

Abstracts

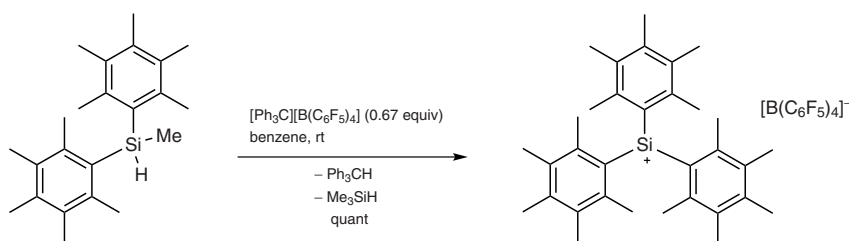
New

p 1

4.4.43 Product Subclass 43: Silylium Ions and Stabilized Silylium Ions

T. Müller

This chapter describes methods for the synthesis of silylium ions and silylium ions stabilized by direct interaction with solvents or counteranions. The applications of these species in Lewis acid catalysis and in bond-activation processes are also summarized.



Keywords: C—F bond activation · borates · Brønsted acids · carbocations · C—Si bonds · hydrosilylation · Lewis acid catalysts · onium ions · silanes · silicon compounds · silyl cations · solvent effects

New

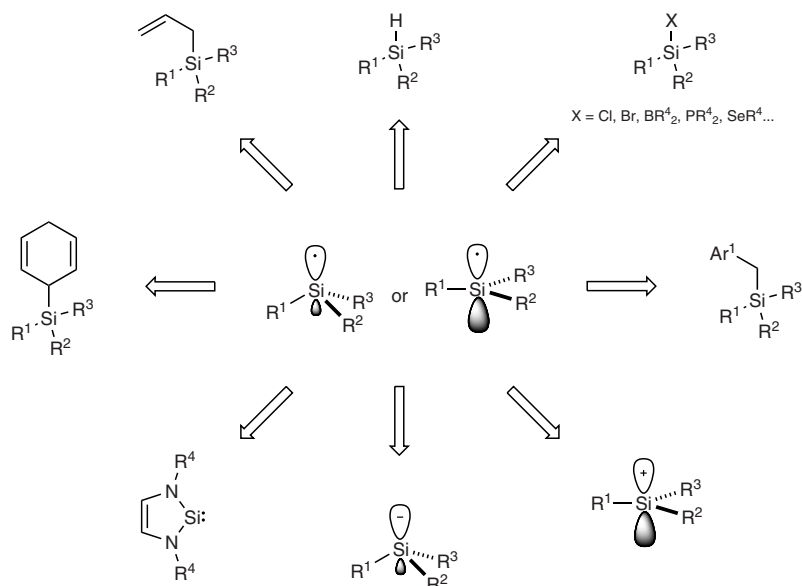
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4.4.44 Product Subclass 44: Silyl Radicals

Y. Landais

Silyl radicals are short-lived species that have found widespread use in various areas, including organic and polymer chemistry and, more recently, material science. These silicon-centered radicals are generated from various sources, including silyl hydrides, disilanes, allylsilanes, silyl halides, and silylenes, and by carbon—heteroatom bond cleavage. Silyl radicals are intermediates in important transformations such as hydrosilylation and reduction processes. They add to unsaturated systems (including alkenes, alkynes, arenes, and carbonyl derivatives) with high rate constants, generating carbon-centered radicals which are then involved in subsequent transformations. The understanding of steric and electronic properties of silyl radicals now allows a better prediction of their reactivity. Silyl radical precursors, such as silyl hydrides, are thus commonly used in the synthesis of complex targets including natural products. These radicals efficiently trigger complex radical cascades as well as rearrangements processes, opening an access to elaborate

architectures that would be otherwise difficult to access. Finally, silyl radicals are key intermediates in the functionalization of silicon surfaces, which have recently received a lot of interest due to the importance of organic films for applications as biomaterials and biochips.



Keywords: radicals · silyl hydrides · abstraction · disilanes · allylsilanes · hydrogen transfer · homolytic substitution · silylenes · silyliums · polarity-reversal catalysis

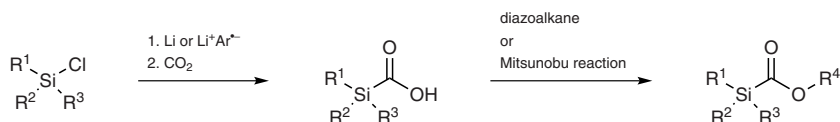
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4.4.45 Product Subclass 45: Silanecarboxylic Acids and Esters

K. Igawa and K. Tomooka

Silanecarboxylic acids having a carboxy group on the silicon atom are synthesized from chlorosilanes via their reductive lithiation and subsequent carboxylation with carbon dioxide. Silanecarboxylic acid esters are synthesized from silanecarboxylic acids by O-alkylation with diazoalkanes or by the Mitsunobu reaction with alcohols.



Keywords: silanecarboxylic acids · silanecarboxylic acid esters · reductive lithiation · carboxylation · esterification

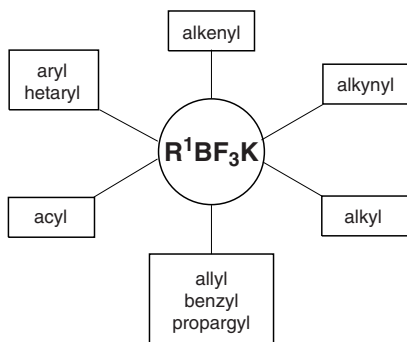
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6.1.6 **Product Subclass 6: Haloborates**

G. A. Molander and F. Beaumard

This chapter is a revision of the earlier *Science of Synthesis* contribution describing methods for the synthesis of haloborates. It focuses on the synthesis of organotrifluoroborates and highlights methods published between 1999 and 2013.



Keywords: organotrifluoroborates · organoboron compounds · C–B bonds · C–H bond activation · hydroboration · transmetalation · borylation

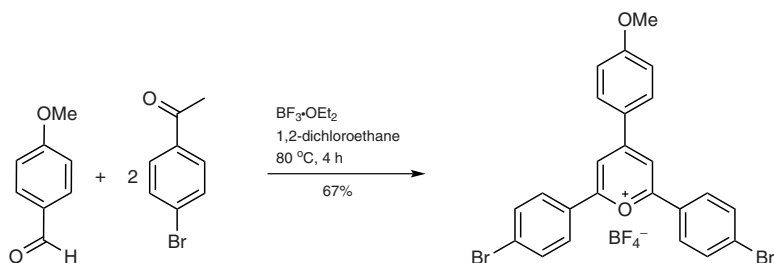
2013

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14.1.5 **Pyrylium Salts**

A. T. Balaban and T. S. Balaban

This update covers the literature from 2000 to the end of 2011; it also includes a few references from 1999 that were not discussed in the original *Science of Synthesis* review of pyrylium salts. In addition to methodologies for preparing pyrylium salts, some new applications of these compounds are also described.



Keywords: pyrylium salts · aldehydes · ketones · 1,5-diones · cyclization · aromatization

2013

Updated Section ·

2013

Completely Revised Contributions ·

New

New Contributions

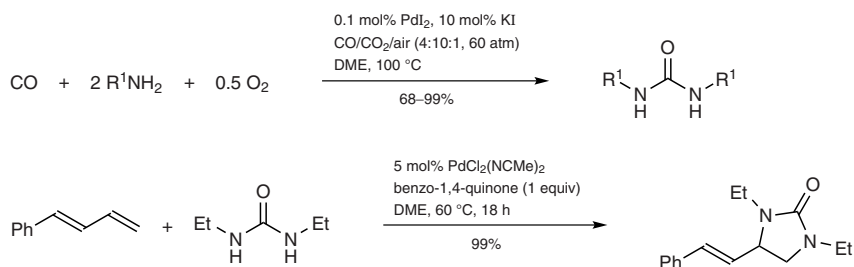
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18.8.22 Acyclic and Cyclic Ureas

S. Kubik

This update summarizes synthetic approaches to acyclic and cyclic ureas, as well as non-functionalized and functionalized derivatives. Syntheses of various urea derivatives are presented that were either not covered, or not treated in such detail, in the earlier *Science of Synthesis* contribution. For example, syntheses of imidazolidine-2,4-diones (hydantoin), 3,4-dihydropyrimidin-2(1H)-ones (Biginelli products), and pyrimidine-2,4,6(1H,3H,5H)-triones (barbiturates) are presented. The literature is covered between the years 2001 and 2012.



Keywords: barbiturates · Biginelli reaction · carbamates · carbon dioxide · carbonylation · 1,2-diamination · hydantoin · isocyanates · multicomponent reactions · ureas

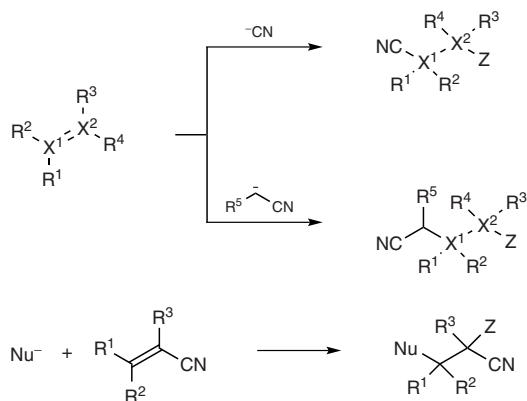
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19.5.14.15 Synthesis from Nitriles with Retention of the Cyano Group

N. Mase

This is an update to the original Section 19.5.14, which deals with synthesis from nitriles with retention of the cyano group. In order to cover significant recent developments, this update focuses on organocatalytic reactions of nitriles. These reactions are classified into two reaction modes: (1) reactions of nucleophiles containing a cyano group with electrophiles, and (2) reactions of nucleophiles with electrophiles containing a cyano group. In this update, significant achievements made employing asymmetric organocatalysts from the years 2000–2012 are highlighted.



Keywords: organocatalysis · nitriles · cyanides · isocyanides · cyanation · nucleophilic addition · nucleophilic substitution · one-pot processes

2013

Updated Section ·

2013

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