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Recent developments in the reactivity of methylene- and alkylidenecyclopropane derivatives

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Abbreviations: Ac, acetyl; AIBN, 2,2′-azobisisobutyronitrile; Ar, aryl; Atm, atmosphere; BARF, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate; Bn, benzyl; bpy, 2,2′-bipyridine; Bu, butyl; Bz, benzoyl; c, *cyclo*; CAN, ceric ammonium nitrate; cod, cyclooctadiene; Cp, cyclopentadienyl; Cy, cyclohexyl; Dba, (*E*,*E*)-dibenzylideneacetone; DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene; DCE, 1,2-dichloroethane; de, diastereomeric excess; DEAD, diethyl azodicarboxylate; DIAD, diisopropyl azodicarboxylate; DME, 1,2-dimethoxyethane; DMF, dimethylformamide; DMSO, dimethylsulfoxide; DPE, 1,2-bis(diphenylphosphino)ethane; E, electrophile; ee, enantiomeric excess; Et, ethyl; fod, 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate; Fu, furyl; Hept, heptyl; Hex, hexyl; HMPA, hexamethylphosphoramide; L, ligand; LDA, lithium diisopropylamide; M, metal; MAD, methylaluminum bis(2,6-*tert*-butyl-4-methylphenoxide); Me, methyl; Ms, mesyl; Naph, naphthyl; NBS, *N*-bromosuccinimide; NFSI, *N*-fluorobenzenesulfonimide; NIS, *N*-iodosuccinimide; NMO, *N*-methylmorpholine *N*-oxide; NMP, *N*-methyl-2-pyrrolidinone; Non, nonyl; Ns, nosyl; Nu, nucleophile; Oct, octyl; Pa, pascal; Pent, pentyl; Ph, phenyl; Piv, pivalate; PMB, *p*-methoxybenzoyl; Pr, propyl; Py, pyridyl; Sc, supercritical; TBAF, tetra-*n*-butylammonium fluoride; TBS, *tert*-butyldimethylsilyl; TEA, triethylamine; TEBAC, triethylbenzylammonium chloride; Tedicyp, *cis*,*cis*,*cis*-1,2,3,4-tetrakis(diphenylphosphinomethyl)cyclopentane; Tf, trifluoromethanesulfonyl; THF, tetrahydrofuran; TMEDA, tetramethylethylenediamine; TMS, trimethylsilyl; Tol, tolyl; Ts, 4-toluenesulfonyl (tosyl).

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1. Introduction

The importance of strained carbocycles such as three-membered rings has long been recognised in organic chemistry.[1] Indeed, organic chemists have always been fascinated by the cyclopropane subunit,[2] which has played and continues to play a prominent role in organic chemistry. Its strained structure, interesting bonding characteristics and value as an internal mechanistic probe have attracted the attention of the physical organic community. Due to the limited degrees of freedom in the system, these conformationally constrained molecules have very pronounced steric, stereoelectronic and directing effects, which make them versatile probes for the study of regio-, diastereo- and enantioselectivity.[3] Furthermore, a diverse reactivity pattern resulting from the significant strain energy accounts for the use of small carbocycles as convenient models for the investigation of organic and organometallic reaction mechanisms. Among the class of cyclopropanes, methylenecyclopropane and alkylidenecyclopropane derivatives have been well documented as useful synthetic intermediates in organic chemistry over the past few decades. Arguably, the chemistry of these compounds is the most rapidly developing among all small-ring compounds. Indeed, alkylidenecyclopropanes and methylenecyclopropanes are highly interesting compounds. Surprisingly, in spite of their highly strained structure ($40\ \mathrm{kcal\ mol^{-1}}$), they usually exist as stable compounds at room temperature, allowing their use in many synthetic applications with an otherwise unattainable chemical reactivity. Because of this strained nature, associated with a large structural differentiation available, methylene- and alkylidenecyclopropanes show various reactivities and have long been widely used in organic synthesis for their enormous potential. It must be noted that numerous efficient and straightforward syntheses of different types of methylene- and alkylidenecyclopropanes have appeared in the literature.[4] The goal of the present review is to cover the recent advances in the reactivity of methylene- and alkylidenecyclopropane derivatives, focussing on those published since 2003. This area was previously reviewed by Brandi et al. in 2003, focussing on the synthesis of heterocycles starting from alkylidenecyclopropanes,[5] and by Yamamoto et al. in 2002, focussing on the transition metal-catalysed reactions[6] of methylene- and alkylidenecyclopropanes.[7] In a more general context, it must be noted that Rubin et al. reported the transition metal chemistry of cyclopropenes and cyclopropanes, in 2007.[8] This review is subdivided into six sections, according to the different types of reactions, such as ring-opening reactions, cycloaddition reactions, rearrangements, radical reactions, polymerisation reactions and miscellaneous reactions including addition reactions with ring conservation and Heck reactions. It must be noted that the transformations of one methylene- or alkylidenecyclopropane into another through a simple functionalisation of the methylene- or alkylidenecyclopropane moiety have not been included in this review, but have been reported in a very recent review dealing with the synthesis of methylene- and alkylidenecyclopropane derivatives.[4f]

2. Ring-opening reactions

Methylene- and alkylidenecyclopropanes undergo a variety of ring-opening reactions because the relief of ring strain provides a potent thermodynamic driving force. These reactions can be achieved by using transition metal catalysts, Lewis acids and also Brønsted acids. Transition metal-catalysed ring-opening reactions of alkylidenecyclopropanes have been widely explored over the past decades.[5,7] On the contrary, less attention has been paid to the Lewis acid- or Brønsted acid-mediated reactions of alkylidenecyclopropanes.[9] Ring-opening reactions of methylene- and alkylidenecyclopropanes can be completed with various nucleophiles, such as amines, alcohols, water, carboxylic acids, thiols, sulfonamides, metal halides, etc. An attractive, but also troublesome, feature of methylene- and alkylidenecyclopropanes is their diverse reactivities that may lead to the formation of a variety of products through the addition to a C=C double bond and cleavage of proximal or distal bonds of the three-membered ring. Moreover, for the reactions with unsymmetrical alkylidenecyclopropanes, the regiochemistry generally affords different possible products. Indeed, the regioselectivity of the ring-opening reaction is one of the attractive issues in exploring this field of chemistry, and the selectivity is controlled by the selection of the metal reagents or catalysts and/or the structure of the cyclopropane substrates. So far, the crucial factor to determine the mode of ring opening of alkylidenecyclopropanes is not clear.

2.1. Ring-opening reactions by amine derivatives

The formation of carbon–nitrogen bonds is one of the most important processes in organic synthesis. In particular, the addition of the nitrogen–hydrogen bond of amines to carbon–carbon multiple bonds (hydroamination) is an ideal and challenging method for this purpose, offering an efficient synthetic route to amines, enamines and imines.[10] In 2003, Shi et al. showed that the ring-opening reaction of alkylidenecyclopropanes with aromatic amines could be performed in an environmentally benign solvent, such as supercritical carbon dioxide at 10 MPa, in the presence of heptadecafluorooctanesulfonic acid as the catalyst, providing an access to the formation of homoallylic amines.[11] Therefore, the reaction proceeded smoothly to give the corresponding dialkylated derivative as the major product along with the corresponding monoalkylated compound, as shown in Scheme 1. The best yields of up to 95% were obtained with aromatic amines bearing an electron-withdrawing group on the benzene ring. Moreover, apart from aromatic amines, this methodology could be applied to sulfonamides, as shown in Scheme 1.

These authors have demonstrated that the ring-opening reaction of diphenylmethylenecyclopropane with aromatic amines in supercritical carbon dioxide could also be catalysed by a Lewis acid, such as $Sn(OTf)_2$, in the presence of an additive, such as perfluorotoluene.[12] As shown in Scheme 2, the reaction led to a mixture of the corresponding mono- and dialkylated amine products in