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Enzyme-Promoted Desymmetrisation of Prochiral Bis(cyanomethyl) Sulfoxide

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Abstract: Prochiral bis(cyanomethyl) sulfoxide has been successfully transformed into the corresponding optically active mono amide and mono acid with enantiomeric excesses ranging from low (10%) to very high (up to 99%) using a broad spectrum of nitrile-hydrolysing enzymes.

Keywords: asymmetric synthesis; cyanides; enzyme catalysis; nitrilases; sulfoxides

Introduction

Nitriles constitute a versatile group of compounds, due to the ease of cyanide introduction, and subsequent conversion into various other functional groups, for example, amines, amides or acids.[1] Possibilities to introduce a cyanide function include substitution of alkyl halides by cyanide anion,[1,2] the reaction of aryl halides under the influence of copper cyanide,[3] dehydration of amides,[4] reaction of ketones with tosylmethyl isocyanide,[5] and the Sandmayer reaction.[6] The hydrolysis, however, of nitriles to the corresponding amides or carboxylic acids usually requires rather harsh conditions, for example, very concentrated acids or bases, heavy metal salts or elevated temperatures.

An alternative for such reactions can be found in the use of nitrile-converting enzymes. In the past two decades the enzymatic hydrolysis of nitriles has been recognised as a method to afford a broad spectrum of useful carboxylic acids and amides.[7] This method is very useful from the synthetic point of view owing to the mildness under which the reactions can be carried out such as in aqueous buffers at neutral pH and at ambient temperature.

Three different enzyme classes can be involved in enzymatic nitrile hydrolysis. Nitrilases are able to convert nitriles directly into the corresponding acids without the amide as an intermediate. Nitrile hydratases (NHases), on the other hand, transform nitriles into the corresponding amides, which under the influence of amidases can be converted into the appropriate acids (Figure 1).[8,9]

Although many enzymatic transformations of nitriles, which have been reported thus far, involve straightforward achiral substrates, stereoselective transformations involving racemic or prochiral substrates are particularly interesting.[10] Mechanisms influencing the stereoselectivity of the nitrile hydrolysis are complicated and may vary depending on the kind

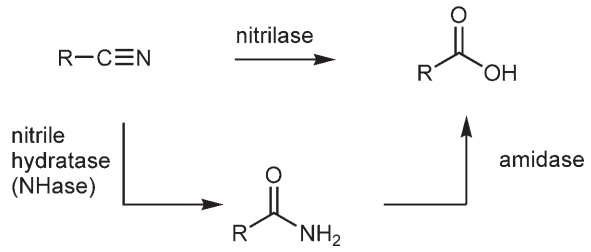

Figure 1. Nitrile hydrolysing enzymes.

of substrates. Thus, in one of the first publications describing the hydrolysis of racemic nitriles, the resolution was assumed to occur in the amide hydrolysis step under influence of the amidase.[11] The lack of enantiomeric enrichment of the recovered substrate and opposite absolute configurations of the resulting amide and acid were taken as proof for such a mechanistic proposal. However, changing the substrate caused an opposite effect leading to the conclusion that the hydratases were responsible for the observed enantioselectivity.[11] A similar assumption was made in the case of the desymmetrisation of prochiral dinitriles, although no amide intermediate was detected.[12] Clearly, both types of enzymes have been shown to exhibit stereoselectivity. In view of the unpredictable nature of enantioselective enzymatic nitrile hydrolysis,[13] a strong interest remains in investigating a variety of new enzymatic transformations of nitriles.

Previous work of our group on the enzymatic desymmetrisation of prochiral compounds and enzymatic resolution of racemic substrates led to particularly efficient syntheses of several classes of optically active heteroatom-containing compounds.[14–17] In all cases simple hydrolytic enzymes were applied and appeared capable of recognising stereogenic or prostereogenic centres located on heteroatoms or heteroatom-bound carbon atoms. In the course of our investigations we turned our attention to heteroorganic nitriles which, in the light of the facts presented above, seemed interesting both from mechanistic and practical points of view. Therefore, we decided to investigate whether nitrile-hydrolysing enzymes are capable of accepting substrates with a prochiral heteroatom. It should be emphasised that such dinitriles have never been used as substrates for these types of enzymes. This contribution focuses on the investigation of enzyme-mediated desymmetrisation of bis(cyanomethyl) sulfoxide.

Results and Discussion

Synthesis of Prochiral Bis(cyanomethyl) Sulfoxide (2)

The starting material, prochiral bis(cyanomethyl) sulfoxide (**2**), was synthesised *via* a two-step method from chloroacetonitrile which, upon treatment with anhydrous sodium sulfide in DME, provided bis(cyanomethyl) sulfide (**1**) in 75% yield. The latter was oxidised in crude form with sodium periodate in a 1:1 mixture of water and ethanol to give the desired sulfoxide **2** in 60% yield after purification (Figure 2). An alternative method for the synthesis of **2**, previously described by Singh and Gandhi[18] using thioacetamide as a sulfur source, in our hands appeared to be unsuccessful.

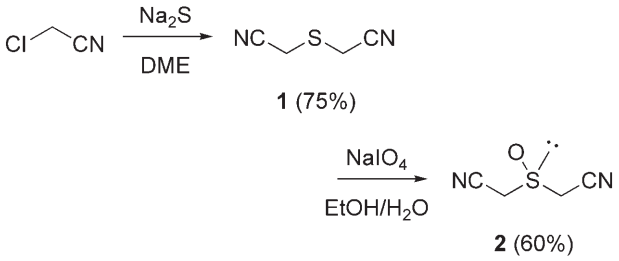

Figure 2. Synthesis of bis(cyanomethyl) sulfoxide (**2**).

Enzymatic Hydrolysis of Prochiral Bis(cyanomethyl) Sulfoxide (2)

The prochiral substrate **2** was subjected to a general enzymatic resolution protocol (vide infra), which can give rise to the five possible products **3–7** (Figure 3). Three of them (**3**, **5** and **6**) may, in principle, be produced in each enantiomeric form. The hydrolyses were performed in different buffer solutions using a broad spectrum of nitrile-converting enzymes, namely a whole cell preparation from *Rhodococcus erythropolis* NCIMB 11540 (freeze dried cells)[13] and a series of commercially available nitrilases. In all cases the

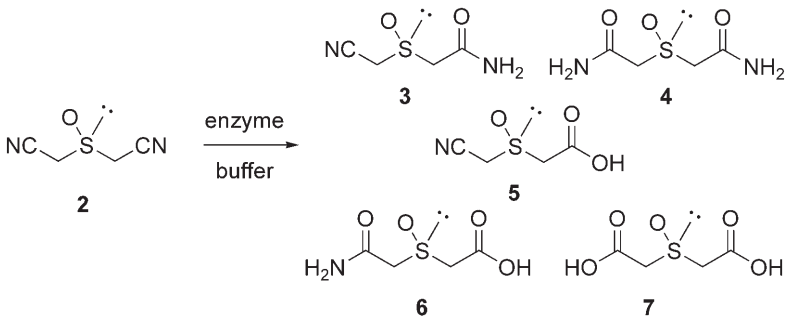

Figure 3. Possible products of hydrolysis of (**2**).

Table 1. Enzymatic hydrolysis of prochiral **2**

Entry	Enzyme	Buffer, pH	After column chromatography Product, yield [%]	After purification with DOWEX® 50W Product, yield [%]	$[\alpha]_D$[a]	ee [%]	Abs. conf.
1	Nitrilase 101	KH_2PO_4/K_2HPO_4, 7.2	**2**, 45.0	**3**, 1.75	+10.0	41[c]	(*S*)
			3, 26.3				
2	Nitrilase 102	KH_2PO_4/K_2HPO_4, 7.2	**7**, 55.8	**7**, 38.8	0	0	-
3	Nitrilase 103	KH_2PO_4/K_2HPO_4, 7.2	**3**, 26.3	**3**, 8.8	-8.0	33[c]	(*R*)
			7, 46.5	**7**, 42.6	0	0	-
4	Nitrilase 105	KH_2PO_4/K_2HPO_4, 7.2	**3**, 8.8	**3**, 4.4	+20.0	82[c]	(*S*)
			5, 43.5	**5**, 26.1	+12.0	52[c]	(*S*)
			7, 23.2	**7**, 19.4	0	0	-
5	Nitrilase 107	KH_2PO_4/K_2HPO_4, 7.2	**3**, 17.5	**3**, 3.5	+18	74[c]	(*S*)
			5, 34.8	**5**, 20.8	-15.0	66[c]	(*R*)
6	Whole cells[d]	KH_2PO_4/K_2HPO_4, 7.2	**3**, 13.2	**3**, 4.4	+12.0	49[c]	(*S*)
			5, 79.1	**5**, 61.7	+8.0	33[c]	(*S*)
7	Nitrilase 103	K_3PO_4, DTT	**2**, 60.0				
		EDTA, pH 7.5	**3**, 39.5	**3**, 27.2	-8.0	33[b]	(*R*)
8	Nitrilase 107	K_3PO_4, DTT	**2**, 30.0				
		EDTA, pH 7.5	**3**, 27.2	**3**, 8.8	+12.0	49[c]	(*S*)
			5, 43.5	**5**, 28.7	+15.0	66[c]	(*S*)
9	Nitrilase 108	K_3PO_4, DTT	**2**, 50.0				
		EDTA, pH 7.5	**3**, 21.9	**3**, 14.9	+10.0	41[c]	(*S*)
			5, 4.4	**5**, 2.6	+15.0	66[c]	(*S*)
10	Nitrilase 104	KH_2PO_4/K_2HPO_4, 7.2	**3**, 61.4	**3**, 57.0	+24.14	>99[c]	(*S*)
			5, 27.2	**5**, 19.9	-17.5	77[c]	(*R*)
11	Nitrilase 107	KH_2PO_4/K_2HPO_4, 7.2	**5**, 50.0	**5**, 35.6	-22.6	>99[b]	(*R*)
			7, 23.2	**7**, 16.5	0	0	-

[a] In D_2O.
[b] Determined by chiral HPLC.
[c] Optical purity, determined by comparison of $[\alpha]_D$ values for the cases, in which *ee*s were determined by chiral HPLC
[d] *Rhodococcus erythropolis* NCIMB 11540 (freeze dried cells).

reaction time was 48 h. The results are summarised in Table 1.

Inspection of Table 1 shows that, of the five expected products, only three that is, cyanomethylsulfinylacetamide (**3**), cyanomethylsulfinylacetic acid (**5**) and sulfinyldiacetic acid (**7**), were formed in different ratios and various enantioselectivities. All these products were isolated by column chromatography and spectroscopically analysed. Their structures were established by ^{1}H NMR, ^{13}C NMR, MS (CI) and elemental analysis and the absolute configurations were determined by X-ray analysis (see Supporting Information). We encountered severe difficulties in separating the desired products *via* chromatography. After standard silica gel column chromatography, products **3**, **5** and **7** were still found to contain an inorganic substance (combustion analysis revealed the presence of an inorganic ash). Therefore, the products were subjected to additional purification involving elution through a strongly acidic ion exchange column. Although this procedure enabled us to remove the inorganic contamination, it also in most cases led to a lowered overall yield of the reaction products.

Nevertheless, both enantiomerically enriched forms of **3** and **5** could be obtained in a ratio depending on the enzyme and conditions used. In the first set of experiments, we used a potassium phosphates buffer solution of pH 7.2, following the suggestion of Turner.[1] The use of buffers containing potassium phosphates, DTT (dithiotreitol) and EDTA with pH 7.5 gave generally poorer results. In these cases, we isolated about 50% of unreacted bis(cyanomethyl) sulfoxide (entries 7–9). Our investigations showed, that the enzymatic hydrolysis of prochiral bis(cyanomethyl) sulfoxide (**2**) was not always chemoselective since in several cases more than one product was formed. In cases of chiral products, the stereoselectivity of these enzymes towards the heteroatom prostereogenic centre (the sulfinyl group) varied from low to excellent depending on the nitrilase, being generally lower in comparison to those reported for *C*-prochiral hydroxyglutaronitriles.[19] An interesting observation is that some nitrilases behaved as nitrile hydratases leading to the preferential formation of the amide. Similar findings have been previously reported by Effenberg and Osswald[20] and recently by Sheldon et al.,[21] who noticed

that such an activity was profoundly enhanced by substrates bearing electron-withdrawing substituents, lower temperature and higher pH. The *ee* values of amides **3** were determined by chiral HPLC (Varian Pro Star 210, Chiralpak AS). In most instances the enzyme led to the (*S*)-amide as the predominant product, although in some cases (*R*)-selectivity was observed (entries 3 and 7). In one instance, the monoamide **3** was obtained in excellent enantioselectivity of over 99%, albeit in a yield of 57% (entry 10). In order to determine the *ee* of acid **5**, the free acid had to be transformed into the corresponding phenacyl derivative **8**, following the general methodology described by Nagao et al. (Figure 4).[22] This involved generation of the carboxylate, followed by alkylation with bromoacetophenone in DMF.

This transformation also allowed us to determine the absolute configuration of the acid **5**, which appeared to depend on the nitrilase involved. While the enantioselectivities varied, in a single instance an excellent *ee* of >99% of the (*R*)-isomer was obtained (entry 11), besides formation of a considerable amount of the diacid.

It is also interesting to compare the outcome of the experiment with the whole cells (entry 6) with the result of enzymatic hydrolysis of the corresponding hydroxy-substituted glutarodinitriles **9** and **10** that was published previously (Figure 5).[23] In the latter cases, the corresponding (*S*)-enantiomers of **11** and **12** were obtained in excess, with a significantly better selectivity for the benzyloxy than for the small hydroxy substituent. This low *ee* value is well in line with relatively low selectivity for the desymmetrisation of the sulfoxide.

As far as the mechanism of the above desymmetrisation is concerned, two courses of the reaction must be considered: In the first one the mono amide **3** and the mono acid **5** are formed concurrently, in the second one the amide is formed first and then subsequently hydrolysed to the acid. Identical absolute configurations of both products obtained in the same reaction (Table 1, entries 4, 6, 8 and 9) undoubtedly speak in favour of the first assumption. The cases in which the amide and the acid formed in the same reaction have opposite absolute configurations (Table 1, entries 5 and 10) may suggest that the real stereorecognition is a result of a kinetic resolution at the stage of the hydrolysis of the initially formed racemic amide. However, also in the latter case the concurrent formation of both products cannot be excluded, as has been shown by Sheldon et al.,[21] who proposed a bidirectional mechanism of action of nitrilases leading to both types of products.

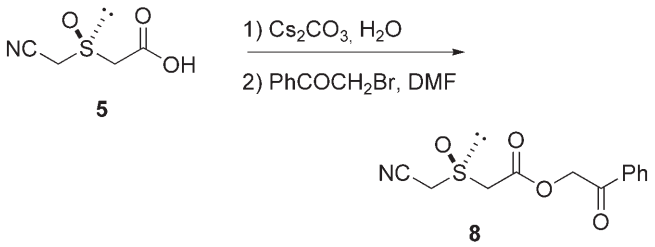

Figure 4. Preparation of benzoylmethyl cyanomethylsulfinylacetate (**8**).

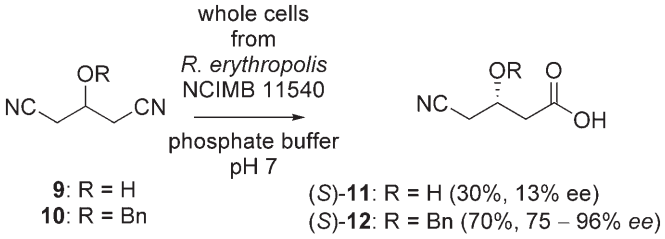

Figure 5. Hydrolysis of hydroxyglutaronitriles.

Conclusions

Enzymatic hydrolysis of prochiral bis(cyanomethyl) sulfoxide was achieved for the first time using a broad spectrum of nitrile-hydrolysing enzymes under mild conditions (buffer solution of pH 7.2, 30 °C). Three products formed were cyanomethylsulfinylacetamide, cyanomethylsulfinylacetic acid and sulfinyldiacetic acid, in different ratios and varying enantioselectivity ranging from 10 to 99% *ee*. Further investigations concerning enzymatic transformations of the substrates bearing other heteroatom prostereogenic centres will be continued.

Experimental Section

General Remarks

The enzymes were purchased from BioCatalytics Europe GmbH, Grambach, Austria. NMR spectra were recorded on Bruker instruments at 200 MHz with D_2O, $CDCl_3$ and CD_3COCD_3 as solvents. Optical rotations were measured on a Perkin–Elmer 241 MC polarimeter. Column chromatography was carried out using Merck 60 silica gel. TLC was performed on Merck 60 F_{254} silica gel plates. The enantiomeric excess (*ee*) values were determined by chiral HPLC (Varian Pro Star 210, Chiralpak AS).

Synthesis of Bis(cyanomethyl) Sulfoxide (2)

To a suspension of anhydrous Na_2S (2.0 g, 0.025 mol) in DME (20 mL) chloroacetonitrile (3.87 g, 0.05 mol) was added. The mixture was stirred at room temperature and the reaction was followed by TLC. After 12 h water was added and the mixture was extracted with chloroform. After

drying over anhydrous $MgSO_4$ and evaporation of $CHCl_3$, compound **1** was obtained as a yellow oil; yield: 2.15 g (75%). ^{1}H NMR ($CDCl_3$): $\delta = 3.57$ (s, 4H); MS (CI): $m/z =$ 113 (M + H).

The crude compound **1** (TLC pure) was directly oxidised to sulfoxide **2**. Thus, crude **1** (2.15 g, 0.019 mol) was dissolved in an ethanol/water mixture (1:1, 20 mL), then $NaIO_4$ (11.3 g, 0.053 mol) was added and the mixture was stirred at room temperature until TLC indicated completion of the reaction (*ca.* 12 h). A white precipitate was filtered off, the filtrate was evaporated and the residue was purified by column chromatography (EtOAc:petroleum ether 40–60, 1:20 to 2:1) to afford **2** as a white powder, which was recrystallized from benzene; yield: 1.47 g (60%); White needles, mp 110–111 °C. ^{1}H NMR (CD_3COCD_3): $\delta = 4.35$ (AB, 4H); ^{13}C NMR (CD_3COCD_3): $\delta = 41.67$, 113.65; MS (CI): $m/z =$ 129 (M + H); anal. calcd. for $C_4H_4N_2OS$: C 37.50, H 3.12, N 21.88, S 25.00; found: C 37.62, H 3.09, N 21.88, S 24.71).

Enzymatic Hydrolysis of 2 – General Procedure

Compound **2** (0.10 g, 0.78 mmol) was dissolved in a buffer solution and an enzyme (10 mg) was added. The reaction was shaken at 30 °C during 48 h and monitored by TLC. After 48 h, water was evaporated and the residue was separated using column chromatography. To remove inorganic substances present in the crude samples, all the products were dissolved in water and the solutions were eluted through a strong acidic ion exchange resin (Dowex® 50W). Lyophilisation of the samples gave the corresponding products **3**, **5** and **7**. The yields and optical rotations are shown in Table 1.

Cyanomethylsulfinylacetamide (3): White crystals (from MeCN), mp 130–133 °C; ^{1}H NMR (D_2O): $\delta = 4.05$ (br. s, 4H); ^{13}C NMR (D_2O): $\delta = 42.7$, 56.2, 112.4, 167.8; MS (CI): $m/z = 147$ (M + H); anal. calcd for $C_4H_4N_2O_2S$: C 32.88, H 4.11, N 19.18, S 21.92; found: C 32.17, H 4.11, N 19.61, S 21.62.

Cyanomethylsulfinylacetic acid (5): Colorless oil; ^{1}H NMR (CD_3COCD_3): $\delta = 4.07$ (AB, 2H), 4.25 (AB, 2H); ^{13}C NMR (CD_3COCD_3): $\delta = 39.07$, 55.99, 112.43, 165.73; MS (CI): $m/z = 148$ (M+H), 104 (M−CO_2); anal. calcd. for $C_4H_5NO_3S$: C 32.65, H 3.40, N 9.52, S 21.77; found: C 32.82, H 3.60, N 9.60, S 21.34.

Sulfinylbisacetic acid (7): White powder, mp 154–157 °C; ^{1}H NMR (D_2O): $\delta = 3.92$ (AB, 4H); MS (CI): $m/z = 167$ (M+H).

Conversion of Acid 5 to Phenacyl Ester 8

Cyanomethylsulfinylacetic acid (**5**; $[\alpha]_D$: −22.6, 85.3 mg, 0.58 mmol) was dissolved in water (10 mL), Cs_2CO_3 (74.9 mg, 0.23 mmol) was added and the mixture was stirred at room temperature for 10 min. After evaporation under vacuum, the residue was treated with *N,N*-dimethylformamide (10 mL) and 2-bromoacetophenone (0.54 mmol) and stirred at room temperature for 30 min. DMF was evaporated under vacuum and the residue was separated by preparative TLC ($CHCl_3$:MeOH, 10:1) to give the corresponding phenacyl ester **8** as a yellow powder; yield: 107 mg (70%). The ester was recrystallized from benzene. Yellow needles, mp 108–110 °C; $[\alpha]_D$: +55.3; ^{1}H NMR ($CDCl_3$): $\delta = 4.24$ (AB, 4H); 5.49 (d, $J = 4.59$ Hz, 2H); 7.51–7.90 (m, 5H); MS (CI): $m/z = 266$ (M + H).

Crystallographic Data

See Supporting Information. Crystallographic data for (+)-**3** and (+)-**8** have been deposited with the Cambridge Crystallographic Data Center, as supplementary publication no. CCDC 634118 and CCDC 634122, respectively and can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) +44–1223/336–033; e-mail: mailto:deposit@ccdc.cam.ac.uk].

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