Chemoselective Reduction

DOI: 10.1002/anie.201104226

Selective Catalytic Monoreduction of Phthalimides and Imidazolidine-2,4-diones**

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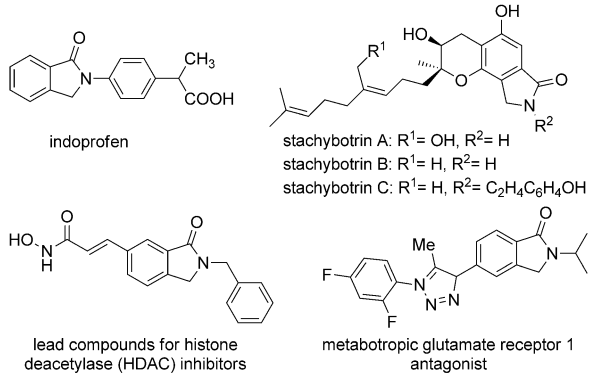
Isoindolinones represent an attractive target for organic synthesis and a valuable scaffold for medicinal chemistry because of their widespread and diverse biological activities (Scheme 1).[1–3] Despite many known methods, there is an ongoing interest in the development of convenient and general protocols for the synthesis of these compounds.



Scheme 1. Selected examples of therapeutically important isoindolinone derivatives.

Hence, in recent years, novel approaches such as rhenium-catalyzed reactions of aromatic aldimines with isocyanates,[4a] acid-catalyzed aza-Nazarov reactions of N-acyliminium ions,[4b] palladium-catalyzed carbonylations of benzylic amines,[4c] and iodoaminations of α-substituted 2-vinylbenzamides[4d] have been developed. In spite of all these achievements, the selective monoreduction of readily available phthalimides represents the most straightforward and efficient route to this class of compounds. Known reductions of phthalimides make use of stoichiometric amounts of tin[5] or zinc[6] in the presence of an acid. On the other hand, the application of more common organometallic hydrides, for example, $LiAlH_4$, leads to complete reduction to give pyrrolidines.[7] Unfortunately, more benign catalytic reductions that use heterogeneous catalysts (Raney nickel) need drastic reaction conditions and are not applicable in the presence of other sensitive functional groups. So far, only few organometallic complexes were explored for the reduction of imides. In this respect, Patton and Drago[8] reported the hydrogenation of *N*-methylsuccinimide at 100 °C in the presence of water-soluble ruthenium catalysts. Nevertheless, the yield of *N*-methylpyrrolidone was low and no general substrate scope was shown. More recently, Bruneau, Dixneuf, and co-workers developed an elegant hydrogenation of aromatic imides by using either $[Ru_4H_6(p\text{-cymene})_4]Cl_2$ or $[RuCl_2(p\text{-cymene})]_2$ in water.[9] However, the arene is reduced in addition to the imide group under this conditions. Notably, Ikariya and co-workers,[10a] as well as Bergens and co-workers[10b] reported the hydrogenation of imides to ω-hydroxy carboxamides by also applying ruthenium catalysts. It should be noted that all of these methods are associated either with expensive transition-metal catalysts or multistep procedures. Furthermore, there is no general methodology known that allows the selective reduction of imides in the presence of other reducible groups.

We recently became interested in the catalytic reduction of carboxylic acid derivatives, especially amides and nitriles.[11] Complementary to catalytic hydrogenations, hydrosilylations that use silanes offer a unique control of chemoselectivity.[12] For example, selective iron- and zinc-catalyzed hydrosilylations of tertiary as well as secondary amides are possible in the presence of various other functional groups.[13] Based on this work, we demonstrate herein that selective reduction of imides is achieved with inexpensive polymethylhydrosiloxane (PMHS) in the presence of catalytic amounts of fluoride ions.

The reaction of *N*-methylphthalimide (**1a**) with different silanes in THF was initially investigated as a model system to identify and optimize the critical reaction parameters (Table 1). As expected, the reaction did not occur in the absence of any catalyst (Table 1, entry 1). Also, when using our previously reported zinc[13a] and iron[13b–c] catalysts, no conversion was observed. However, use of $PhSiH_3$ in the presence of 5 mol% simple tetra-*n*-butylammonium fluoride (TBAF)[14] gave *N*-methylisoindolinone (**2a**) in 40% yield (Table 1, entry 2). When Ph_2SiH_2 was used, an excellent yield (80%) of **2a** was obtained (Table 1, entry 3). Other fluoride sources, such as CsF, KF, and TBAF hydrate showed less activity, whereas the corresponding bromide (TBABr) was completely inactive (Table 1, entries 8–11).

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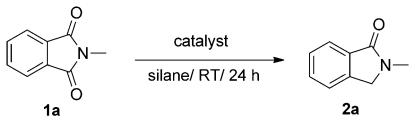
[**] This work was funded by the State of Mecklenburg-Western Pomerania, the BMBF, and the DFG (Leibniz Prize). We thank Dr. W. Baumann, Dr. C. Fischer, S. Buchholz, S. Schareina, A. Kammer, A. Koch, B. Wendt, S. Rossmeisl, and K. Mevius (all at the LIKAT) for their excellent technical and analytical support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201104226.

Table 1: Optimization of the conditions for the monoreduction of imides.[a]



Entry	Catalyst (mol%)	Silane (equiv)	Solvent	Yield[b] [%]
1	–	$PhSiH_3$ (2)	THF	–
2	TBAF (5)	$PhSiH_3$ (2)	THF	40
3	TBAF (5)	Ph_2SiH_2 (3)	THF	80
4	TBAF (5)	$(EtO)_2MeSiH$ (3)	THF	69
5[c]	**TBAF (5)**	**PMHS (5)**	**THF**	**85**
6	TBAF (5)	Et_3SiH(3)	THF	2
7	TBAF (5)	TMDS (3)	THF	35
8	TBABr (5)	PMHS (5)	THF	0
9	CsF (10)	PMHS (5)	THF	35
10	KO*t*Bu (20)	PMHS (5)	THF	25
11	TBAF hydrate (3)	PMHS (5)	THF	75
12	TBAF (5)	PMHS (5)	Toluene	78
13	TBAF (5)	PMHS (5)	DME	70
14	TBAF (5)	PMHS (5)	CH_2Cl_2	18

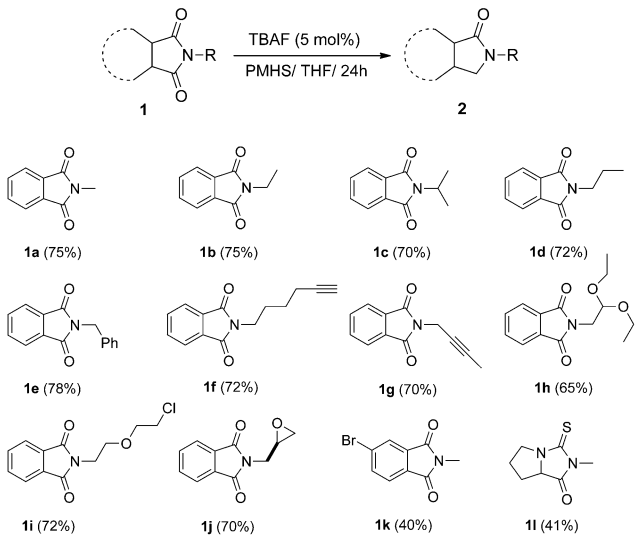
[a] Reaction conditions: **1a** (1.0 mmol), catalyst, silane, solvent (3 mL), RT, 24 h. [b] Determined by gas chromatography with hexadecane as an internal standard. [c] 1 mmol PMHS = 0.06 mL. Entry in bold represents the optimized reaction conditions.

To our delight, variation of different silanes demonstrated that less expensive and nontoxic PMHS[15] is a more suitable hydride source than other more special silanes. Hence, the reduction of *N*-methylphthalimide (**1a**) at room temperature in the presence of five equivalents of PMHS gave **2a** in 85% yield (Table 1, entry 5). Notably, no further reduction was observed. Expediently, PMHS can be easily separated from the reaction mixture because of its polymeric nature. Among other solvents, the reaction works well in THF, toluene, and DME (Table 1, entries 12–14).

Once suitable reaction conditions for the model system were identified, the scope and limitations of this novel fluoride-catalyzed reduction of imides with PMHS were explored. As shown in Scheme 2, 12 different N-substituted phthalimides (**1**) are smoothly reduced to the corresponding isoindolinones (**2**).

Notably, we did not observe further reduction toward the corresponding isoindolines in any of the cases. From a synthetic point of view, it is important that a range of functional groups, including halides, ethers, acetals, epoxides, and internal and terminal alkynes, are well-tolerated in this catalytic protocol (Scheme 2). To the best of our knowledge, similar functional-group tolerance has not been shown in imide reductions. While most reactions proceeded smoothly at room temperature, a slightly higher temperature (65 °C) was needed in case of *N*-methyl-4-bromophthalimide (**1k**), and the isoindolinone was obtained as a 1:1 mixture of two regioisomers.

Furthermore, the reaction was easily scaled up to a 100 mmol scale, and 12 g of **2a** were isolated straightforwardly from the reaction of **1a**. Interestingly, when **1l** was



Scheme 2. Fluoride-catalyzed reduction of aromatic imides **1a–1k** and substrate **1l**. Yields of isolated products **2** are given in brackets. Substrate **1k** and **1l** react at 65 °C.

used as substrate, a chemoselective reduction of the carbonyl group took place in the presence of the thiocarbonyl group.

To obtain more information on the mechanism of this catalytic reduction, simultaneous in situ ATR-FTIR and UV/Vis spectroscopic measurements were carried out to study the model reaction between **1a** and Ph_2SiH_2 with TBAF as catalyst. The obtained in situ ATR-FTIR and UV/Vis spectra are shown in Figures 1 and 2. Besides the bands of the solvent (THF), **1a** showed characteristic bands at 1773, 1719, and 1380 cm^{-1}, which are assigned to $\nu_s C{=}O$, $\nu_{as} C{=}O$, and $\delta_s CH_3$, respectively (Figure 1).[16,17] These band positions were not affected by addition of TBAF. Addition of one equivalent of Ph_2SiH_2 led to a new $\delta_s CH_3$ band at 1394 cm^{-1}. The additional bands at 1126 and 1117 cm^{-1} can be assigned to νSi–Ph.[17]

The observed splitting of the νSi–Ph band is surprising because the spectrum of Ph_2SiH_2 in THF contains only one band at 1122 cm^{-1}, the position of which shifts to 1120 cm^{-1} by adding TBAF (see also Figure S1 in the Supporting Information). After 10 minutes reaction time, the $\nu_{as} C{=}O$ band

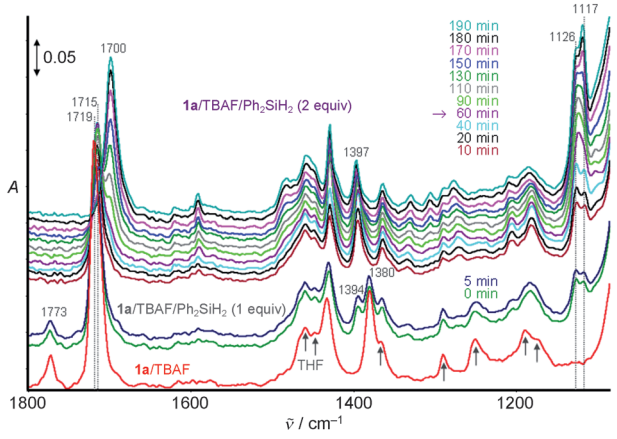


Figure 1. In situ ATR-FTIR spectra recorded during reaction of **1a** and Ph_2SiH_2 with TBAF as catalyst at room temperature.

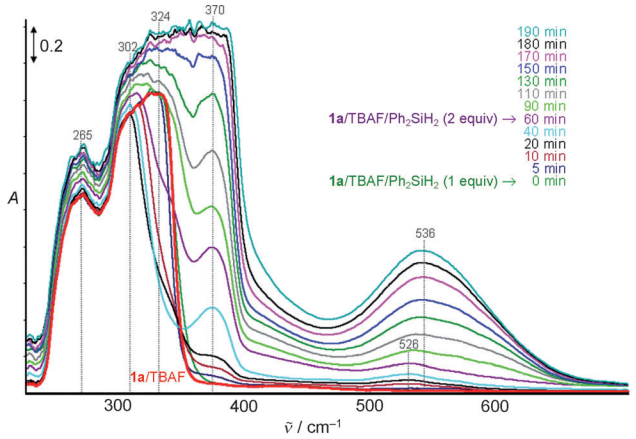


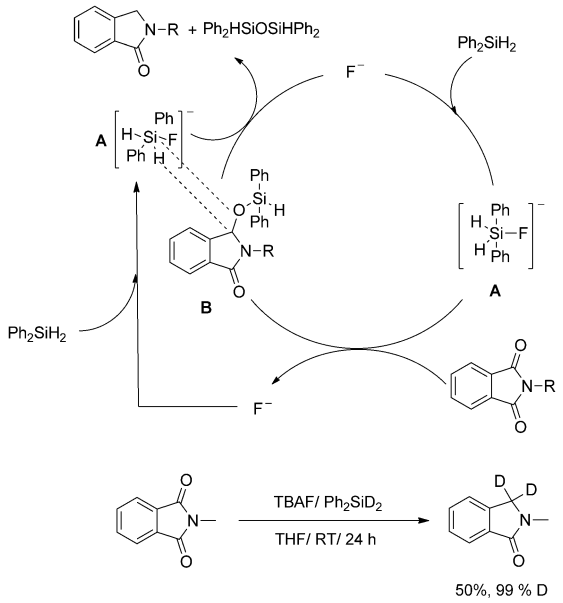
Figure 2. In situ UV/Vis spectra recorded during reaction of **1a** and Ph_2SiH_2 with TBAF as catalyst at room temperature.

showed a slight shift from 1719 to 1715 cm^{-1}, while the $\nu_s C{=}O$ band at 1773 cm^{-1} and the $\delta_s CH_3$ band at 1380 cm^{-1} disappeared completely. In turn, the $\delta_s CH_3$ band at 1394 cm^{-1} became dominant.

The UV/Vis spectrum of the reactant **1a** in THF did not change after the addition of TBAF, and was characterized by bands at 265, 302, and 324 nm; these bands result from the conjugated interaction of the two carbonyl chromophores with the electron pair of the nitrogen atom (Figure 2). The addition of one equivalent of Ph_2SiH_2 did not cause significant changes within the first 5 minutes of the reaction. However, after 10 minutes the band at 324 nm vanished, thus indicating the reduction of one carbonyl group. Simultaneously, a new band at 370 nm started to appear, which resulted from product **2a** as confirmed by a separate measurement of the UV/Vis spectrum of the product in THF.

The results of the in situ measurements suggest that, in the first step of the catalytic cycle, the fluoride ion is coordinated to the silicon atom of Ph_2SiH_2 (band shift of νSi–Ph as detected by ATR-FTIR) to form a reactive pentacoordinated silicon species **A** (Scheme 3), which immediately attacks the carbonyl group of **1a** to give a hexacoordinated silicon species within which the hydride transfer can take place.[18] Consumption of the respective bands in the ATR-FTIR as well as in the UV/Vis spectra confirmed this assumption. Changes of the coordination sphere of silicon are additionally indicated by the splitting of the νSi–Ph band.

During the course of the reaction, the formation of product **2a** is observed by an increase in the intensity of the respective bands in the ATR-FTIR (1700 cm^{-1}) as well as in the UV/Vis (370 nm) spectra. The addition of a second equivalent of Ph_2SiH_2 after 55 minutes caused a distinct increase in the amount of product formed (see Figure S2 in the Supporting Information). As shown in the ATR-FTIR spectra, the intensities of the νC=O band at 1700 cm^{-1} (product **2a**) and the νSi–Ph band at 1126/1117 cm^{-1} increased simultaneously (Figure 1). Considering the fact that both Si–O–Si and Si–O–Ph vibrations are observed in this region,[17] the latter effect is obviously caused by the formation of $Ph_2HSi{-}O{-}SiHPh_2$. This result implies the interaction of another activated pentacoordinated silicon



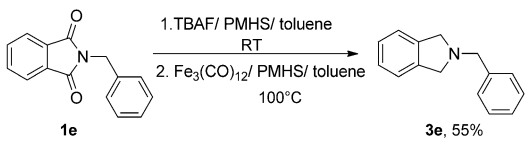
Scheme 3. Proposed reaction mechanism for the monoreduction of imides.

species to transfer the second hydride atom and to form $Ph_2HSi{-}O{-}SiHPh_2$. As can be seen from the UV/Vis spectra in Figure 2, an additional band appeared at 536 nm and increased in intensity as the amount of product increased. The appearance of absorption bands at such high wavelengths points to the formation of small amounts of molecules with highly conjugated chromophores as side products.

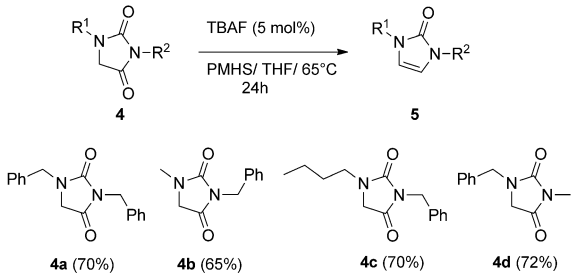
The proposed mechanism, which is based on the in situ spectroscopic measurements, is illustrated in Scheme 3. This mechanistic proposal is also supported by the reaction of **1a** with Ph_2SiD_2, the deuterium atoms of which were incorporated in the product **2a** (Scheme 3).

Fluoride-activated silanes are clearly unable to reduce the corresponding isoindolinones further to the corresponding isoindolines. However, by simply adding an $Fe_3(CO)_{12}$ catalyst system in the presence of PMHS,[19] complete reduction took place. By using this dual catalyst system, *N*-benzylisoindoline (**3e**) was obtained from *N*-benzylphthalimide (**1e**) in 55% yield of isolated product without optimization (Scheme 4).

Selective reduction of one or both carbonyl groups of the imide is possible by simple variation of the catalyst system. Finally, we performed some reduction reactions of other imide derivatives. Because of the chemoselective transformation of **1l** shown in Scheme 2, we focused our efforts on imidazolidine-2,4-diones (**4**; Scheme 5). By using the above-mentioned optimized conditions, smooth reductions occurred



Scheme 4. One-pot reduction of *N*-benzylphthalimide to *N*-benzylisoindoline.



Scheme 5. Fluoride-catalyzed reduction of imidazolidine-2,4-diones **4**. Yields of isolated products **5** are given in brackets.

at 65 °C. Surprisingly, the obtained products were not the simple deoxygenated compounds; instead formation of new double bonds in place of the amide bonds occurred (**5**; Scheme 5). To the best of our knowledge, this kind of transformation has not been observed previously for imidazolidinone derivatives. The mechanism shown in Scheme 3 can well explain the formation of the double bond in case of imidazolinone derivatives. Because of the presence of hydrogen atoms in α-position to the carbonyl group, elimination of water and formation of a double bond from species **B** is preferred; the absence of a hydrogen atom on the α-carbon atom in phthalimide derivatives leads to the selective monoreduction of imides. Interestingly, the reaction with secondary amides of imidazolidine-2,4-dione derivatives did not work at all.

In summary, we have developed novel chemoselective reduction reactions of phthalimides and imidazolidine-2,4-diones. By using low-cost polymethylhydrosiloxane in the presence of readily available fluoride ions as catalyst, good to excellent yields are obtained for different imides. Notable features of our novel protocols are the chemoselectivity, operational simplicity, and safe and mild reaction conditions. In situ spectroscopic investigations allowed for a concise mechanistic proposal. In addition, by combining fluoride- and iron-catalyzed hydrosilylations, full reduction of phthalimides to isoindolines is also possible.

Experimental Section

General procedure for the reduction of imides: A dried 10 mL Schlenk tube containing a stirrer bar was charged with TBAF (1M solution in THF, 50 μL, 5 mol %) and the imide (1 mmol). Dry THF (3 mL) and PMHS (300 μL, 5 mmol) were added sequentially after purging the Schlenk tube with argon. The mixture was stirred at room temperature and monitored by thin-layer chromatography. After complete disappearance of the substrates, the reaction mixture was filtered through Celite and washed with ethyl acetate. The combined fractions were concentrated under reduced pressure. The residue was then purified by column chromatography on silica gel by using a mixture of ethyl acetate and hexane as the eluent.

2-methylisoindolin-1-one (2a): Yield: 75 %. ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 7.76$ (d, $J = 7.44$, 1H), 7.44 (dd, $J^1 = 1.22$, $J^2 = 7.33$, 1H), 7.37 (m, 2H), 4.3 (s, 2H), 3.12 ppm (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 29.5$, 52.0, 122.6, 123.6, 128.0, 131.2, 133.0, 141.0, 168.7; ATR-IR (cm^{-1}) (neat) 1666 (s), 1615 (w), 1480 (m), 1442 (w), 1420 (w), 1396 (s), 1330 (w), 1273 (s), 1222 (w), 1206 (m), 1088 (w), 1053 (m), 1017 (w), 996 (w), 941 (w), 873 (w), 827 (w), 797 (m), 764 (w), 739 (s), 683 (s), 669 (w), 587 (s), 528 (s), 491 (s), 417 ppm (s); MS (EI): *m*/*z* (rel. int.) 147. HRMS (EI, *m*/*z*) calculated for C_9H_9ON, 148.07569; found 148.07568.

Received: June 19, 2011
Published online: August 24, 2011

Keywords: amides · amines · fluorides · homogeneous catalysis · reduction

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