Abstracts

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5.2.1 Product Subclass 1: Tin Hydrides

K. Tchabanenko

This chapter is a revision of an earlier *Science of Synthesis* contribution describing methods for the synthesis and synthetic applications of tin hydrides. Synthetic methods based on free-radical chain reactions promoted by tin hydrides are discussed, including cascade reactions that proceed with rearrangement of radical intermediates. Free-radical and transition-metal-catalyzed hydrostannylations of multiple carbon—carbon bonds are also discussed in the chapter.

Keywords: stannanes \cdot radical reactions \cdot cyclizations \cdot rearrangements \cdot C—C bond formation \cdot C—Sn bond formation \cdot transition-metal catalysis \cdot cascade reactions

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7.6.11.21 Grignard Reagents with Transition Metals

Z. Song and T. Takahashi

This chapter is an update to *Science of Synthesis* Section 7.6.11, which describes the reactions of Grignard reagents in conjunction with transition metals. This update briefly summarizes the related publications that appeared from 2004 onwards.

$$R^1MgX^1 + R^2X^2$$
 transition metal R^1-R^2

Keywords: Grignard reagents \cdot C—C coupling \cdot enantioselectivity \cdot transition metals \cdot transmetalation

7.7



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Product Class 7: Calcium Compounds

M. Hatano

This chapter is a revision of the earlier *Science of Synthesis* contribution describing methods for the synthesis of calcium compounds. Recent interest in this area has in part been generated by the observation that complexes of calcium with chiral diols, diamines, or phosphoric acids possess potent activity in asymmetric catalysis.

Keywords: alkylation \cdot amination \cdot arylation \cdot 1,1'-binaphthalene-2,2'-diols \cdot bis(oxazolines) \cdot C—C bond formation \cdot cyclization \cdot diamines \cdot diols \cdot oxidation \cdot phosphoric acids \cdot pybox ligands

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9.13.5 **1***H***-Pyrroles**

W. D. Lubell, D. J. St-Cyr, J. Dufour-Gallant, R. Hopewell, N. Boutard, T. Kassem, A. Dörr, and R. Zelli

This chapter updates the previous *Science of Synthesis* contribution on 1*H*-pyrroles, which covers the literature up to 1998. This update includes the literature to 2011, with coverage of >900 references. Modern advances in pyrrole synthesis, reactivity, and functional-group modification, are described, including syntheses of nitrogen-, oxygen-, and sulfur-substituted pyrroles, multicomponent and annulation reactions, selective modifications at the 1-, 2-, and 3-positions of the pyrrole ring, and enantioselective additions of chiral side chains. Various annulation, ring-contraction, and ring-expansion approaches to the heterocycle, as well as modifications of pyrrole by carbon—hydrogen, carbon—halogen, carbon—heteroatom, and carbon—carboxylate transformations, and substituent migration strategies, all are covered in detail, along with many other recent synthetic developments. In addition, examples of various applications of pyrrole chemistry are presented to illustrate the growing importance of this heterocycle in fields such as medicinal chemistry, materials science, and natural product synthesis.

syntheses
$$\mathbb{R}^3$$
 \mathbb{R}^4 \mathbb{R}^5 applications

Keywords: pyrrole · Paal–Knorr condensation · Knorr-type reactions · tosylmethyl isocyanide · Barton–Zard type reactions · 1,3-dipolar cycloaddition · halopyrroles · cross coupling · direct arylation · Vilsmeier reaction · enantioselective alkylation · lamellarins · distamycin · prodigiosin · netropsin



16.9.5 **Cinnolines**

 $R^1 = Bu, s-Bu$

R. Krishnamoorthy

This chapter is an update to the earlier published *Science of Synthesis* report on the synthesis of cinnolines. The literature on cinnolines published from 2000 onwards is covered.

Keywords: cinnolines \cdot fused cinnolines \cdot diazotization \cdot cyclization \cdot arenediazonium salts \cdot arylhydrazones \cdot alkynyltriazenes \cdot *N*-oxides \cdot Richter reaction \cdot Suzuki reaction \cdot Sonogashira reaction

This chapter is an update to the earlier *Science of Synthesis* contribution describing the methods for the preparation of various diphosphinines. The focus is on the literature published in the period 2003–2011.

Keywords: diphosphinines · dimerization · palladium complexes