Efficient Brønsted Acid Catalyzed Hydrations and Hydroaminations of (Dicyclopropylmethylene)cyclopropane

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Abstract: (Dicyclopropylmethylene)cyclopropane underwent efficient Brønsted acid catalyzed hydrations and hydroaminations with H_2O and basic amines, respectively, occurring with conservation of all three cyclopropane rings.

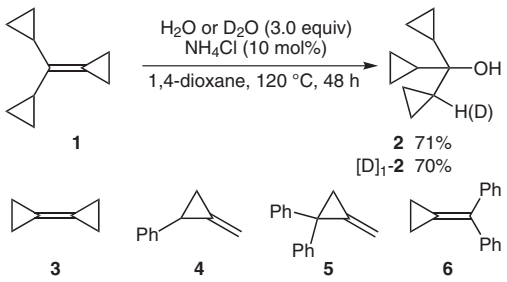
Key words: Brønsted acids, catalysis, hydroaminations, methylenecyclopropanes, ring conservation

Among numerous transition-metal-catalyzed reactions applied in synthetic organic chemistry,[1] intra- and intermolecular additions of amines onto C–C multiple bonds, hydroamination reactions, have received significant attention as an ecologically and economically friendly approach to nitrogen-containing compounds.[2,3] Yet, applications of less expensive Lewis or Brønsted acids as catalysts bear remarkable potential as user-friendly alternatives.[4]

Highly strained methylenecyclopropanes[5] (MCPs) can be considered as promising substrates to probe hydroamination catalysts, because their enhanced reactivities allow to explore fundamental concepts in organic chemistry and enable the development of useful synthetic methodologies. Thus, metal-mediated or -catalyzed reactions of MCPs were studied extensively in recent years.[5,6] Notably, all previously reported hydroaminations of MCPs employing palladium,[7] gold,[8] titanium[9] or lanthanum[10] catalysts proceeded exclusively via opening of at least one cyclopropane ring,[6] whereas formation of cyclopropane-containing compounds was observed as a side reaction only. Likewise, Lewis and Brønsted acid catalyzed (hydro)amination reactions occurred with ring opening,[11,12] a feature which can be rationalized with the electrophilic activation reaction manifold.[13,14]

Recently we have developed the first intermolecular hydroarylation of highly strained methylenecyclopropanes (MCPs) with conservation of cyclopropane rings via C–H bond functionalizations[15] through the use of a highly chemoselective ruthenium catalyst.[16] However, selected MCPs such as (dicyclopropylmethylene)cyclopropane (**1**) did not undergo this transformation. Contrarily, attempted hydroarylations employing $[RuCl_2(cod)]_n$ as precatalyst modified with a representative set of commonly used ligands in wet 1,4-dioxane or NMP as the solvent provided minor quantities of tricyclopropylmethanol (**2**).[17] Subsequent studies demonstrated that the ruthenium catalyst served as a source of chloride anions in these intermolecular hydrations. These results prompted us to explore acid-catalyzed additions onto MCPs by nitrogen- or oxygen-containing nucleophiles, on which we wish to report herein.

Thus, when using an excess of H_2O or D_2O in the presence of catalytic amounts of inexpensive Brønsted acids, such as ammonium chloride,[18] a chemoselective hydration to give **2** or $[D]_1$-**2** with conservation of all three cyclopropane rings was observed (Scheme 1).



Scheme 1 NH_4Cl-catalyzed hydrations of methylenecyclopropane **1**

On the contrary, bicyclopropylidene (**3**), 2-phenylmethylenecyclopropane (**4**), 2,2-diphenylmethylenecyclopropane (**5**) and (diphenylmethylene)cyclopropane (**6**) did not undergo this addition reaction. Moreover, no conversion of MCP **1** was accomplished with benzyl alcohol under otherwise identical reaction conditions.

Surprisingly, primary benzyl- and phenethylamines reacted with MCP **1** when using NH_4Cl as the precatalyst, furnishing hydroamination products **7a** and **7b** in 80% and 75% isolated yield, respectively, a reaction that notably occurred with retention of all three cyclopropane rings.[19] However, hydroaminations of MCP **1** with *n*-octylamine or cyclohexylamine proceeded with reduced efficacy (Scheme 2).[20]

Furthermore, hydroaminated products could not be obtained from reactions of MCP **1** with aniline or secondary dibenzylamine and *N*-benzyl-*N*-methylamine (not shown in Scheme 2), even after prolonged heating. Notably, the

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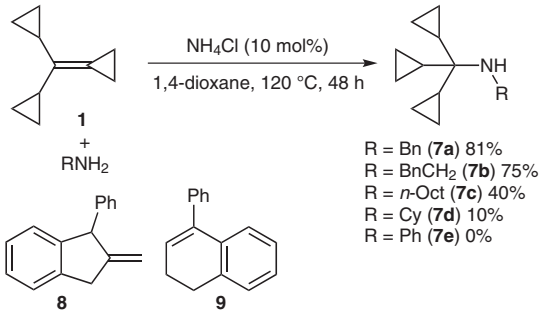


Scheme 2 NH_4Cl-catalyzed hydroaminations of MCP **1**

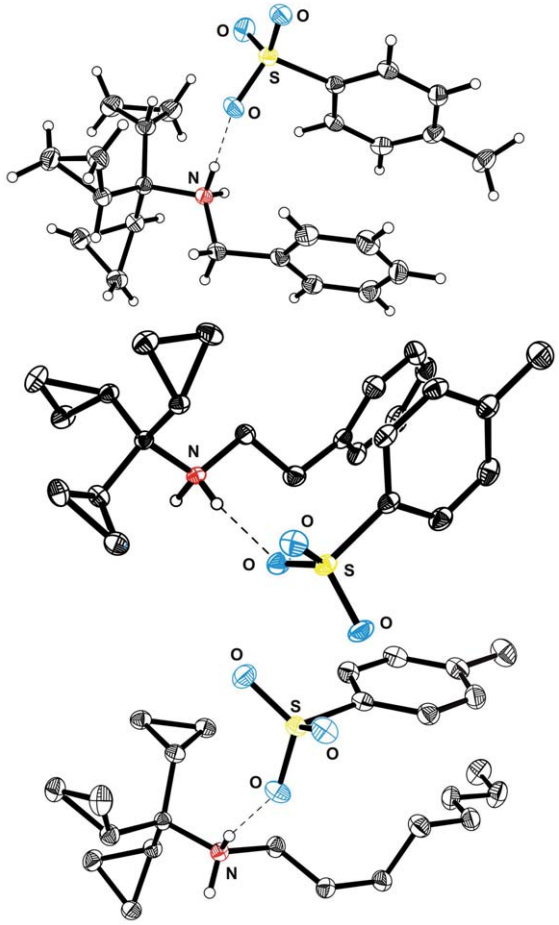


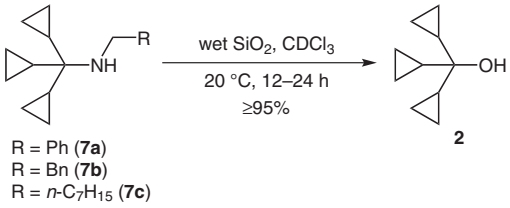
Figure 1 Molecular structures of *p*-toluenesulfonates **7a**·*p*-TsOH (top), **7b**·*p*-TsOH (middle) and **7c**·*p*-TsOH (bottom) in the crystal

yield of product **7a** dropped to 40% when dibenzylamine (0.5 equiv.) was used as additive in the hydroamination of MCP **1** with benzylamine under otherwise identical reaction conditions. Moreover, MCPs **3** and **4** either remained unchanged (**4**) or underwent polymerization reactions (**3**), while intramolecular Friedel–Crafts-type isomerization occurred with 2,2-diphenylmethylenecyclopropane (**5**) and benzhydrylidenecyclopropane (**6**) to yield 2-methylene-1-phenylindane (**8**, 46% yield) and 4-phenyl-1,2-dihydronaphthalene (**9**, 25–40% yield), respectively. The formation of dihydronaphthalene **9** from MCP **6** under palladium[21] catalysis has only recently been observed.

It is important to note that all isolated hydroamination products **7a–d** contained conserved cyclopropane moieties. Thus, the connectivity of amines **7a–7c** was unambiguously established by X-ray diffraction analysis of their *p*-toluenesulfonate salts **7a**·*p*-TsOH (top), **7b**·*p*-TsOH (middle) and **7c**·*p*-TsOH (bottom) (Figure 1).[22] The conformations of tricyclopropylmethyl moieties in these three compounds were found to be comparable.[23]

As to the reaction mechanism, we propose an initial protonation of MCP **1** to produce the tricyclopropylcarbenium ion, along with a subsequent nucleophilic attack by H_2O or the corresponding amine. Thus, the extraordinary stability of the tricyclopropylcarbenium ion[24] is likely responsible for its unique reactivity, resulting in the conservation of all three cyclopropane moieties.

Finally, we observed an unusual chemical behavior of secondary amines **7a–c**. Hence, stirring these hydroamination products in the presence of wet silica gel in $CDCl_3$ almost quantitatively delivered tricyclopropylmethanol (**2**; Scheme 3). Such a phenomenon has previously solely been observed for *N*-tricyclopropylmethylbenzamides,[23b] but, to the best of our knowledge, as of yet not for amines with reduced nucleofugalities.



Scheme 3 Hydrolysis of secondary amines **7a–c**

In summary, we have reported on an efficient acid-catalyzed hydration as well as hydroamination of (dicyclopropylmethylene)cyclopropane (**1**) with nucleophilic amines. A valuable asset of these user-friendly methods is represented by their high chemoselectivity, resulting in the formation of hydroamination products with conserved cyclopropane moieties. These reactions are of practical interest, since organic compounds with a (tricyclopropylmethyl)amine moiety demonstrate enhanced biological activity as herbicides and plant growth regulators,[25] while their syntheses continue to be challenging.[26]

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(20) **General Procedure for the Preparation of Benzyl(tricyclopropylmethyl)amine (7a), Phenethyl(tricyclopropylmethyl)amine (7b) and *n*-Octyl(tricyclopropylmethyl)amine (7c)**: A flame-dried Schlenk flask was cooled and charged with **1**, (402.6 mg, 442.1 μL, 3.0 mmol), the corresponding amine (1.0 equiv) and NH_4Cl (16.0 mg, 10 mol%) in anhyd 1,4-dioxane (3.0 mL) under Ar. After stirring the reaction mixture for 48 h at 120 °C, Et_2O (50 mL) was added at ambient temperature, and the reaction mixture was extracted with aq HCl (0.1 N, 2 × 80 mL). The combined aqueous phases were washed with Et_2O (2 × 50 mL) and, after addition of aq NaOH (1 N, 25 mL), extracted with CH_2Cl_2 (3 × 40 mL). The combined organic phases were dried over K_2CO_3 and concentrated under reduced pressure. The residue was dissolved in MeOH (20 mL), stirred with charcoal (2.0 g) at ambient temperature overnight, quickly filtered through a thin pad of silica gel and concentrated in vacuo. Amines **7a–c** (1.0 mmol) were dissolved in CH_2Cl_2 (5.0 mL), and a solution of *p*-TsOH·H_2O (190.2 mg, 1.0 mmol, 1.0 equiv) in MeOH (2.0 mL) was

added in one portion at ambient temperature. After an additional stirring for 10 min, the reaction mixture was evaporated, and the corresponding *p*-toluenesulfonate was purified by slow evaporation of its solution in CH_2Cl_2–octane (**7a**·*p*-TsOH: 92% yield, and **7c**·*p*-TsOH: 94% yield) or in THF–octane (**7b**·*p*-TsOH: 95% yield) at +4 °C. Compound **7a**: colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.21–7.38 (m, 5 H), 3.98 (s, 2 H), 1.53 (br s, 1 H), 0.69–0.71 (m, 3 H), 0.48–0.53 (m, 6 H), 0.29–0.35 (m, 6 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 142.3 (C), 128.0 (CH), 127.8 (CH), 126.6 (CH), 52.9 (C), 46.7 (CH_2), 15.9 (CH), 0.0 (CH_2). Compound **7a**×*p*-TsOH: colorless crystals; mp 137–139 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.34 (br s, 2 H), 7.65 (d, *J* = 8.0 Hz, 2 H), 7.52–7.56 (m, 2 H), 7.20–7.26 (m, 3 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 4.29 (t, *J* = 5.6 Hz, 2 H), 2.37 (s, 3 H), 0.65–0.75 (m, 9 H), 0.40–0.47 (m, 6 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 142.4 (C), 139.9 (C), 132.4 (C), 130.2 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 125.9 (CH), 67.0 (C), 46.5 (CH_2), 21.3 (Me), 11.5 (CH), 1.8 (CH_2). Compound **7b**: colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.17–7.29 (m, 5 H), 3.05 (t, *J* = 7.3 Hz, 2 H), 2.75 (t, *J* = 7.3 Hz, 2 H), 1.53 (br s, 1 H), 0.51–0.60 (m, 3 H), 0.36–0.42 (m, 6 H), 0.20–0.32 (m, 6 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 140.6 (C), 128.7 (CH), 128.1 (CH), 125.8 (CH), 52.9 (C), 43.8 (CH_2), 37.5 (CH_2), 15.6 (CH), 0.0 (CH_2). Compound **7b**·*p*-TsOH: colorless crystals; mp 149–150 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.48 (br s, 2 H), 7.80 (d, *J* = 8.0 Hz, 2 H), 7.12–7.26 (m, 7 H), 3.25–3.41 (m, 4 H), 2.38 (s, 3 H), 0.72–0.75 (m, 9 H), 0.41–0.46 (m, 6 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 142.8 (C), 140.0 (C), 137.8 (C), 129.0 (CH), 128.8 (CH), 128.5 (CH), 126.6 (CH), 125.8 (CH), 65.2 (C), 43.9 (CH_2), 32.7 (CH_2), 21.3 (Me), 11.0 (CH), 1.4 (CH_2). Compound **7c**: colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.75 (t, *J* = 7.0 Hz, 2 H), 1.65 (br s, 1 H), 1.35–1.51 (m, 2 H), 1.27 (m, 10 H), 0.88 (t, *J* = 6.5 Hz, 3 H), 0.54–0.63 (m, 3 H), 0.37–0.45 (m, 6 H), 0.23–0.30 (m, 6 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 42.4 (C), 31.8 (CH_2), 31.4 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 27.5 (CH_2), 26.4 (CH_2), 22.6 (CH_2), 15.7 (CH), 14.1 (Me), 0.0 (CH_2). Compound **7c**·*p*-TsOH: colorless crystals; mp 159–161 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.18 (br s, 2 H), 7.71 (d, *J* = 8.3 Hz, 2 H), 7.14 (d, *J* = 8.3 Hz, 2 H), 3.03 (m, 2 H), 2.35 (s, 3 H), 1.92 (m, 2 H), 1.22 (m, 10 H), 0.88 (t, *J* = 6.5 Hz, 3 H), 0.73–0.75 (m, 9 H), 0.42–0.50 (m, 6 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 143.0 (C), 139.6 (C), 128.6 (CH), 125.7 (CH), 64.8 (C), 42.3 (CH_2), 31.8 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 27.4 (CH_2), 26.4 (CH_2), 22.6 (CH_2), 21.3 (Me), 14.1 (Me), 11.0 (CH), 1.4 (CH_2).

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