

Abstracts

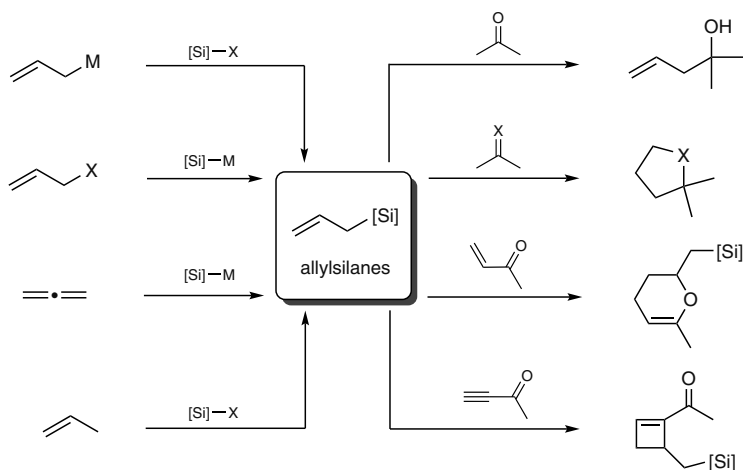
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4.4.40.72 Allylsilanes

K. Okamoto and K. Ohe

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 4.4.40), which describes methods for the synthesis of allylsilanes as well as their applications in organic synthesis. This update summarizes the recently reported (from 2001 to 2018) efficient synthetic methods and synthetic applications of allylsilanes involving transition-metal-catalyzed reactions.



Keywords: allylsilanes · vinylsilanes · alkenes · allenes · dienes · silanes · carbonyl compounds · cycloaddition reactions · organosilicon chemistry · transition-metal catalysis

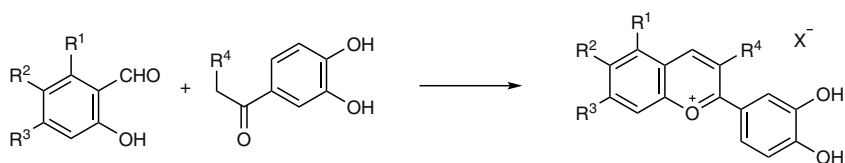
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14.2.5 Benzopyrylium Salts

F. Wu and S. Zhu

This chapter is an update to the earlier *Science of Synthesis* contribution describing methods for the synthesis of benzopyrylium salts (1-benzopyrylium salts, 2-benzopyrylium salts, and dibenzo[*b,e*]pyrylium salts). Classical routes to benzopyrylium salts involve intermolecular or intramolecular cyclization, aromatization, and oxidation processes, while recent developments with alternative approaches are also included.



Keywords: benzopyrylium · flavylum · xanthylum · chromenium · cyclization · condensation · oxidation

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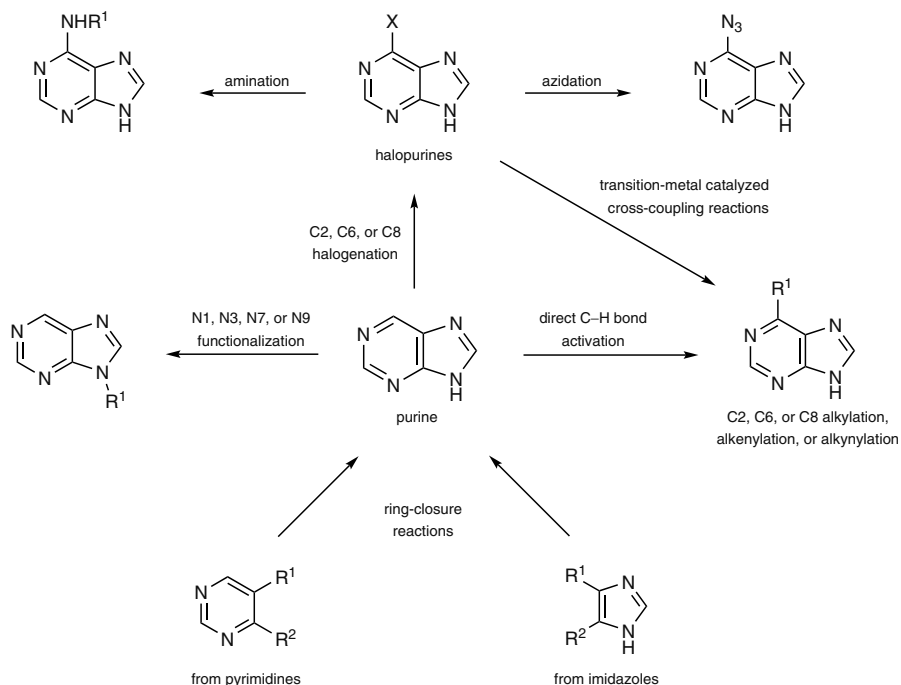
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New Contributions

16.17.7 Purines

Y. Liang,^{1b} Z. Wen,^{1b} M. Cabrera,^{1b} A. H. Howlader,^{1b} and S. F. Wnuk^{1b}

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 16.17) describing methods for the synthesis and chemical modification of purine and purine derivatives. It focuses on the literature published in the period 2002–2019, with a particular emphasis on regioselective direct C–H functionalization of purines, transition-metal-catalyzed cross-coupling reactions of halopurines, and synthesis of purine analogues, including azidopurines, by exchange of substituents.



Keywords: adenines · alkenylation · alkylation · alkynylation · amination · arylation · azidopurines · Buchwald–Hartwig reaction · carbon–carbon coupling · C–H bond activation · click reactions · cross-coupling reactions · cyclization · double C–H activation · fluorination · fused purines · guanines · halogen-exchange reactions · halogenation · halopurines · hypoxanthines · imidazoles · Negishi coupling · nucleosides · organometallic reagents · palladium catalysts · purines · pyrimidines · radical reactions · ring closure · Sonogashira coupling · Stille coupling · Suzuki–Miyaura coupling · transition metals

New

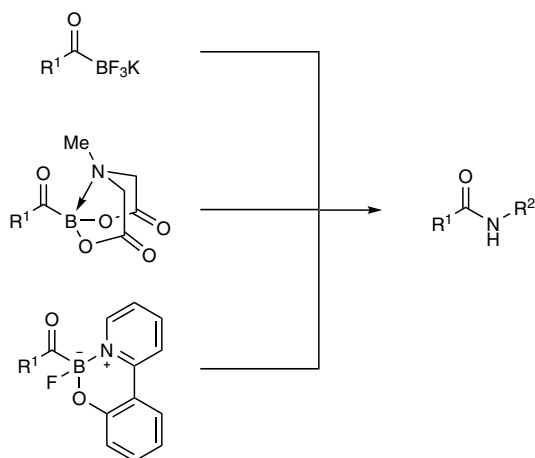
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21.1.7

Synthesis of Amides from Acylboron Compounds*A. Osuna Gálvez and J. W. Bode*

Recently, acylboronates have been shown to be applicable in the fast and chemoselective synthesis of amides. The methods covered in this review include the use of potassium acyltrifluoroborates (KATs), *N*-methyliminodiacetyl (MIDA) acylboronates, and monofluoro(acyl)boronates.

Acylboronates are, in general, bench-stable solids that can be easily handled in the laboratory. Among them, potassium acyltrifluoroborates stand out as remarkably stable salts that resist a variety of reaction conditions including acid, base, and heating. *N*-Methyliminodiacetyl acylboronates have the advantage of being amenable to purification by column chromatography and they exhibit high reactivity in amide ligation, but are limited by their poor stability under aqueous conditions. Monofluoro(acyl)boronates lie in between the above two classes, having acceptable half-life values in solution and improved overall reactivities compared to potassium acyltrifluoroborate reagents.



Keywords: acylboronates · amides · potassium acyltrifluoroborates (KATs) · *N*-methyliminodiacetyl acylboronates (MIDA boronates) · monofluoro(acyl)boronates · amide bond formation · azides · hydroxylamines · *N*-chloroamines

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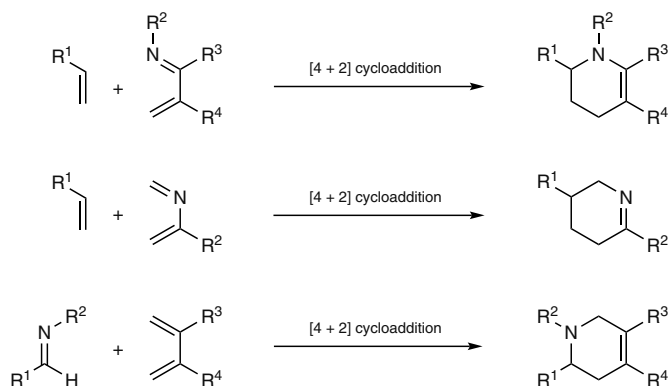
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40.1.1.3.3.6 **Synthesis of Amines by Pericyclic Reactions Involving C=N Units**

W. Maison

The synthesis of nitrogen heterocycles, such as piperidines and tetrahydroquinolines, with high chemo-, regio-, and stereoselectivity can be achieved via cycloaddition reactions that involve imine derivatives either as dienes or dienophiles. This topic was previously covered in Section 40.1.1.3.3, to which this chapter is an update, covering the literature from 2008 to 2019. The field has seen significant advances in recent years; this is particularly true for catalytic, enantioselective variants and new hetero-Diels–Alder variants using aza-*o*-quinone methides as reactive 1-azabutadienes. Both topics are therefore a special focus of this update.



Keywords: aza-Diels–Alder reactions · imines · dienes · dienophiles · pericyclic reactions · piperidines · tetrahydroquinolines · [4 + 2] cycloaddition · Povarov reactions · Lewis acid catalysis · Brønsted acid catalysis · stereoselective synthesis

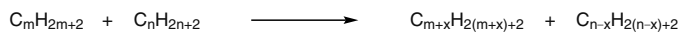
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48.1.6.4 **Alkane Metathesis**

G. Liu and Z. Huang

Alkane metathesis is a class of chemical reaction in which alkanes are covalently rearranged and exchange carbon atoms to form a new distribution of alkane products. The process involves both cleavage and formation of C–H and C–C bonds, and usually proceeds through a sequence containing dehydrogenation of alkanes to form alkenes, alkene (olefin) metathesis, and hydrogenation of the new alkenes. Both single-site systems and tandem dual-catalytic systems have been developed to effect this process. Alkane metathesis has been applied in the transformation of medium-weight alkanes into a mixture of longer and shorter alkanes, upgrading short-chain alkanes, and for the degradation of polyethylenes.



Keywords: alkanes · catalysis · dehydrogenation · iridium · metathesis

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