

Abstracts

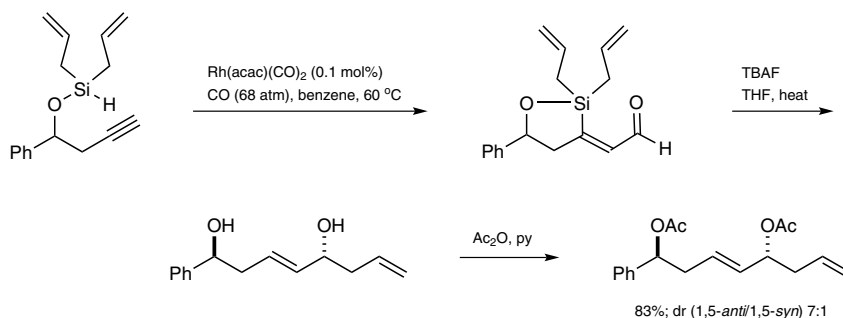
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4.4.4.8 Silyl Hydrides

R. W. Clark and S. L. Wiskur

This chapter is an update to the earlier article in *Science of Synthesis* (Section 4.4.4) covering the synthesis and use of silyl hydrides. Recent advances in synthetic preparations of silyl hydrides are explored, as well as the use of silyl hydrides for hydrosilylation, reduction, and dehydrogenative silylation.



Keywords: silyl hydrides · silanes · organosilanes · chiral silanes · hydrosilylation · dehydrogenative silylation · reduction

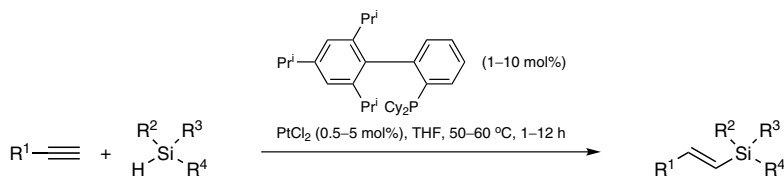
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4.4.34.35 Vinylsilanes

E. A. Anderson and D. S. W. Lim

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 4.4.34) describing methods for the synthesis of vinylsilanes. It focuses on the literature published in the period 2000–2014, with a particular emphasis on metal-catalyzed methods.



Keywords: vinylsilanes · vinylmetals · transition-metal catalysis · hydrosilylation · alkynes · silylmetalation · alkynylsilanes · hydrogenation · hydrometalation · coupling reactions · dehydrogenative silylation · alkenes · carbometalation · metathesis · rearrangements

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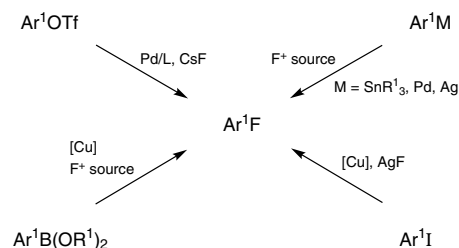
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31.1.2 Fluoroarenes

A. Harsanyi and G. Sandford

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 31.1) describing methods for the synthesis of fluoroarenes. It focuses on the literature published in the period 2007–2014, with a particular emphasis on transition-metal-mediated fluorination processes.



Keywords: organofluorine · fluoroarenes · fluoroaromatics · fluorination · transition-metal-mediated fluorination

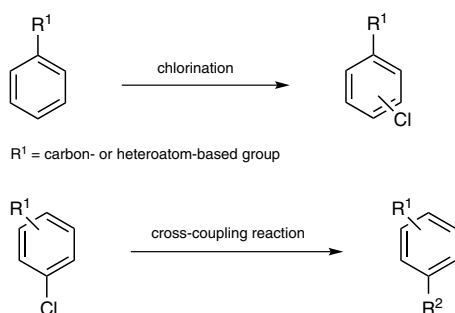
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31.2.3 Chloroarenes

S. P. Stanforth

This chapter updates the previous *Science of Synthesis* contribution (Section 31.2) published in 2007. Methods for the chlorination of arenes are described. The application of chloroarenes in synthesis, principally in transition-metal-catalyzed cross-coupling reactions, is discussed.

R¹ = carbon- or heteroatom-based groupR¹ = any atom or group; R² = carbon- or heteroatom-based group

Keywords: chlorination · cross-coupling reactions · transition-metal-catalyzed reactions · aryl–carbon bond formation · aryl–heteroatom bond formation

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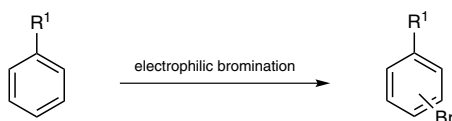
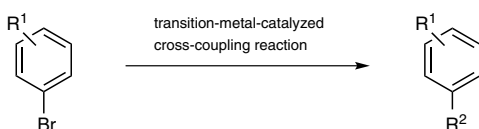
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31.3.3

Bromoarenes

S. P. Stanforth

This chapter updates the previous *Science of Synthesis* contribution (Section 31.3), published in 2007, describing the preparation of bromoarenes and their applications in synthesis. In recent years, the use of bromoarenes in transition-metal-catalyzed cross-coupling reactions has attracted considerable interest.

R¹ = carbon- or heteroatom-based groupR¹ = any atom or group; R² = carbon- or heteroatom-based group

Keywords: bromoarenes · bromination · cross-coupling reactions · Suzuki reaction · Sonogashira reaction · Buchwald–Hartwig reaction · hydrodebromination · transhalogenation

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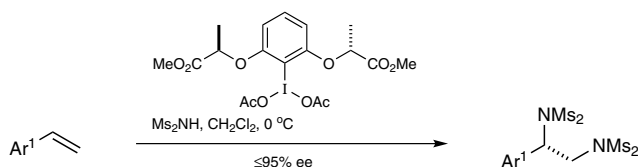
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31.4.1.3

Hypervalent Iodoarenes and Aryliodonium Salts

V. V. Zhdankin

This chapter provides an update to the earlier *Science of Synthesis* contribution (Section 31.4.1) describing the preparation and synthetic applications of hypervalent iodoarenes and aryliodonium salts. Recently, the chemistry of hypervalent iodine compounds has experienced several significant new developments, the most important of which are represented by the discovery of catalytic reactions promoted by in situ generated hypervalent iodine species, the development of highly enantioselective reactions of chiral hypervalent iodine reagents, and the preparation and synthetic application of numerous recyclable hypervalent iodine reagents.



Keywords: iodine · iodonium compounds · alkynylation · arylation · trifluoromethylation · oxidation · oxidative cleavage · catalysts · chiral compounds · fluorination · iodination · Hofmann rearrangement

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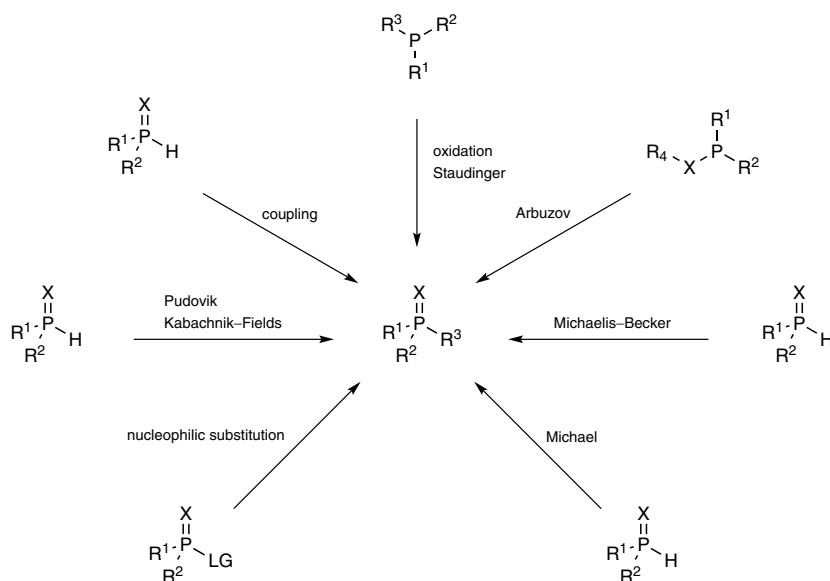
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Arylphosphine Oxides and Heteroatom Derivatives

O. M. Demchuk, M. Stankevič, and K. M. Pietrusiewicz

This chapter is an expanded update to the earlier *Science of Synthesis* contribution (Section 31.41), describing methods for the synthesis of arylphosphine oxides, arylphosphine sulfides, arylphosphine selenides, and aryl(imino)phosphoranes. Classical routes to arylphosphine chalcogenides involve the oxidation of parent phosphines by the pertinent chalcogenide oxidant. Other methods involve the formation of the lacking P–C bond(s) in oxidized electrophilic, nucleophilic, and radical phosphorus(V) precursors. Newer methods are based on hydrophosphinylation and coupling processes catalyzed by transition-metal complexes. Classical synthesis of aryl(imino)phosphoranes involves the reaction of the parent phosphines with organic azides (the Staudinger reaction), but methods based on the use of aminophosphonium intermediates are also reviewed. Approaches involving modifications of the carbon skeleton in existing arylphosphine chalcogenides are included as well.



Keywords: phosphorus compounds · phosphines · phosphine oxides · phosphine sulfides · phosphine selenides · iminophosphoranes · phosphorus heterocycles · phosphinylation · addition reactions · nucleophilic substitution · coupling reactions · cycloadditions · 1,3-dipolar cycloaddition · oxidation · radical addition · P–C bond formation · P–C bond cleavage

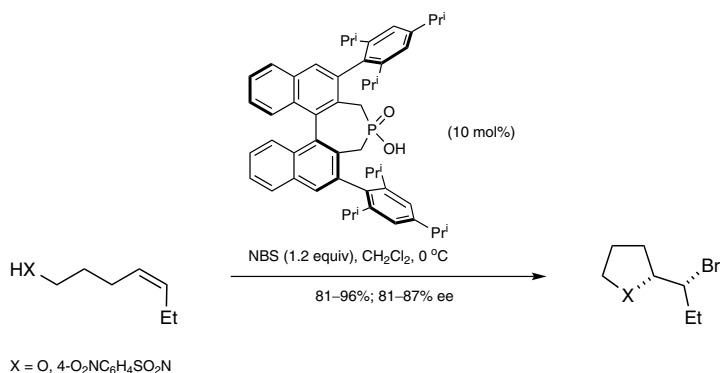
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35.2.5.1.9 **Synthesis by Addition across C=C Bonds**

G. Dagousset and G. Masson

This chapter is an update to the earlier *Science of Synthesis* Section 35.2.5.1, written by Troll in 2006, on the synthesis of 1-bromo-n-heteroatom-functionalized alkanes ($n \geq 2$), with both functions formed simultaneously by addition across C=C bonds. It focuses on recent advances in the field of bromofunctionalization of alkenes in the period 2007–2014, in particular on catalytic enantioselective syntheses.



Keywords: bromine compounds · carbon–bromine bonds · carbon–heteroatom bonds · bromination of alkenes · alkoxybromination of alkenes · bromolactonization · aminobromination · catalytic enantioselective reactions

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