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Catalytic Reduction

Selective Reduction of Carboxylic Acid Derivatives by Catalytic Hydrosilylation

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amides · esters · hydrosilylation · reduction · synthetic methods

In the last decade, an increasing number of useful catalytic reductions of carboxylic acid derivatives with hydrosilanes have been developed. Notably, the combination of an appropriate silane and catalyst enables unprecedented chemoselectivity that is not possible with traditional organometallic hydrides or hydrogenation catalysts. For example, amides and esters can be reduced preferentially in the presence of ketones or even aldehydes. We believe that catalytic hydrosilylations will be used more often in the future in challenging organic syntheses, as the reaction procedures are straightforward, and the reactivity of the silane can be fine-tuned. So far, the synthetic potential of these processes has clearly been underestimated. They even hold promise for industrial applications, as inexpensive and readily available silanes, such as polymethylhydrosiloxane, offer useful possibilities on a larger scale.

1. Introduction

The catalytic reduction of ketones, aldehydes, imines, and nitriles to alcohols and amines is one of the most fundamental and widely employed transformations in synthetic organic chemistry.[1] In these reactions, hydrogen is generally used as a benign and atom-efficient reducing agent in the presence of one of a multitude of metal complexes. On the other hand, similar reactions of esters, acids, and amides are scarcely known.[2] Sodium borohydride, lithium aluminum hydride, and other stoichiometric reducing agents still prevail in small- and medium-scale reductions of carboxylic acid derivatives.[3] Clearly, increased demand for more-atom-efficient synthetic methods as well as straightforward workup procedures make the use of these stoichiometric reagents disadvantageous. Furthermore, the use of catalysts enables the fine-tuning of activity, which might result in improved chemo- and regioselectivities for the conversion of carboxylic acid derivatives into alcohols, ethers, and amines.

It is well-known that hydrosilanes are easy-to-use and practical reducing agents that can be activated under mild conditions.[4] On the one hand, hydrosilylation under mild reaction conditions without high-pressure equipment is very attractive, but on the other hand, the varying price of hydrosilanes, which are used in stoichiometric amounts, has to be regarded. Whereas metal-catalyzed hydrosilylations of carbonyl compounds have been known for more than five decades, transition-metal-free hydrosilylations in the presence of either a Brønsted or Lewis acid[5] as a promoter or a Lewis base[6] as an activator are also established reactions for the reduction of imines and carbonyl compounds. In general, carboxylic acid derivatives were considered to be inert substrates under these conditions;[7] however, more recently it has been demonstrated that these compounds can also be reduced conveniently and highly selectively by catalytic hydrosilylation. Herein, we describe developments in this area.

2. General Considerations

With respect to their reactivity at the carbonyl group, carboxylic acid derivatives are more challenging substrates than ketones and aldehydes (Scheme 1). Esters and amides are the most interesting substrates for this kind of reaction. Clearly, in hydrosilylation reactions, acid halides and anhy-

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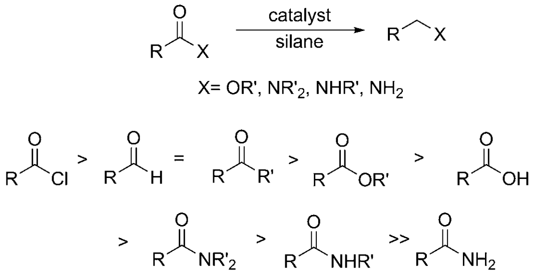

Scheme 1. General order of reactivity for the hydrosilylation of different functional groups.

drides are more reactive than esters, which in turn are more reactive than amides. A remarkable exception was provided by Nagashima and co-workers, who reduced tertiary amides selectively in the presence of esters and ketones.[24d] Among the different classes of amides, tertiary amides are reduced more readily than secondary amides, whereas primary amides tend to undergo dehydration to form nitriles.[8] Carboxylic acids react in a different way with hydrosilanes to give silyl esters.[9]

An advantage of silanes as reducing agents over hydrogen and organometallic hydrides is that their reactivity can be fine-tuned by the substituents on the silicon atom. The general order of reactivity of various silanes is: PMHS < $Et_2(MeO)SiH$ < $(EtO)_3SiH$ < Ph_3SiH < Ph_2SiH_2 < $PhSiH_3$ (PMHS = polymethylhydrosiloxane). On the other hand, the price and availability of different silanes varies substantially. Whereas expensive silanes, such as $PhSiH_3$, may only be useful for small-scale synthesis in the laboratory, the use of PMHS and 1,1,3,3-tetramethyldisiloxane (TMDS) are also suitable for larger-scale applications in industry. The prices of typically used silanes (for reactions on a laboratory scale) are given for comparison in Table 1.

Table 1: Cost of different silanes.

Entry	Hydrosilane	Price [€ (mmol silane)$^{-1}$]
1	$Me(OEt)_2SiH$	0.22
2	$TMSOSiMe_2H$[a]	0.16
3	$PhSiH_3$	0.72
4	Et_2MeSiH	0.10
5	Et_3SiH	0.15
6	$(EtO)_3SiH$	0.26
7	PMHS	0.01
8	$Me_2SiHSiHMe_2$	16.9
9	Ph_2SiH_2	0.38

[a] TMS = trimethylsilyl.

3. Reduction of Esters

The first transition-metal-catalyzed hydrosilylation of esters was described by Tsurugi and co-workers as early as 1973.[10] However, it took 20 years before this transformation became more popular. At the beginning of 1990s, Buchwald

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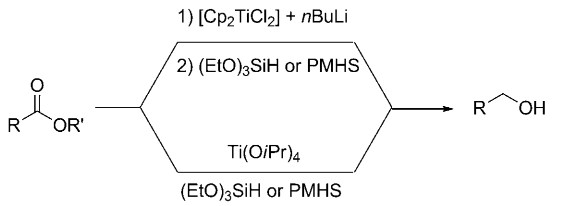
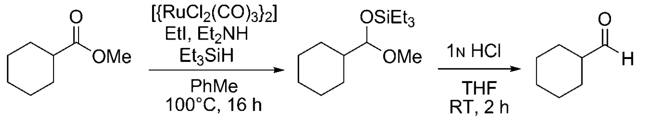
and co-workers started a thorough investigation on the use of titanocene and titanium alkoxide catalysts.[11] They were able to reduce a number of aliphatic and aromatic esters to the respective alcohols with these two systems. The titanocene-based catalyst was prepared in situ by the treatment of dichlorotitanocene with *n*-butyllithium at low temperature under inert conditions, whereas the titanium alkoxide catalyst was more robust and air-stable, but needed longer reaction times and higher temperatures. After the initial use of triethoxysilane as the reducing agent, it was found that inexpensive PMHS was also effective (Scheme 2).



Scheme 2. Reduction of esters with titanium catalysts.

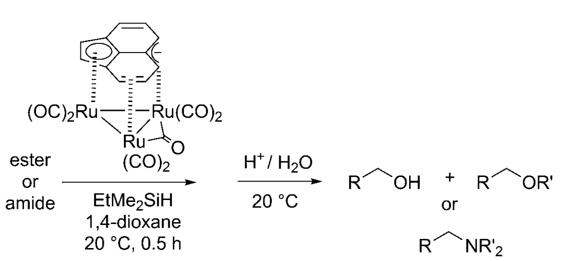
In 2005, Furukawa and co-workers reported the reduction of carboxylic acid derivatives with hydrosilanes in the presence of rhodium complexes, such as [{RhCl(cod)}$_2$]/4 PPh$_3$ (cod = 1,5-cyclooctadiene) and [RhCl(PPh$_3$)$_3$].[12] Carboxylic esters were reduced to alcohols with diphenylsilane at room temperature in up to 99 % yield. For example, ethyl decanoate and ethyl phenylacetate were converted into decanol and 2-phenylethanol in 98 and 92 % yield, respectively. Mimoun earlier reported an inexpensive catalyst system based on zinc hydride, which was produced in situ with PMHS. This inexpensive catalyst system was able to reduce a great variety of carbonyl compounds.[13] Typically, the hydrosilylation of nonfunctionalized esters to the respective alcohols proceeded in 4 h at 70 °C in excellent yields. Unfortunately, this system did not show high chemoselectivity in the presence of other functional groups, except for double bonds.

Ruthenium catalysts for the hydrosilylation of esters were first introduced by Igarashi and Fuchikami. They used [Ru$_3$(CO)$_{12}$] or [{RuCl$_2$(CO)$_3$}$_2$] to reduce esters to the corresponding alkylsilyl acetals; an acidic workup then gave the corresponding aldehydes (Scheme 3).[14]



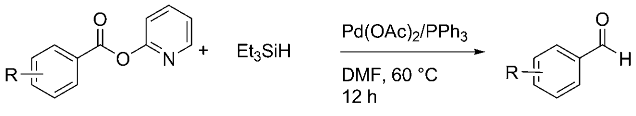
Scheme 3. Ruthenium-catalyzed reduction of an ester to an aldehyde.

In 2002, Nagashima and co-workers presented an efficient reduction of carboxylic acids, esters, and amides with trialkyl silanes in the presence of a specific triruthenium carbonyl cluster as a catalyst. Preactivation of the catalyst with trialkyl silanes accelerated the reduction of carboxylic acids and amides to produce the corresponding silyl ethers and amines, respectively (Scheme 4). The reduction of esters gave a mixture of silyl and alkyl ethers, the proportions of which could be controlled by changing the silane and the solvent.[15]



Scheme 4. Reaction developed by Nagashima and co-workers for the hydrosilylation of esters and amides.

Following the development of successful reactions with ruthenium, titanium, and rhodium complexes, palladium catalysts were also tested for the hydrosilylation of esters. Chatani and co-workers presented a palladium-catalyzed reduction of 2-pyridynyl esters to aldehydes with hydrosilanes. Interestingly, other substituents or functional groups, such as fluoro, methoxy, aldehyde, acetal, and ester groups, were tolerated under these conditions (Scheme 5).[16] Notably, in the absence of triphenylphosphane, the product is the corresponding silyl ether.

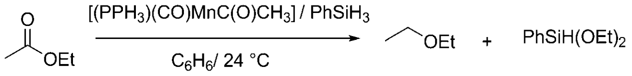


Scheme 5. Palladium-catalyzed reduction of pyridinyl esters to aldehydes.

The hydrosilylation of esters has also been investigated with Lewis acid catalysts. For example, Piers and co-workers reduced some simple esters with triphenylsilane in the presence of a catalytic amount of B(C$_6$F$_5$)$_3$.[17]

Furthermore, Fernandes and Romão used [MoO$_2$Cl$_2$] for the reduction of aliphatic and aromatic esters to the corresponding alcohols.[18] Their results demonstrated the catalytic potential of high-valent oxo complexes in reductions: an unexpected addition to their well-established ability to catalyze oxygen transfer to olefins, phosphines, and sulphites.

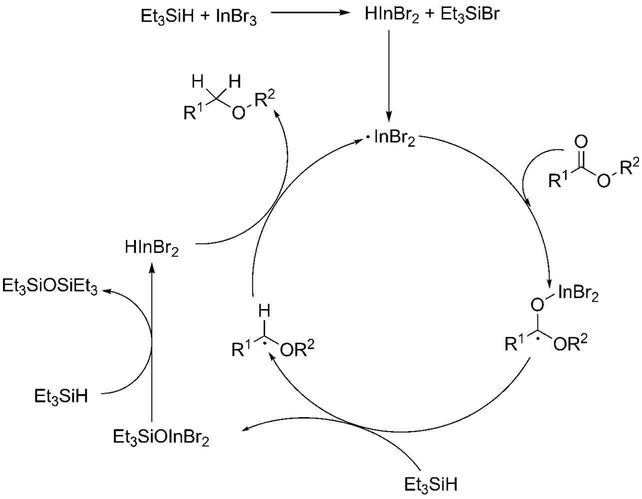
Although versatile hydrosilylation reactions have been developed for the selective reduction of esters to alcohols, the reduction of esters to ethers has not been well explored. The classical methods for the preparation of ethers involve the reaction of alkoxy anions with alkyl halides/sulfonates under basic conditions (Williamson synthesis) and the acid-promoted condensation of alcohols. In 1995, Cutler and co-workers reported the first example of the catalytic reduction of an ester to an ether. In this process, manganese acetyl complexes catalyzed the hydrosilation of esters with phenylsilane to give the respective silyl acetal, and subsequently the ether or alkoxysilane product. However, the generality of this reaction



Scheme 6. Manganese-catalyzed reduction of an ester to an ether.

was not demonstrated, as only one ester was cleanly converted into the corresponding ether (Scheme 6).[19]

More recently, Sakai et al. reported a more general system for the reduction of esters to ethers. They used indium bromide as the catalyst and triethyl silane as the hydride source.[20] A number of aliphatic esters were reduced to the corresponding ethers; however, the selective conversion of aromatic esters remains a challenge. A radical reduction mechanism was proposed (Scheme 7). When 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO), a radical scavenger, was added to the reaction mixture containing the ester, $InBr_3$, and Et_3SiH, the desired reduction was fully suppressed, and the starting ester was recovered. The proposed reaction pathway involves transmetalation between Et_3SiH and $InBr_3$ as the initial step, the abstraction of a hydrogen atom from Et_3SiH by the radical intermediate and formation of the ether product, and finally, regeneration of the indium radical species. Accordingly, in the case of aromatic esters ($R^1 =$ Ph), resonance stabilization of the generated benzyl radical hinders hydrogen abstraction and thus results in the sluggish reduction of the benzoate.



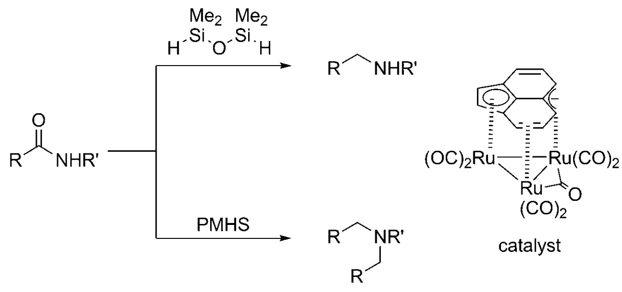
Scheme 7. Mechanism for the indium-catalyzed reduction of esters to ethers.

4. Reduction of Amides

In a pioneering study in this field in the early 1980s, Corriu et al. showed that the hydrosilylation of *N,N*-diethylphenylacetamide with the Wilkinson catalyst and 1,2-bis(dimethylsilyl)benzene as the hydrosilane led to an enamine through deoxygenation of the amide.[21] In the last decade, the selective hydrosilylation of amides has continuously attracted attention. In an early study reported by Ito and co-workers in 1998, the reduction of a range of tertiary amides with 2 equivalents of diphenylsilane was promoted by $[RhH(CO)(PPh_3)_3]$ at room temperature to afford the corresponding tertiary amines in good yields.[22] The synthetic utility of this protocol was demonstrated by the chemoselective reduction of amides in the presence of esters and epoxides, which are not compatible with conventional reductions with metal hydrides. Later, Fuchikami and Igarashi showed that the reaction of amides with hydrosilanes is catalyzed by different transition-metal complexes in the presence or absence of halides and amines as cocatalysts to give the corresponding amines in good yields.[23]

Essential developments in the catalytic hydrosilylation of carboxylic acid derivatives have come from the research group of Nagashima.[15,24] A notable improvement in their first protocol for the hydrosilylation of tertiary amides was the use of inexpensive PMHS as the hydrogen source. At the end of the reaction, the amines were readily separated by washing of the polymeric support with ether, while the ruthenium catalyst remained trapped in the resin.[24b] In the course of their studies, they also examined a similar reduction of amides with PMHS in the presence of self-encapsulated metal species. When they applied $[H_2PtCl_6]$ and other platinum compounds that are widely used for the catalytic hydrosilylation of alkenes, the reduction of the amide group proceeded chemoselectively even in presence of double bonds at relatively low temperatures (generally 50–60 °C).[24c]

In 2007, Nagashima and co-workers showed that tertiary amides could be reduced in the presence of ketones or esters by using a ruthenium catalyst in combination with a stoichiometric amount of triethylamine and $PhMe_2SiH$.[24d] Triethylamine inhibited the reduction of the other functional groups. Notably, in competitive experiments in which *N,N*-dimethylhexanamide and 2-heptanone or methyl hexanoate were present in a ratio of 1:5, selective hydrosilylation of the amide was observed. In the same year, Nagashima and co-workers also developed two different procedures for the reduction of secondary amides, which are more difficult substrates (Scheme 8).[24e] Secondary amines could be formed selectively through the use of a higher concentration of the catalyst with a bifunctional hydrosilane, such as 1,1,3,3-tetramethyldisiloxane (TMDS). Acidic workup of the reaction mixture afforded the corresponding ammonium salts, which after treatment with a base were isolated readily as secondary amines with

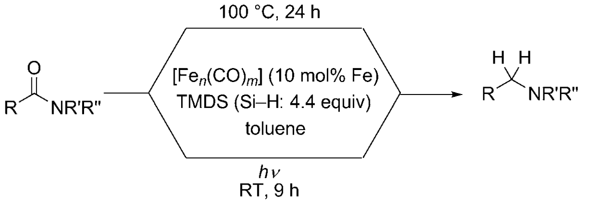


Scheme 8. Hydrosilylation of secondary amides with a special ruthenium cluster.

high purity. In contrast, tertiary amines were formed with high selectivity when a lower concentration of the ruthenium cluster (1 mol %) was used in combination with PMHS as the reducing agent. Reduction with PMHS causes encapsulation of the ruthenium catalyst and organic by-products in the insoluble silicone resin. Application of the ruthenium cluster to the more challenging hydrosilylation of primary amides gave the corresponding nitrile as the only product through a dehydration mechanism.[8a]

More recently, Nagashima and co-workers again used platinum catalysts to show the synergetic effect of two Si–H groups in the reduction of carboxamides to amines under mild conditions.[24f] The rate of the reaction was dependent on the distance between the two Si–H groups; 1,1,3,3-tetramethyldisiloxane and 1,2-bis(dimethylsilyl)benzene were found to be effective reducing reagents. Notably, the reduction of amides with other sensitive functional groups, such as NO_2, CO_2R, CN, C=C, Cl, and Br groups, proceeded selectively. Thus, this method provides reliable access to functionalized amine derivatives. The platinum-catalyzed reduction of amides with PMHS also proceeded under mild conditions with the further advantage of the automatic removal of both platinum and silicon waste products as insoluble silicone resin.

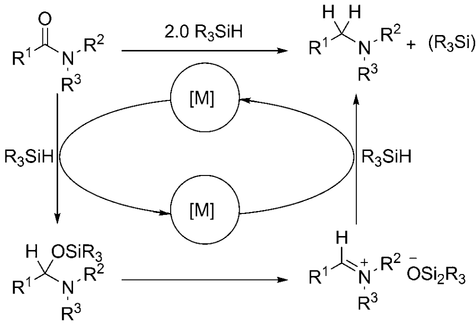
In 2009, in parallel to our own studies,[25] Nagashima and co-workers found that $[Fe(CO)_5]$ and $[Fe_3(CO)_{12}]$ are useful catalysts for the thermal and photoassisted reduction of tertiary amides to tertiary amines with TMDS and PMHS as reducing agents (Scheme 9).[24g] Importantly, the photoassisted reaction occurred at room temperature. Although both the thermal and photoassisted reactions required a larger amount of the catalyst than the corresponding reactions catalyzed by platinum or ruthenium compounds, the use of inexpensive iron as the catalyst metal is beneficial.



Scheme 9. Thermal and photoassisted hydrosilylation of tertiary amides with iron catalysts.

Fernandes and Romão reported the use of a simple molybdenum catalyst for the hydrosilylation of various amides at reflux in toluene with phenylsilane as the hydrosilylation agent.[26] Product yields were in general good to excellent in the case of tertiary amides and moderate in the case of secondary amides. Another simple and practical procedure for the direct reductive conversion of a variety of tertiary amides into the corresponding tertiary amines was developed by Sakai et al. with their $InBr_3/Et_3SiH$ reducing system.[27]

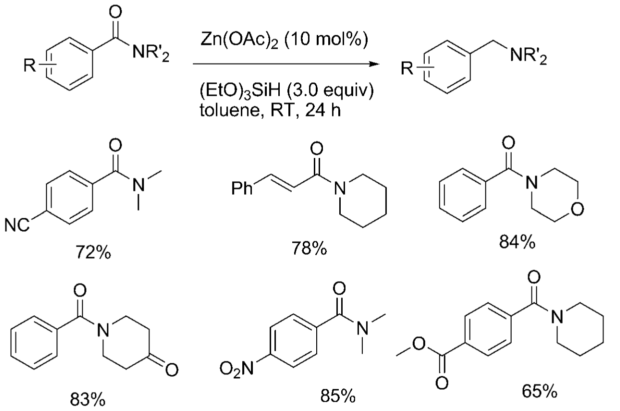
As a result of our interest in the application of biorelevant metal catalysis,[28] we recently also started to explore the catalytic potential of zinc- and iron-based catalysts for the hydrosilylation of amides to amines.[29] To our delight, inexpensive and readily available iron carbonyl clusters, such as $[Fe_3(CO)_{12}]$, enabled the selective reduction of tertiary amides in combination with PMHS.[25] A mechanism proposed on the basis of isotopic labeling experiments is shown in Scheme 10. This procedure also showed good functional-group tolerance. Thus, esters, halogens, olefins, and alkoxy groups remained stable under the reaction conditions.



Scheme 10. Proposed mechanism for the iron-catalyzed reduction of tertiary amides.

In further investigations to find milder conditions for the hydrosilylation of amides, a system combining zinc acetate and $(EtO)_3SiH$ showed excellent activity for the reduction of many tertiary amides at room temperature.[30] In this case, the amide group was reduced selectively in the presence of other functional groups. Ester, cyano, nitro, and diazo groups, C=C double bonds, and even ketones remained untouched during the reaction, which furnished only the corresponding tertiary amine (Scheme 11).

Note that when the reducing agent triethoxysilane was used in the reduction of a methyl ester on a 90 mmol scale, a pyrophoric gas (probably SiH_4) was formed, which resulted in a fire and an explosion.[31] During our studies on the reduction of amides, we have never experienced any safety problems when using triethoxysilane, which is used on an industrial scale in the silane and silicone industry for the production of

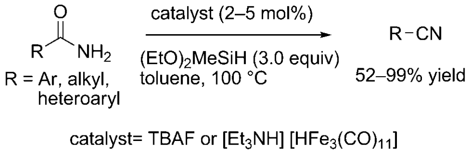


Scheme 11. Zinc-catalyzed hydrosilylation of tertiary amides. Substrates are shown with the product yields.

organofunctional coupling agents, low-temperature-vulcanizing (ltv) silicone rubbers and elastomers, and specialty monomers. However, owing to the previous safety problems experienced during ester reductions, we advise the use of methyldiethoxysilane instead of triethoxysilane for the reduction of amides on a multigram scale. Since Si–C bonds and Si–O–Si linkages are strong, alkyl hydrosilanes (in particular, trialkyl hydrosilanes) and PMHS can not produce SiH_4. The procedures based on the use of these hydrosilanes are important. For example, methyldiethoxysilane and other organosilanes can also be used for the reduction of amides at a slightly higher temperature, for example, at 60 °C.

Very recently, we further developed zinc-catalyzed reductions of amides. Key to the success of the hydrosilylation of secondary amides was again the use of a silane with a dual Si–H moiety. The production of secondary amines was completely selective in the presence of ester, nitro, nitrile, and ether groups, as well as C–C double bonds and azo bonds.[32]

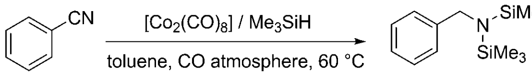
Besides iron-based catalysts, we also investigated the tetrabutylammonium fluoride (TBAF) catalyzed hydrosilylation of primary amides to amines with methyldiethoxysilane $(EtO)_2MeSiH$.[8b,33] With benzamide as the model substrate, the exclusive formation of benzonitrile took place (Scheme 12). The general applicability of the method and the functional-group tolerance of the catalytic systems TBAF and $[Et_3NH][HFe_3(CO)_{11}]$ with $(EtO)_2MeSiH$ were shown in the dehydration of 18 different aromatic, heteroaromatic, and aliphatic amides.



Scheme 12. Dehydration of primary amides.

5. Reduction of Nitriles

Although transition-metal-catalyzed hydrosilylations of acetylenes are well-established in silicon chemistry, very little is known about the hydrosilylation of C–N triple bonds. Indeed, the cyano group was believed to be inert under the usual hydrosilylation conditions. In the early 1980s, Corriu et al. reported that the hydrosilylation of nitriles with the Wilkinson catalyst and 1,2-bis(dimethylsilyl)benzene as the hydrosilane gave a mixture of *trans-N,N*-disilylated enamines and *N,N*-disilylated amines.[21] Almost a decade later, Murai et al. demonstrated the hydrosilylation of nitriles in the presence of a catalytic amount of $[Co_2(CO)_8]$ at 60 °C to give *N,N*-disilyl amines in good yields (Scheme 13). Electron-donating groups on the aromatic nitriles facilitated the reaction, whereas electron-withdrawing groups decreased the reaction rate. For aliphatic nitriles, a higher reaction temperature (100 °C) was required; as in the case of α,β-unsaturated nitriles, four products were obtained.[34a] Later on, Caporusso et al. developed a novel hydrosilylation of nitriles catalyzed by rhodium metal particles. They demonstrated the broad scope of the reaction with respect to the substrate, as well as the use of different hydrosilanes.[34b]

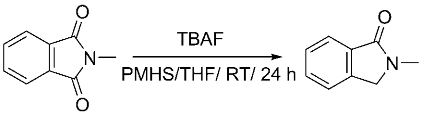


Scheme 13. Hydrosilylation of benzonitrile.

Recently, Gutsulyak and Nikonov discovered an elegant and efficient ruthenium-catalyzed hydrosilylation of nitriles that showed unprecedented chemoselectivity as well as compatibility with most common functional groups. The catalyst is air-stable and can be synthesized readily from commercially available compounds. Moreover, the catalyst is recyclable, which makes the system particularly attractive for practical use.[34c]

6. Miscellaneous Reductions

Recently, effort has also been devoted to the hydrosilylation of imides and nitro groups. Such reactions open up viable routes to functionalized amines. For example, we developed the first fluoride-catalyzed reduction of imides with inexpensive PMHS (Scheme 14). Good to excellent product yields were observed for a variety of aromatic imides. By combining fluoride- and iron-catalyzed hydrosilylation reactions, the full reduction of phthalimides to isoindolines is also possible.[35]



Scheme 14. Hydrosilylation of an imide.

We also carried out a comprehensive study on the selective iron-catalyzed reduction of nitroarenes with organosilanes. The inexpensive and convenient catalytic system $FeBr_2/PPh_3$ reduced a variety of nitro-substituted arenes and heteroarenes under optimized reaction conditions (with $FeBr_2$, PPh_3, and $PhSiH_3$ (2.5 equiv) in toluene at 110 °C) in good to excellent yields. Notably, other reducible functional groups, such as cyano, nitro, ester, ether, and alcohol groups, as well as C=C double bonds, were not affected under these conditions.[36] During their studies on the iron-catalyzed reduction of amides, Nagashima and co-workers observed a selective catalytic reduction of nitroarenes to anilines with TMDS. Notably, this reduction proceeded preferentially in the presence of the amide group, which was not the case for catalysis by platinum or ruthenium compounds.[24g]

7. Summary

A number of interesting catalytic reductions of carboxylic acid derivatives with hydrosilanes have been developed in the last decade. Notably, some of the procedures enable unprecedented chemoselectivity that is not attainable with traditional organometallic hydrides. For example, amides and esters can be reduced preferentially in the presence of ketones! Because of the straightforward reaction procedures and the ability to fine-tune the reactivity of the reducing systems, we believe that catalytic hydrosilylations will be used more often in challenging organic syntheses in the future. So far, their potential has clearly been underestimated. However, when it comes to larger-scale applications, the cost of the silane must be considered. In this case, inexpensive and readily available silanes, such as PMHS, should be used preferentially.

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