Hydrodefluorination

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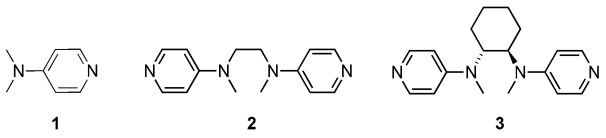
Selective Catalytic Hydrodefluorination as a Key Step for the Synthesis of Hitherto Inaccessible Aminopyridine Derivatives**

Gabriel Podolan, Dieter Lentz, and Hans-Ulrich Reissig**

Dedicated to the Bayer company on the occasion of its 150th anniversary

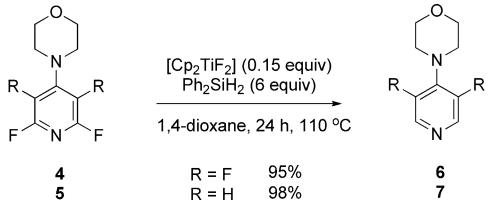
The synthesis of specifically substituted pyridines is a permanent challenge since new derivatives of this class of heterocycles are required as building blocks for supramolecular chemistry, as components of new materials, and also in pharmaceutical science.[1] 4-(Dimethylamino)pyridine (DMAP) (**1**) is a frequently used basic catalyst in many important synthetic transformations,[2] but it also strongly stabilizes nanoparticles by coordination of the Lewis basic nitrogen to the metal surface.[3] Due to our interest in multivalent ligands[4] we set out to synthesize divalent analogues of **1**, in particular, compounds **2** and **3** (Scheme 1).[5] Whereas compound **2** was available in moderate yield by the nucleophilic substitution of 4-chloropyridine employing the appropriate diamine, the chiral divalent compound **3** with a more rigid backbone could not be prepared. Neither were the nucleophilic substitutions of 4-halopyridines with *trans*-1,2-diaminocyclohexane in the presence or absence of palladium catalysts successful,[6] nor were reactions with 4-(methylamino)pyridine as the nucleophile in its reactions with difunctionalized cyclohexane derivatives.[5] The high steric hindrance seems to hamper these substitution reactions.



Scheme 1. DMAP **1**, divalent BiDMAP **2**, and cyclic divalent BiDMAP **3**.

Thus we developed a new synthetic strategy for the preparation of **3** based on two key reactions: nucleophilic substitution of the (oligo)fluorinated pyridines[7] and subsequent conversion of C–F into C–H bonds by catalytic hydrodefluorination (HDF).[8,9] The strong electron-withdrawing effect of the fluorine substituents in fluorinated pyridine derivatives allows the selective substitution of fluoride by nucleophiles at the 4- or 2-/6-positions of the heterocyclic ring.[7] Hence 4-aminopyridine derivatives with additional fluorine substituents on the ring are easily accessible[10] and serve as potential precursors for compounds such as **2** and **3**. The catalytic hydrodefluorination (HDF), that is, the conversion of C–F into C–H bonds, has been extensively studied;[8] however, due to the high cost of most reagents and catalysts as well as limitations in the substrate scope it is scarcely used for synthetic applications.[9] Our synthetic strategy to prepare hitherto inaccessible aminopyridine derivatives used the detour employing the nucleophilic aromatic substitution to create the C–N bond followed by catalytic HDF. For this purpose we used the $[Cp_2TiF_2]$/diphenylsilane system, recently developed for the defluorination of fluoroalkenes.[11,12]

To prove the viability of the catalytic HDF of fluorinated aminopyridines, we used 2,3,5,6-tetrafluoro-4-morpholinopyridine (**4**) as a model substrate in 1,4-dioxane as the solvent (Scheme 2). Under optimized conditions at temperatures between 90 to 110 °C with 15 mol% of the precatalyst we obtained the twofold hydrodefluorinated product **6** in 95% yield. These conditions allow the regioselective substitution of the more reactive fluorine atoms at C-2 and C-6.[7] Lower loadings of the precatalyst did not lead to full conversion. Interestingly, the use of 1,2-dimethoxyethane as a solvent led to a decrease of the reaction rate; a reaction time of 96 h was necessary to obtain a similar yield of 92%. Higher catalyst loadings apparently caused decomposition of precursor **4** or of the possible intermediates, and the completely hydrodefluorinated 4-morpholinopyridine (**7**) could not be detected. To demonstrate that the "inert" fluorine atoms at C-3 and C-5 of **4** are not required for a successful HDF, we also examined 2,6-difluoro-4-morpholinopyridine (**5**) under



Scheme 2. Regioselective catalytic hydrodefluorination of model substrates **4** and **5**.

[*] Dr. G. Podolan, Prof. Dr. D. Lentz, Prof. Dr. H.-U. Reissig
Institut für Chemie und Biochemie
Freie Universität Berlin
Takustrasse 3, 14195 Berlin (Germany)
E-mail: dieter.lentz@fu-berlin.de
hans.reissig@chemie.fu-berlin.de

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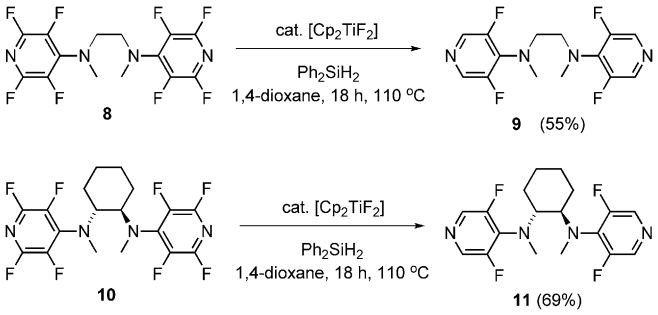
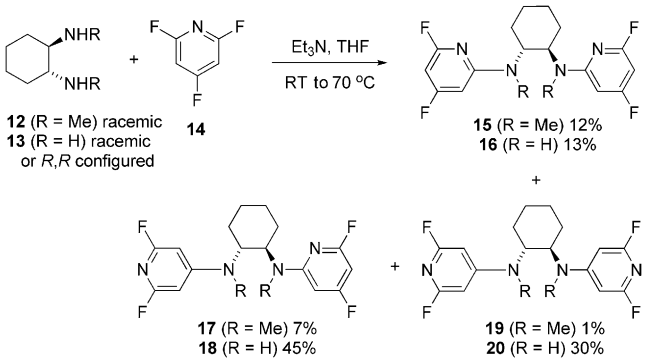
the optimized reaction conditions. The expected 4-morpholinopyridine (**7**) was isolated in excellent yield, thus demonstrating the feasibility of the developed method for the synthesis of entirely defluorinated aminopyridine derivatives.

After establishing efficient conditions for the HDF of simple aminopyridine derivatives, we extended the method to other oligofluorinated pyridine derivatives. The bis(aminotetrafluoroaminopyridine) derivatives **8** and **10** bearing different spacer moieties were readily available by nucleophilic substitution of pentafluoropyridine with the corresponding diamines. The substitution occurred with high selectivity at the 4-position of the pyridine ring. The catalytic HDF was executed with 30 mol% of the precatalyst since two pyridine rings were involved. The expected products **9** and **11** were obtained regioselectively in good yields (Scheme 3).



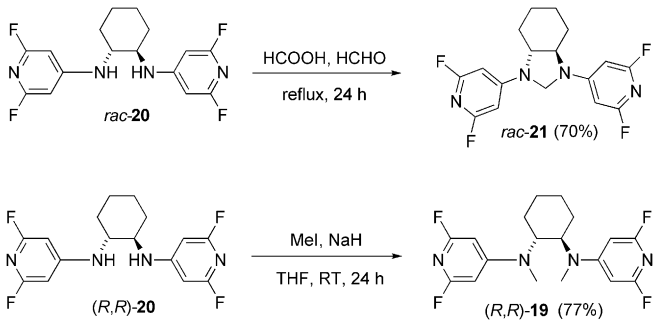
Scheme 3. Regioselective HDF of divalent pyridine derivatives **8** and **10** (compounds **10** and **11** are racemic mixtures).

Whereas the nucleophilic substitution of pentafluoropyridine occurs regioselectively at C-4, the reaction of 2,4,6-trifluoropyridine as the electrophile shows a surprising dependency on the degree of substitution of the nitrogen atoms of *trans*-1,2-diaminocyclohexane. The bis(*N*-methyl)-substituted compound **12** furnished the desired product **19** in only 1% yield (as result of a twofold substitution at C-4), but the two regioisomers **15** and **17** were isolated in yields of 12% and 7%, respectively (Scheme 4). The C-4/C-4 disubstitution reaction of the primary diamine **13** (used as a racemic mixture or as the *R*,*R* enantiomer) proceeded more efficiently leading to the desired compound **20** at least in 30% yield. The three regioisomers **16**, **18**, and **20** were easily separable by column chromatography. Apparently, the regioselectivity of the nucleophilic substitution is strongly dependent on the steric hindrance of the attacking nitrogen atom.



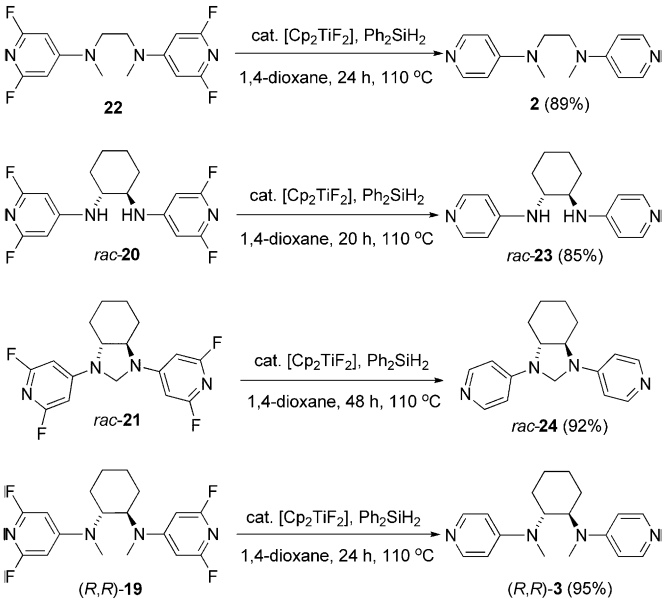
Scheme 4. Nucleophilic substitutions of *trans*-1,2-diaminocyclohexane derivatives **12** and **13** with 2,4,6-trifluoropyridine.

We tried to methylate NH groups of **20** by reductive alkylation with formaldehyde, but surprisingly obtained the bicyclic compound **21**. However, by deprotonation of **20** with sodium hydride and subsequent reaction with methyl iodide the desired precursor **19** for the catalytic HDF could be prepared in good yield (Scheme 5).



Scheme 5. *N*-Alkylations of aminopyridine **20** to **21** and **19**.

With the bis(2,6-difluoropyridyl) compounds **22** (synthesis described in the Supporting Information), **20**, **21**, and **19** we performed the catalytic HDF under standard conditions (i.e. 7.5 mol% of precatalyst per fluorine substituent): the substrates were converted into divalent DMPA analogues **2**, **23**, **24**, and **3** in excellent yields of 85–92% (Scheme 6). The synthesis of the long-awaited compound **3** in racemic and enantiomerically pure form (*R*,*R* enantiomer) should be emphasized here.



Scheme 6. Catalytic HDF of pyridine derivatives **22**, **20**, **21**, and **19** leading to divalent DMAP analogues **2**, **23**, **24**, and **3**.

Mechanistic studies of the HDF of fluoroalkenes indicate that a titanium(III) hydride is the catalytically active species. On reaction with the substrate, biscyclopentadienylfluoridotitanium(III) is formed and subsequently retransformed to the hydride by reaction with the silane.[11b,c] The HDF step has been suggested to proceed by an insertion/β-fluoride elimination mechanism or by a σ-bond metathesis mechanism. However, given the considerable differences between pyridine derivatives and alkenes as well as the entirely different reaction conditions, it is possible that other species and mechanisms are involved.

In conclusion, we have demonstrated that the combination of nucleophilic aromatic substitution of (oligo)fluorinated pyridines with a catalytic HDF offers excellent opportunities for the preparation of hitherto inaccessible aminopyridine derivatives. In the nucleophilic substitution the fluoro substituents act as activating and as leaving groups, but in the crucial HDF step they were regioselectively removed despite the strength of the C–F bond of approximately 500 kJ mol^{-1}.[13] This key reaction proceeds without expensive catalysts. Compounds such as the enantiomerically pure DMPA analogue **3** should have interesting properties as Lewis bases or as chiral ligands.[14] Our HDF method should also allow the preparation of fluoro-substituted pharmaceuticals[15] and should be of interest in the context of recently developed methods for C–C couplings with C–F bonds.[16]

Experimental Section

Typical procedure for the titanium-induced HDF of pyridine derivative **4**: 2,3,5,6-Tetrafluoro-4-morpholinopyridine (**4**) (50 mg, 0.21 mmol), titanocene difluoride (7 mg, 0.032 mmol, 15 mol%), diphenylsilane (0.235 mL, 1.27 mmol, 6 equiv, distilled from CaH_2), and anhydrous 1,4-dioxane (2 mL) were placed in a single-necked Schlenk flask equipped with a Young tap. The resulting mixture was subsequently degassed by repeated freeze–pump–thaw cycles. The mixture was briefly heated with a heat gun until the color changed from yellow to dark-brown and the solution was then stirred for 1 d at 110 °C. The reaction was quenched with MeOH (2 mL) and water (20 mL) was added. Extraction with Et_2O (3 × 30 mL), drying with Na_2SO_4, filtration, and concentration furnished the crude product. Purification by flash column chromatography (ethyl acetate/hexanes 1:4 to 1:1) gave compound **6** as a colorless solid (40 mg, 95%, mp 56–58 °C).

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