Chemoselective Hydrogenation of α,β-Unsaturated Nitriles

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Abstract: The chemoselective hydrogenation of cinnamonitrile to 3-phenylallylamine proceeds with up to 80% selectivity at conversions of >90% with Raney cobalt and up to 60% selectivity with Raney nickel catalysts. Best results were obtained with a doped Raney cobalt catalyst (RaCo/Cr/Ni/Fe 2724) in ammonia saturated methanol at 100 °C and 80 bar. Major problems are the formation of hydrocinnamonitrile and of secondary amines, and overreduction to 3-phenylpropylamine. Important parameters are the catalyst type and composition, the solvent type and the presence and concentration of ammonia. The catalytic system tolerates functional groups like OH, OMe, Cl, C=O, but not aromatic nitro groups. Preliminary experiments indicate that other unsaturated nitriles with di- or trisubstituted C=C bonds are also suitable substrates.

Keywords: allylamines; chemoselective hydrogenation of unsaturated nitriles; Cr-modified Raney cobalt; effect of ammonia addition; Raney nickel

Introduction

The catalytic hydrogenation of nitriles is one of the basic methods to obtain primary amines, and especially diamines are of high industrial importance. While many different catalytic systems have been studied, the open literature is rather scattered and only two recent up-to-date reviews exist.[1] Reactions are often carried out in a liquid phase, at temperatures up to 100 °C and pressures up to 100 bar with Raney nickel (RaNi) or Raney cobalt (RaCo) as industrially preferred catalysts, but Pd and Pt catalysts are also suitable. The activity and selectivity of RaNi catalysts is often improved by adding metals such as chromium, iron or molybdenum.

Besides the usually desired primary amines, secondary and tertiary amines can be formed *via* condensation of reaction intermediates and control of this chemoselectivity problem is one of the main issues of nitrile hydrogenation (see below). Addition of ammonia is most widely used to improve the selectivity for primary amines,[1] but recently it was reported that less toxic bases such as NaOH[2] and LiOH[3] are also effective for Raney Ni and Co catalysts. The OH^- ions not only prevent catalyst deactivation by inhibiting polyamine formation on the catalyst surface for the hydrogenation of dinitriles,[2a] but also seem to block active sites responsible for by-product formation.[2b]

For fine chemicals applications, functional group tolerance is an important issue. When hydrogenating nitriles in the presence of other reducible groups, substituents like aryl groups, benzylic functions or C−Hal are usually not reduced with skeletal Ni or Co catalysts. More difficult to conserve are heteroaromatic or heteroaryl halogen functions, ketones, aldehydes or a second C≡N group, but with the proper catalyst, solvent and additives success is often possible.[1] In contrast, the selective hydrogenation of C≡N groups in the presence of C=C bonds has long been an unsolved problem, particularly if conjugated or in close proximity.[4–6] We could find only three examples with reasonable chemoselectivities (see Figure 1): A non-conjugated, sterically hindered C=C bond was left intact with unspecified cobalt and nickel catalysts in liquid ammonia,[7] high selectivity was described for an unsaturated fatty acid nitrile where the reduction of a remote C≡N function is possible by applying a Ziegler-type Co-Fe catalyst even in absence of NH_3,[8] and, finally, it was claimed that cinnamonitrile can be reduced selectively over an *in situ* prepared Ni-B catalyst.[9]

We started to investigate the hydrogenation of α,β-unsaturated nitriles in more detail since this could be an attractive procedure for preparing allylamines. As model substrate for our study we chose cinnamonitrile which is reasonably stable, not too volatile and has an activated, not very sterically hindered C=C bond. The hydrogenation of cinnamonitrile **1** can proceed along two major pathways as shown in Figure 2. In the more frequently observed route, the C=C bond of cinnamonitrile is reduced first to give hydrocinnamonitrile **2** which is transformed *via* the saturated imine **3** to the final product,

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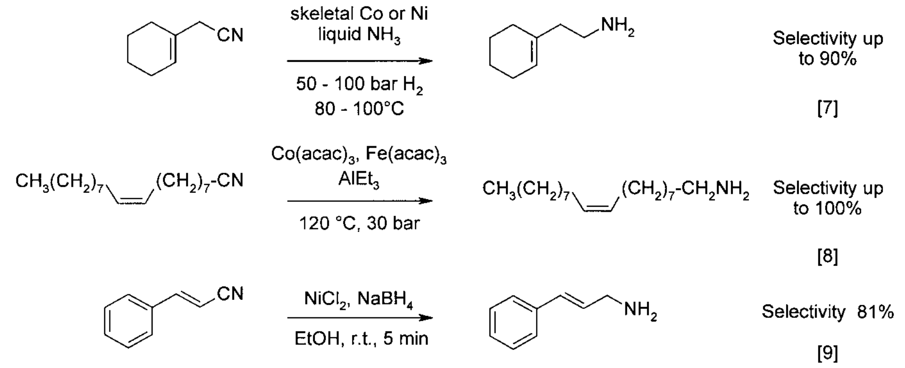

Figure 1. Chemoselective reduction of C≡N functions in presence of a C=C bond.

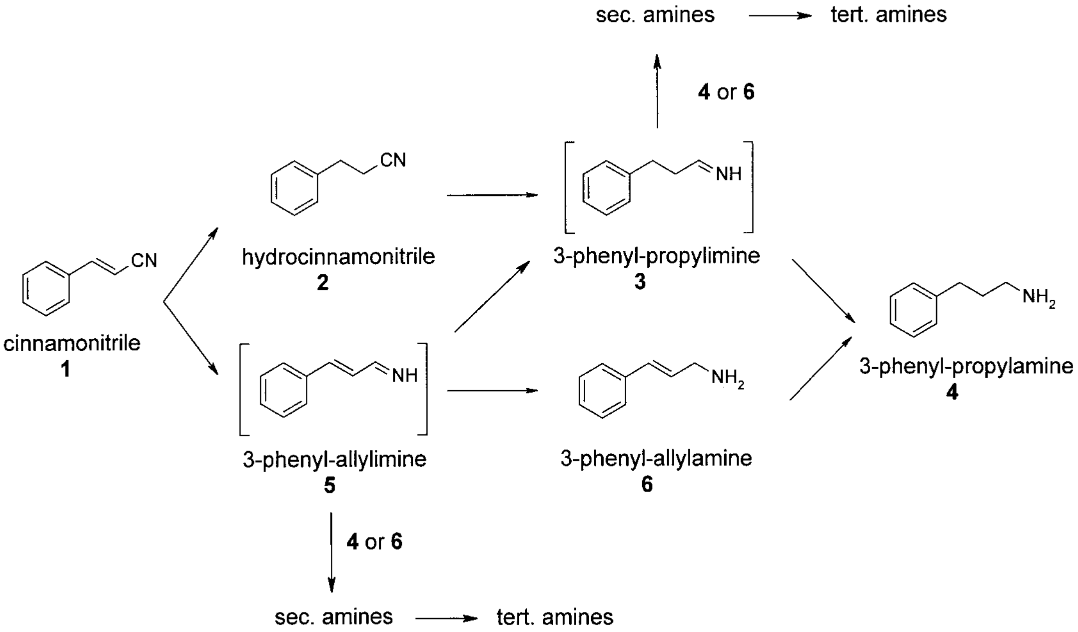

Figure 2. Possible reaction paths for the cinnamonitrile hydrogenation.

3-phenyl-propylamine **4**. Alternatively, H_2 can add to the nitrile forming the unsaturated conjugated imine **5**, which can either react to **3** or to the desired 3-phenyl-allylamine **6**. Consecutive hydrogenation of **6** leads again to the fully hydrogenated **4**. In addition, the two imine intermediates **3** and **5** can react with already formed **4** or **6** to form various secondary amines (which in turn can react even further to give tertiary amines). In this contribution we describe the development of Raney nickel- and Raney cobalt-based catalyst systems for the chemoselective hydrogenation of cinnamonitrile yielding up to 70% of 3-phenylallylamine **6**.

Results and Discussion

In a first phase, we tested a broad spectrum of catalysts such as (modified) noble metals on various supports, selected Ni catalysts and some other types (see Table 1 in the Supporting Information). We decided to use only commercially available catalysts since in this phase of our investigation, we were primarily interested to develop a synthetically useful catalytic system. Commercial catalysts have the advantage to be available in reproducible quality, on the negative side often little information is available on their preparation and detailed structure. Not unexpectedly, these experiments which were carried out in various solvents (methanol, toluene, and THF) without base addition resulted mainly in the preferential hydrogenation of the C=C double bond giving 3-phenylpropionitrile **2** and subsequently 3-phenylpropylamine **4**. In addition, up to 50% formation of secondary amines was observed. Nevertheless, some unsaturated amine **6** was observed with Raney nickel (RaNi) and Raney cobalt (RaCo) and we decided to investigate the effect of base addition to suppress secondary amine

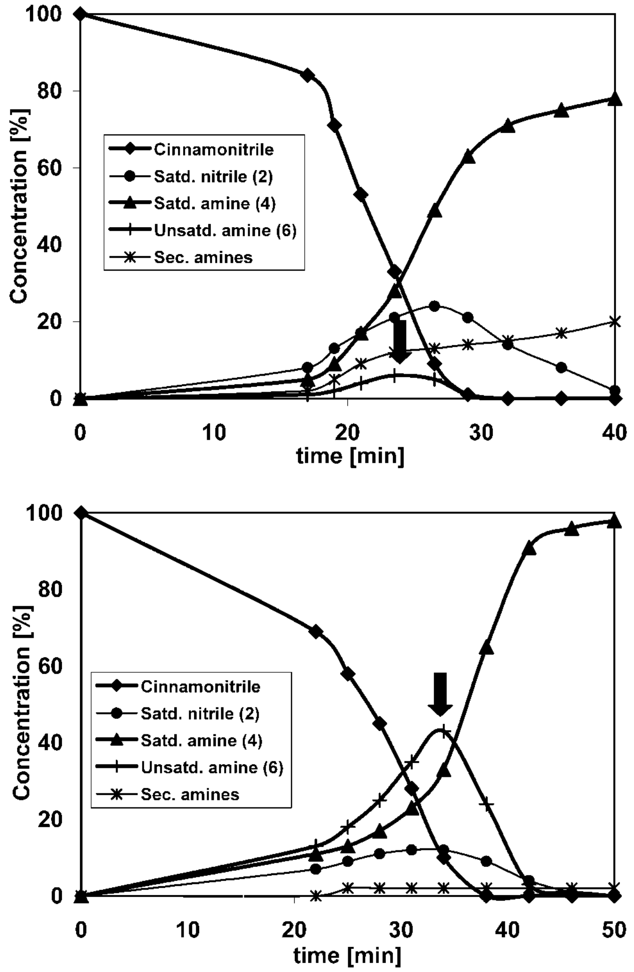

Figure 3. Typical reaction profiles. *Top:* RaNi in MeOH, no base. *Bottom:* RaNi in MeOH saturated with NH_3. Arrow shows maximum concentration of unsaturated amine **6**.

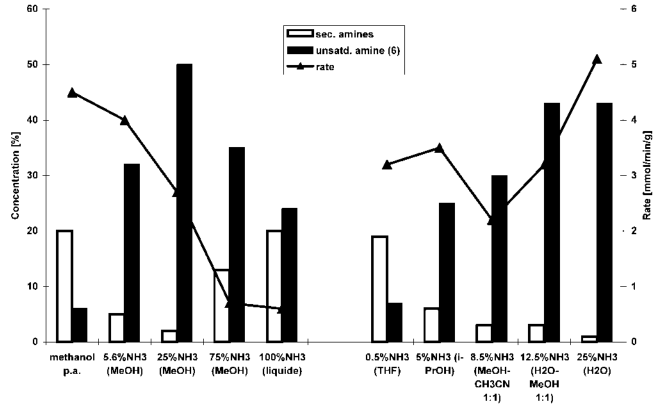

Figure 4. Effect of ammonia concentration (wt %) in various solvents on the formation of unsaturated amine **6** (maximum concentration), of secondary amines (end of reaction) and on the reaction rate (at 50% conversion). Reaction conditions: 250 mg wet RaNi-H_2O Doducco Actimet M, 3 mL substrate, 27 mL solvent, 100 °C, 8 MPa.

formation with these two catalyst types. Selected results are summarized in Table 1 and two typical concentrations profiles are depicted in Figure 3.

Without going into detail, some observations warrant a comment. i) Figure 3 demonstrates that we in fact deal with consecutive reactions where the intermediates **2** and **6** are hydrogenated further to the saturated amine **4**. The secondary amines appear only after much of the substrate has disappeared and their concentration remains almost unchanged over a long period. The apparent induction period is due to the fact that the reaction temperature of 100 °C is reached only after about 12 min. ii) While the addition of either hydroxide and even more pronounced of ammonia led to the expected decrease in secondary amines (determined at the end of the reaction), it also had a surprising beneficial effect on the selectivity to unsaturated amine **6** expressed as SEL_{uncat}, defined as %**6**/[%**2**+%**4**+%**6**] at the maximum concentration of **6** (arrows in Figure 3). iii) RaCo achieved similar selectivities but much lower rates than RaNi. iv) On the negative side, relatively high amounts of by-products were formed, especially in presence of aqueous ammonia, and base addition caused a rate decrease for all RaNi catalysts.

These trends were confirmed by a series of experiments designed to give a more quantitative picture of the effect of ammonia concentration on selectivities

Table 1. Preliminary experiments with RaNi and RaCo in methanol, influence of various bases.

Catalyst	Base	Secondary amine %	By-product %	SEL_{unsat}[a]	$Rate_{50\%}$ mmol/min/gcat
RaNi-H_2O (Doducco)	None	20	<1	0.11	4.5
RaNi-H_2O (Doducco)	0.1 M NaOH	11	7	0.15	3.3
RaNi-H_2O (Doducco)	1.0 M LiOH	16	5	0.13	4.1
RaNi-H_2O (Doducco)	25 wt % NH_3	1	<1	0.56	2.7
RaNi-H_2O (Doducco)	25% NH_4OH[b]	1	9	0.51	5.1
RaCo-EtOH (Degussa)	None	41	<5	0.26	0.3
RaCo-EtOH (Degussa)	14 wt % NH_3	3	7	0.49	0.9[c]

Reaction conditions: 250 mg wet catalyst, 3 mL substrate, 27 mL MeOH, 100 °C, 8 MPa.

[a] SEL_{uncat}, defined as %**6**/[%**2**+%**4**+%**6**].

[b] Solvent H_2O.

[c] Reaction temperature 120 °C.

Table 2. Comparison of Raney nickel catalysts supplied by different manufacturers.

Entry	Catalyst	NH_3 conc. %	SEL_{unsat}[a]	Conv.[b] %	$Rate_{50\%}$ mmol/min/gcat
1	Actimet M (Doducco)	12%	0.50	90	3.6
2	Actimet M (Doducco)	17%	0.53	95	3.3
3	Actimet M (Doducco)	25%	0.56	95	2.7
4	BLM 112 W (Degussa)	12%	0.38	83	3.6
5	RaNi+2%Cu B113 (Degussa)	14%	0.60	88	2.1
6	RaNi-1%V BP113 (Degussa)	14%	0.45	91	4.2
7	E117-EtOH (Engelhard)	12%	0.42	78	4.7
8	E014-H2O (Engelhard)	14%	0.49	93	3.4
9	RaNi 1250 (Metcat)	17%	0.38	89	2.7
10	RaNi/Cr/Fe 1254 (Metcat)	17%	0.21	90	4.2
11	RaNi/Mo 3110 (Grace)	14%	0.35	90	3.9
12	RaNi/Cr/Fe 2400 (Grace)	14%	0.28	91	4.2

Reaction conditions: 250 mg catalyst, 3 mL cinnamonitrile, 27 mL MeOH, 100 °C, 80 bar H_2.

[a] Concentration of secondary amines <3%, no by-products.

[b] At maximum concentration of **6**.

and rate and the results are graphically summarized in Figure 4. In methanol, increasing ammonia concentrations up to 25% led to a strong decrease in secondary amine formation combined with a significantly higher amount of unsaturated amine, however, at NH_3 concentrations >25%, this trend was reversed. The reaction rate decreased continually with increasing ammonia content. In other solvents, higher ammonia concentrations always gave an increase of the desired selectivities too, whereas the rate no longer had a clear trend.

While we are not able to interpret all these observations, it is plausible that competitive adsorption of ammonia leads to a lower overall rate. Since the nitrile group adsorbs much more strongly on Ni surfaces than a C=C bond[6] the adsorption of latter could be blocked by ammonia more effectively than that of the nitrile, explaining the preferential formation of the allylamine **6**. However, it should be stressed that simple adsorption considerations are not able to explain the basic difficulty to obtain unsaturated amines.[6]

Protic solvents seem to be better suited giving higher rates and often better selectivities both concerning the formation of secondary as well as unsaturated amines. The effects of the hydrogen pressure (40–120 bar), temperature (80–120 °C) and of the amount of cinnamonitrile (1.5–6 mL) were also briefly examined (results not shown). All parameters had relatively small effects on the formation of secondary amines (<3%) and on SEL_{unsat} (0.46–0.56), except for low substrate concentrations with an SEL_{unsat} of 0.35, maybe due to a lower nitrile coverage. The rates were mainly influenced by the reaction temperatures and increased from 2.1 to 3.9 mmol/min/g. For all further studies we worked at 100 °C and 80 bar with 3 mL cinnamonitrile in 27 mL of ammonia saturated methanol as solvent, as these conditions represented the best compromise between selectivity and rate. Furthermore, due to the relatively slow reaction we are confident that under these conditions there are no diffusion limitations.

It is well known that different Raney nickel catalysts can have quite different catalytic performances. Therefore, a series of catalysts from the major suppliers was tested and since Raney catalysts can easily be doped with a second metal, we also used several modified samples. The results listed in Table 2 show that all investigated catalysts are suitable with relatively small differences in catalyst performance. The beneficial effect of higher ammonia concentrations is confirmed (compare entries 1–3) and a remarkable selectivity of 0.56 to the desired unsaturated amine **6** at a conversion of 95% was observed for the Actimet M catalyst from Doducco. The effects of doping were contradictory. While doping of the Degussa RaNi with Cu or V had a beneficial effect (entries 4–6) leading to a catalyst with the highest SEL_{unsat}, albeit at only 88% conversion, adding Cr and Fe to the Metcat catalyst was detrimental (entries 9 and 10) and the Mo and Cr-Fe doped Grace catalysts were among the least selective of all tested catalysts (entries 11 and 12). In most cases, doping led to somewhat more active catalysts but the highest rate was observed with E117-EtOH from Engelhard stored under ethanol.

Under the same optimized reaction conditions some supported nickel catalysts (SiO_2, Al_2O_3), Raney Cu and Cu chromite as well as *in situ* prepared Ni–B catalyst[9] and the Ziegler-type Co-Fe catalyst[8] (see Figure 1) were also tested. These catalysts were not investigated any further since all showed either low SEL_{unsat}, low rates or both (results not shown).

Since we could not further improve the catalyst performance with Ni catalysts, we returned to the Raney cobalt catalysts, even though the pre-screening results indicated them to have rather low activities. Again, several doped and undoped catalyst samples of different catalyst manufacturers were tested (see Table 3). The results need little comment since it is immediately obvious that

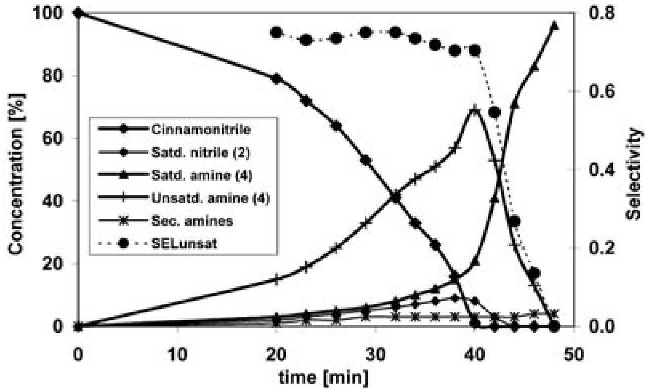

Figure 5. Reaction profiles with RaCo/Cr/Ni/Fe 2724 (entry 8).

all doped RaCo catalyst exhibited very high selectivities to the desired allylamine **6**. Obviously, Cr sometimes in combination of Fe increased SEL_{unsat} up to 0.81 at very high conversions. The rates were also positively affected, especially for the Grace catalyst doped with Cr, Fe and Ni (entry 7). As already observed with the Ni catalysts, LiOH gave even higher rates but lower selectivities (entries 8 and 9). As a slight drawback, somewhat higher levels of secondary amines were formed than with the Ni catalysts. Examination of the reaction profile with a doped Co catalyst depicted in Figure 5 reveals that SEL_{unsat} remains constant up to the point where all nitrile is consumed and then rapidly decreases. This points to a preferential adsorption of the C≡N group in competition with the C=C bond on the catalyst surface thereby preventing its reduction. At this time we cannot explain the positive effect of doping the RaCo catalysts with Cr and Fe since we do not have any information on the oxidation state or the location of the dopants. Making the interpretation even more difficult is the fact that the same dopants led to lower selectivities when RaNi catalysts were employed (Table 2).

We also tried to replace ammonia with hydroxide ions since we had shown in our preliminary study that these also had a weak positive effect on the selectivity without lowering the reaction rates very much (see Table 1). However, only rather low selectivities were obtained with the exception of the Grace catalyst in the presence of LiOH (Table 3, entries 8 and 9) which showed very high rates and acceptable levels of unsaturated amine. Unfortunately, in MeOH rather high amounts of secondary amines were formed.

For application in the fine chemicals industry, the functional group tolerance of a catalytic system is important. To get a first idea in this respect, we carried out a few preliminary experiments in the presence of anisole and 4-hydroxyphenylethanol (OH, OMe groups), chlorobenzene (C–Cl), acetophenone (C=O), nitrobenzene and 4-nitro-2-methoxyaniline (NO_2, NH_2). The reactions were carried out using the best Raney cobalt catalyst with one equivalent of tested molecule with respect to cinnamonitrile. The results are shown in Table 4.

As expected, MeO, Cl, and OH groups do not interfere with the cinnamonitrile hydrogenation and only slight differences in catalytic performance were observed. The same was true in the first phase for acetophenone but the C=O group was reduced as soon as all nitrile groups had been hydrogenated. Phenylethylamine (*via* reductive amination) and phenylethanol were formed, again a case of competitive adsorption of the nitrile and the C=O or the C=N group. The influence of an aromatic nitro group was tested with 4-nitro-2-methoxyaniline and nitrobenzene. With both substrates the reaction was strongly inhibited and several by-products were formed. To observe a measurable reaction rate with nitrobenzene, the reaction temperature had to be increased to 120 °C, the catalyst amount had to be doubled, and lithium hydroxide was used instead of ammonia. The low catalyst activity points to a nitro group very strongly adsorbed on the catalyst surface. Furthermore, the aniline derivatives formed by hydrogenation, prob-

Table 3. Comparison of Raney cobalt catalysts supplied by different manufacturers.

Entry	Catalyst	T [°C]	Sec. amines %	By-product %	SEL_{unsat}	Conv.[a] %	$Rate_{50\%}$ mmol/min/gcat
1	RaCo Degussa B2112 – F014	120	3	7	0.49	100	0.9
2	RaCo/Cr Degussa MC200X	100	10	<2	0.73	92	0.9
3	RaCo/Cr/Ni Degussa MC201X	120	8	<2	0.69	99	1.2
4	RaCo/Cr/Fe Degussa MC202X	100	7	<2	0.81	99	1.0
5	RaCo/Cr/Fe Degussa MC202X	120	10	<2	0.78	94	1.7
6	RaCo 2700 (Grace)	100	3	–	0.51	88	1.0
7	RaCo/Cr/Ni/Fe 2724 (Grace)	100	3	–	0.75	99	3.8
8	RaCo/Cr/Ni/Fe 2724 (Grace)[b]	100	28	<1	0.70	90	12.2
9	RaCo/Cr/Ni/Fe 2724 (Grace)[c]	100	3	<1	0.63	80	7.2

Reaction conditions: 250 mg catalyst, 3 mL cinnamonitrile, 27 mL 14% NH_3 in MeOH, 80 bar H_2.

[a] At maximum concentration of **6**.

[b] 100 mg catalyst, methanol with 200 mg $LiOH \cdot H_2O$.

[c] 100 mg catalyst, THF with 200 mg $LiOH \cdot H_2O$.

Table 4. Hydrogenation of cinnamonitrile in presence of a second substrate.

Entry	2nd Substrate	SEL_{unsat}	Sec. amines %	$Rate_{50\%}$ mmol/min/gcat	$Rate_{2nd\ Substrate}$ mmol/min/gcat
1	None	0.75	<3	3.2	0.0
2	Anisole	0.73	6	4.0	0.0
3	Chlorobenzene	0.65	5	2.9	0.0
4	4-Hydroxyphenylethanol	0.61	2	2.5	0.0
5	Acetophenone	0.68	9	3.4	1.7
6	4-Nitro-2-methoxyaniline[a]	0.56	2	1.1	1.6
8	Nitrobenzene (120 °C)[b]	0	24	0.7	0.7

Reaction conditions: 1 equiv. additive, 3 mL cinnamonitrile, 250 mg RaCo/Cr/Ni/Fe 2724, 27 mL 17% NH_3 in MeOH, 100 °C, 80 bar.

[a] 5% unknown by-products.

[b] 500 mg RaCo/Cr/Ni/Fe 2724, 500 mg $LiOH.H_2O$, 1 mL H_2O, 27 mL MeOH.

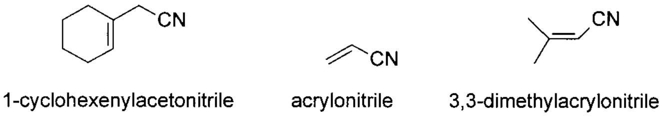

Figure 6. Structures of the tested unsaturated nitriles.

ably stay adsorbed and react with imine intermediates to give various secondary amines.

Finally we carried out a few preliminary experiments with three other unsaturated nitriles (Figure 6) with the best catalyst systems in 17% NH_3/MeOH at 100 °C, 80 bar. The hydrogenation of 1-cyclohexenylacetonitrile gave similar results as reported by Poeple and Gaube.[7]. With RaCo (RaCo/Cr/Ni/Fe 2724) selectivity to primary amines was 99% and SEL_{unsat} reached 90%, while it was again a bit lower (80%) with RaNi (Doducco Actimet M). The selective reduction of acrylonitrile could be a very attractive way for producing allylamine. However, no trace of allylamine was found when using RaCo/Cr/Ni/Fe 2427 in 25% NH_3/MeOH. The major products were 3-methoxypropionitrile (20%, addition of MeOH), 3-aminopropionitrile (65%) and propionitrile (15%). The more sterically hindered 3,3-dimethylacrylonitrile gave SEL_{unsat} up to 0.45 under similar reaction conditions with RaCo. The results indicate that the degree of substitution as well as the position of the C=C bond relative to the nitrile crucially determine the chemoselectivity. These as well as additional substrates will be investigated further and details will be described in a future publication.

Conclusions

The chemoselective hydrogenation of cinnamonitrile to 3-phenylallylamine is possible with chemoselectivities up to 80% in the presence of selected Raney nickel and Raney cobalt catalysts in methanolic ammonia solutions. The best chemoselectivities are obtained in methanol with a doped Raney cobalt catalyst, RaCo/Cr/Ni/Fe 2724 from Grace. The presence of ammonia is essential to enhance both the selectivity to allylamine and to suppress the formation of unwanted secondary amines. Replacing ammonia by sodium or lithium hydroxides leads to more active but significantly less selective catalysts. Various functional groups (OH, OMe, Cl, C=O) do not affect the reaction, whereas the presence of a nitro group is either not tolerated or strongly disturbs the catalyst. Preliminary experiments with other unsaturated nitriles show that the degree of substitution as well as the position of the C=C bond relative to the nitrile group have a strong influence on the chemoselectivity.

Experimental Section

General Remarks

Devices used: Varian GC. (Star 3400cx equipped with autosampler and a special chromatographic column for separation of amines (RTX 5-Amine from Restek Co.); Bruker NMR (300 MHz) with autosampler; Varian GC-MS (sector) – measurements performed by Syngenta.

Chemicals

Cinnamonitrile (97% trans, Fluka), hydrocinnamonitrile (Aldrich) and 3-phenylpropylamine (Fluka) were available commercially. 3-Phenylallylamine was prepared from cinnamonitrile by reduction with $LiAlH_4$.

Secondary amines were isolated from the reaction mixture by column chromatography and were characterized by GC and NMR. To compare the results obtained by GC and NMR, the hydrogenation was stopped close to the maximum concentration of intermediates. The mixture was separated by column chromatography (SiO_2, 100:20:1 CH_2Cl_2:MeOH:25% aqueous NH_4OH), fractions were evaporated and their amounts and compositions were compared with the GC results obtained directly from the reaction mixture. It was confirmed that the results obtained by these two independent methods were in good agreement.

Catalysts

Tested catalysts were commercial samples supplied by different companies (Degussa, Engelhard, Grace Davison, Doducco, Kata Leuna and Metal Catalysts Technology). A list of all applied catalysts is available as Supporting Information. Ziegler catalyst[8] and nickel boride[9] were prepared right before use, following procedures described in the literature.

Raney catalysts were supplied and stored under water and were weighed following the instructions of their manufacturers. Usually the water was removed from the container as well as a first layer of decanted catalyst, and then an appropriate amount of catalyst suspension containing approximately 50% of water was taken for weighing.

Hydrogenation Procedure

Hydrogenation reactions were performed in the liquid phase in a 50-mL three-phase slurry reactor with a magnetic stirring bar and a small baffle. The catalyst and solvent were placed into the reactor and an appropriate amount of substrate was added. The autoclave was closed, and the air was displaced first with argon (3 times) and then with hydrogen (3 times). The autoclave was pressurized with hydrogen to the desired value and a leak-test was carried out (10 min). The reaction was started at room temperature by turning on the magnetic stirrer (ca. 1100 rpm). After saturation of the liquid phase with hydrogen (1.5 min), the reactor was heated up to the reaction temperature (usually 12 min from 25 to 100 °C). The samples were withdrawn periodically until there was no observable consumption of hydrogen. Then, the reaction was stopped, the pressure was released and the hydrogen was displaced by argon. Withdrawn samples and product were filtered in order to remove the catalyst before the analytical measurements.

Analytics

The samples of the reaction mixture withdrawn during the reaction were analyzed by GC (column RTX-5 Amine, Restek), carrier gas: helium 13 psi, temperatures: injector 250 °C, detector 280 °C, oven temperature program: 100 °C (1 min), 5 °C/min to 170 °C (0 min), 20 °C/min to 290 °C (9 min) with the following retention times: 12.0 min (3-phenylpropylamine); 12.8 min (hydrocinnamonitrile); 12.9 min (*cis*-cinnamonitrile); 14.1 min (3-phenylallylamine); 14.3 min (*trans*-cinnamonitrile); 15.0–18.0 min (other by-products, usually $<3\%$, not fully characterized, but probably including alkylated primary and secondary amines formed by the reaction with solvent); 22.0–25.0 min [secondary amines such as bis(3-phenylpropyl)amine, (3-phenylallyl)(3-phenylpropyl)amine and bis(3-phenylallyl)amine].

Some of the samples were also characterized by NMR (Bruker, 300 MHz) and by GC-MS (Varian) in order to compare the results obtained by independent methods. The standard compounds were also analyzed and the results were compared with the analyses of the reaction mixtures.

trans-*Cinnamonitrile:* ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=$ 5.88 (d, =CH-C≡N, 1H), 7.35–7.47 (m, Ph-CH=, 6H); MS (EI): *m/z* (rel. intensity) = 129(100), 102(40), 76(22), 63(18), 51(24).

Hydrocinnamonitrile: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=2.61$ (t, $-CH_2-C\equiv N$, 2H), 2.96 (t, $Ph-CH_2-$, 2H); MS (EI): *m/z* (rel. intensity) = 131(83), 91(100), 77(18), 65(23), 51(13), 39(15).

3-Phenylallylamine: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.49$ (brs, $-NH_2$, 2H), 3.48 (d, CH_2-NH_2, 2H), 6.32 (dt, Ph-CH=CH-, 1H), 6.51 (d, Ph-CH=CH-, 1H), 7.18–7.41 (m, Ph, 5H); MS (EI): *m/z* (rel. intensity) = 133(100), 132(89), 115(67), 91(34), 77(21), 56(23), 51(17).

3-Phenylpropylamine: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=$ 1.19 (brs, $-NH_2$, 2H), 1.78 (m, $CH_2CH_2NH_2$, 2H), 2.65 (t, $-CH_2-NH_2$, 2H), 2.72 (t, $Ph-CH_2-$, 2H), 7.11–7.34 (m, Ph, 5H); MS (EI): *m/z* (rel. intensity) = 135(15), 118(100), 117(65), 91(61), 77(44), 65(53), 51(39), 42(19).

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