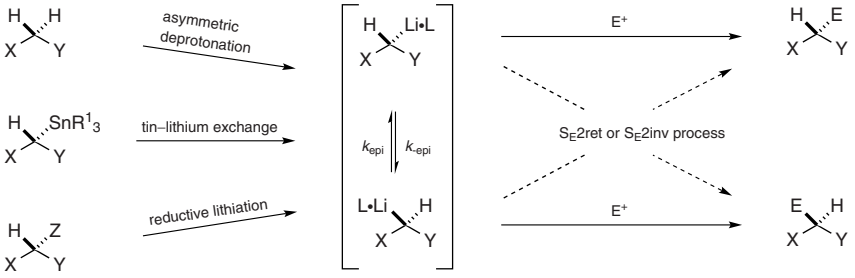
New p 85

8.1.34 **Asymmetric Lithiation**

J.-C. Kizirian

This section deals with processes that produce a chiral lithiated species by an asymmetric lithiation. The lithium atom can be introduced on an sp^3 carbon atom (centered chirality) or an sp^2 carbon atom (axial or planar chirality). The C—Li bond can be formed by one of three main methods: deprotonation (of a C—H bond), transmetalation (usually from tin), or reductive lithiation (from halo, cyano, arylsulfanyl, arylselanyl, or aryltellanyl derivatives). The configurational stability of the lithiated species determines the stereochemical pathway of the reaction, but is not a necessary condition to have a selective process. The

product is formed by one of the following mechanisms: enantioselective deprotonation, dynamic thermodynamic resolution, or dynamic kinetic resolution. Furthermore, the electrophilic substitution step can take place with inversion or retention of configuration.



X ≠ Y ≠ Z; X = alkyl, aryl; Y = heteroatom bearing an activated group; Z = CN, Cl, Br, I, SAr^1, $SeAr^1$, $TeAr^1$
E^+ = electrophile

Keywords: lithium compounds · dynamic thermodynamic resolution · dynamic kinetic resolution · enantioselective deprotonation · diastereoselective deprotonation · Wittig rearrangement · tin–lithium exchange · reductive lithiation · carbolithiation

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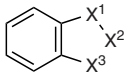
13.32 **Product Class 32: 1,2,3-Trithioles, Their Benzo Derivatives, and Selenium and Tellurium Analogues**

R. A. Aitken

This chapter covers methods for the synthesis of 1,2,3-trithioles, 1,2,3-benzotrithioles, and a range of eleven different analogues with one or more sulfur atoms replaced by selenium or tellurium. None of these ring systems has previously been included in *Science of Synthesis*.

X = S, Te



X^1, X^2, X^3 = S, Se, Te

Keywords: sulfur heterocycles · selenium compounds · tellurium compounds · trithioles · dithiatelluroles · benzotrithioles · benzodithiaselenoles · benzothiadiselenoles · benzotriselenoles · benzodithiatelluroles · benzothiaselenatelluroles · benzodiselenatelluroles

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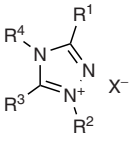
13.33 **Product Class 33: 1,2,4-Triazolium Salts**

C. A. Gondo and J. W. Bode

A 1,2,4-triazolium salt is composed of a cationic five-membered ring associated with a negatively charged counterion. These compounds are stable precursors for N-heterocyclic carbenes (NHCs), which are used either as ligands for metal-based catalysts or as organic catalysts. In this survey, the major routes for the synthesis of 1,2,4-triazolium salts are reviewed.



Keywords: heterocycle · N-heterocyclic carbene · ligand · organocatalyst · ring-closure reactions · ring transformation · substituent modification · 1,2,4-triazolium salts

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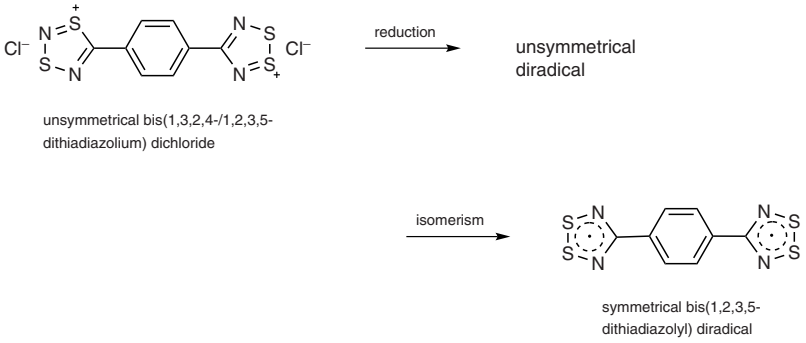
13.34 **Product Class 34: Dithiadiazolium Salts and Dithiadiazolyl-Containing Compounds**

R. J. Pearson

This chapter describes the preparation of 1,2,3,5-dithiadiazolium salts and their corresponding radicals and dimers. These crystalline and brightly colored compounds are most commonly synthesized, in varying yields, by ring-closure reactions involving amidines, amidoximes, nitriles, azines, and alkenes. The synthetic routes to the less stable 1,3,2,4-isomers are also discussed, together with the conditions for their complete isomerism to the dominant 1,2,3,5-isomers.



Keywords: dithiadiazole · radical · dimerization · isomerism · ring closure · ring transformation

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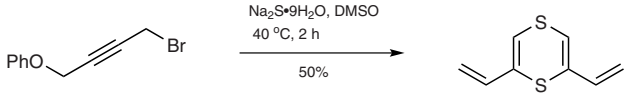
16.4.6 **1,4-Dithiins**

S. A. Kosarev

This chapter is an update to the earlier *Science of Synthesis* contribution describing methods for the synthesis of monocyclic 1,4-dithiins and their annulated analogues. It focuses on the literature published in the period 2003–2011.



Keywords: alkynes · chromium catalysts · dihalides · diimides · diketones · 1,4-dithiins · diols · dithianes · dithiols · sulfides · sulfinates · sulfur compounds · sulfur heterocycles · thiadiazoles · thiolates · thiophenes

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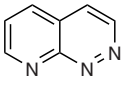
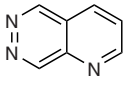
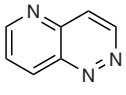
16.18.7 **Pyridopyridazines**

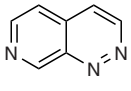
S. Lou and J. Zhang

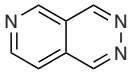
This update presents the state of the art in the synthesis of pyridopyridazine heterocyclic systems from 2001 to 2011. The synthetic methodologies are grouped based on the isomeric pyridopyridazine structures and typical experimental procedures are included. Some pyridopyridazine derivatives have been used as drug candidates and brief discussions are given of their pharmaceutical activities in the treatment of cancers, allergies, pain states, inflammatory diseases, and erectile dysfunction.

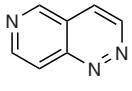

pyrido[2,3-*c*]pyridazine


pyrido[2,3-*d*]pyridazine


pyrido[3,2-*c*]pyridazine


pyrido[3,4-*c*]pyridazine


pyrido[3,4-*d*]pyridazine


pyrido[4,3-*c*]pyridazine

Keywords: pyridopyridazine · heterocycles · pyridine · pyridazine · pyridopyridazinone · hydrazine · dicarbonyl

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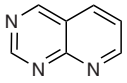
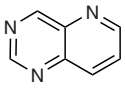
16.19.5 **Pyridopyrimidines**

Y.-J. Wu

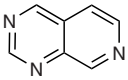
This chapter in an update to the previous *Science of Synthesis* contribution describing the the synthesis of all four isomeric pyridopyrimidines and their saturated derivatives. It covers syntheses described from 2002 until 2011.



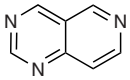
pyrido[2,3-*d*]pyrimidine



pyrido[3,2-*d*]pyrimidine



pyrido[3,4-*d*]pyrimidine



pyrido[4,3-*d*]pyrimidine

Keywords: pyrido[2,3-*d*]pyrimidine · pyrido[3,2-*d*]pyrimidine · pyrido[3,4-*d*]pyrimidine · pyrido[4,3-*d*]pyrimidine

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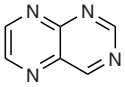
16.21.4 **Pteridines and Related Structures**

T. Ishikawa

This review is an update to the earlier *Science of Synthesis* contribution describing the synthesis of pteridines and pteridinones. It focuses on syntheses described since 2003.



Keywords: pteridine · pteridinone · ring closure · ring transformation · substituent modification

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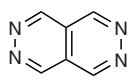
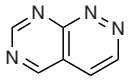
16.22.6 **Other Diazinodiazines**

T. Ishikawa

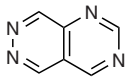
This review is an update to the earlier *Science of Synthesis* contribution describing the synthesis of diazinodiazines other than pteridines. It focuses on syntheses described since 2003.



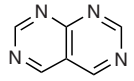
pyridazino[4,5-*d*]pyridazine



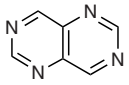
pyrimido[4,5-*c*]pyridazine



pyrimido[4,5-*d*]pyridazine



pyrimido[4,5-*o*]pyrimidine



pyrimido[5,4-*o*]pyrimidine

Keywords: diazinodiazine · pyridazinopyridazine · pyrimidopyridazine · pyrimidopyrimidine · addition · ring closure · substituent modification

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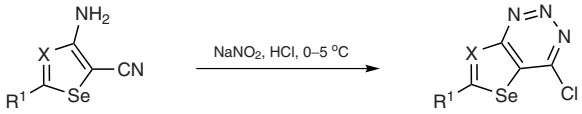
17.2.1.9 **1,2,3-Triazines and Phosphorus Analogues**

P. Aggarwal and M. W. P. Bebbington

This manuscript is an update to the earlier *Science of Synthesis* contribution describing methods for the synthesis of 1,2,3-triazines. The reported diazotization method is of particular note, as the substrate scope has broadened in recent years.



Keywords: alkylation · arylation · condensation reactions · cyclization · diazotization · dipolar cycloaddition · nucleophilic aromatic substitution · nucleophilic addition · ring-closure reactions · triazines

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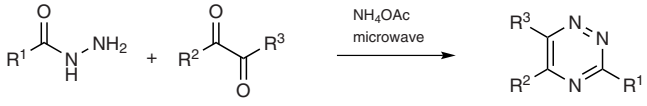
17.2.2.3 **1,2,4-Triazines**

P. Aggarwal and M. W. P. Bebbington

This manuscript is an update to the earlier *Science of Synthesis* contribution describing methods for the synthesis of 1,2,4-triazines. Of particular note are the microwave-assisted reactions that have emerged in recent years in addition to more conventional methods.



Keywords: condensation reactions · cyclization · dehydration · diazo compounds · microwave-assisted reactions · multicomponent reactions · nucleophilic addition · ring closure · ring formation · 1,2,4-triazines

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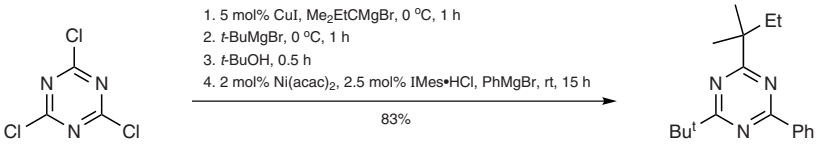
17.2.3.6 **1,3,5-Triazines and Phosphorus Analogues**

P. Aggarwal and M. W. P. Bebbington

This manuscript is an update to the earlier *Science of Synthesis* edition describing methods for the synthesis of 1,3,5-triazines. A number of transition-metal-catalyzed techniques have emerged in recent years to complement traditional methods.



IMes•HCl = 1,3-dimesityl-1*H*-imidazol-3-ium chloride

Keywords: condensation reactions · cross-coupling reactions · multicomponent reactions · nucleophilic aromatic substitution · ring closure · ring formation · transition metals · 1,3,5-triazines

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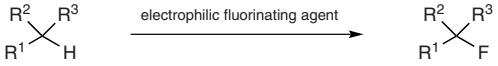
34.1.1.7 **Synthesis by Substitution of Hydrogen**

G. Sandford

Recent methods for the selective fluorination of sp^3-hybridized carbon atoms in aliphatic systems by reaction of an electrophilic fluorinating agent with a sufficiently nucleophilic C—H bond via electrophilic aliphatic substitution processes are discussed in this update.



Keywords: organofluorine · electrophilic aliphatic substitution · elemental fluorine · Selectfluor · selective fluorination