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Some observations on the enantio- and diastereo-selective synthesis of 1-substituted-1,2,3,4-tetrahydroisoquinolines

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Abstract

Several approaches to the synthesis of optically active 1-aryl-1,2,3,4-tetrahydroisoquinoline alkaloids, cryptostylines (**1–3**) from dihydroisoquinoline precursors **5, 6, 11** and **12** have been tried. Reductions of the 1-aryldihydroisoquinoline **5** and the 1-methyl analogue **7** as well as of their methiodides **6** and **9** with yeast are unsuccessful. Reduction of the quaternary salts **6, 11, 12** and **9** with sodium tris-acyloxyborohydrides gives the tetrahydroisoquinoline alkaloids **1–3** and **10**, respectively, in unsatisfactory enantiomeric excess. (±) Norcryptostyline **4** is resolved with (–) and (+) tartaric acid into (–)S and (+)R enantiomers **14** and **17**, respectively, which are converted to their camphorsulphonyl derivatives **15** and **16**. Reaction of camphorsulphonyl homoveratryl amine **13** with piperonal affords a mixture of **16** and **15** in the ratio of 4:3, whereas camphorsulphonylation of racemic **4** gives **16** much in excess of **15** (4:1).

Key words: Asymmetric reduction, diastereoselective synthesis, cryptostylines, chiral tetrahydroisoquinolines, yeast reduction, acyloxyborohydrides.

1. Introduction

The alkaloids cryptostyline I, II and III (**1, 2** and **3**, respectively) are unique in being the first 1-aryl-1, 2, 3, 4-tetrahydroisoquinoline alkaloids to be found in nature. The dextrorotatory enantiomers isolated by Leander and Luning from *Cryptostylis fulva* Schltr[1] have the S-configuration at C-1[2]. The (–) (1R) cryptostylines have been encountered in *Cryptostylis erythroglossa*[2]. The S and R enantiomers have been obtained by conventional resolution of the synthetic racemic 1-aryl-1,2,3,4-tetrahydroisoquinolines[3]. There has been one report of synthesis of (+) (1S) **1** from the laevorotatory nor derivative **4** obtained by enantioselective reduction of the corresponding 3,4-dihydroisoquinoline **5**[4]. We have carried out extensive experiments in this direction which we report in this paper. In particular, while there is a lot of published literature on the asymmetric reduction of ketones including the use of fermenting yeast, less is known about similiar reduction of imines such as **5**. Outlined below are the results of various approaches we have made.

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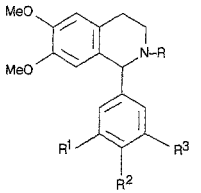
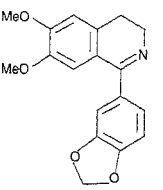
2. Reductions with yeast

The reduction of various organic compounds by yeast has become very popular in recent years[5], especially of prochiral ketones to optically active alcohols, *e.g.*, methyl and trifluoromethyl ketones, beta-keto esters, diketones and aryl alkyl ketones.

Enantioselective reduction of prochiral carbon–carbon double bonds has also been reported as well as of α-methylene-β-hydroxyketones to the α-methyl-β-hydroxyketones. Reduction with yeast under non-fermenting conditions is claimed to give better enantioselectivity than fermenting conditions[6]. However, the reduction of imines by yeast had not been reported when we initiated our work. But in 1990, the first asymmetric reduction of a prochiral oxime to chiral 2-aminobutane was published albeit with unsatisfactory enantiomeric excess (ee) of 24–54%[7].

With the objective of reducing it to an enantiomer of norcryptostyline **4**, we treated 1-(3,4-methylenedioxyphenyl)-3,4-dihydro-6,7-dimethoxyisoquinoline **5** with fermenting baker's yeast (made from tap water, yeast and sugar) at room temperature for several hours but





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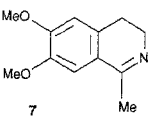


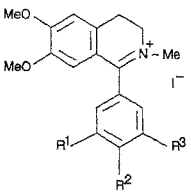
7 **9** **7.** MeI

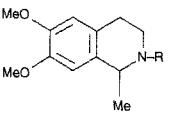
1 R = Me; R¹ R² = –OCH_2O–; R³ = H

2 R = Me; R¹ = R² = OMe; R³ = H

3 R = Me; R¹ = R² = R³ = OMe

4 R = R³ = H; R¹ R² = –OCH_2O–





8 R = H

10 R = Me

6 R¹ R² = –OCH_2O–; R³ = H

11 R¹ = R² = OMe; R³ = H

12 R¹ = R² = R³ = OMe

observed no reduction. We next prepared the quaternary methiodide **6** (itself an alkaloid[2]) of **5** with a view to activating the iminium bond for reduction as well as to provide some water solubility. Exposure of **6** however did not lead to any detectable formation of **1**.

In yet another approach, we attempted the reduction of 1-methyl-3,4-dihydroisoquinoline **7** with yeast, hoping that the substitution of an aryl group in **1** by methyl would decongest the prochiral centre, provide greater dissymmetry and encourage the desired reaction. The result was again negative since the product, salsolidine **8** was not formed. As a final resort, the methiodide **9** was prepared and added to the yeast medium, but again the expected tetrahydroisoquinoline, carnegine **10** was not formed.

In a control experiment, we were able to reduce ethyl acetoacetate with fermenting baker's yeast according to the directions of Seebach *et al*[8] and isolate (S) (+) ethyl 3-hydroxybutyrate in 85% ee. Hence, our failure to reduce the dihydroisoquinolines is to be attributed to the intransigence of the iminium bond rather than to our ineptitude.

3. Chemical reductions

In recent years, asymmetric reduction of prochiral ketones to optically active alcohols with chiral metal hydride reagents has been widely studied. A large variety of highly promising chiral-reducing agents offering excellent optical induction for prochiral ketones have been developed[9]. There have been fewer reports on the asymmetric reduction of prochiral imines. Yamada *et al*[4] have achieved the reduction of cyclic imines **5** and **7** to laevorotatory **4** and **8** with 70–86% ee using chiral sodium triacyloxyborohydrides derived from $NaBH_4$ and three equivalents of N-acyl-α-amino acids, esp., (S)-N-benzyloxycarbonylproline.

Using the last reagent, we carried out the reduction of the quaternary salts **6**, **11**, **12** and **9** to yield the alkaloids cryptostylines I, II and III (**1**, **2** and **3**, respectively) and carnegine **10**, but with unimpressive optical purity of 11–25% ee (Table I). We also studied the reduction of **6** using other optically active acids such as d-naproxen, S-pyroglutamic acid and (S)-N-α-phenethyl oxamic acid, obtained by us for the first time from (S)-α-phenethyl amine by reaction with diethyl oxalate followed by hydrolysis. (S) (+) Cryptostyline I (**1**) was obtained in the last two cases but the optical purity was low. In the case of d-naproxen, interestingly, the product had a slight excess of (R) (–)cryptostyline I.

In yet another probe we attempted to reduce **6** with a complex made from $NaBH_4$, 1 equivalent of (+)2,2'-binaphthic acid and 1 equivalent of acetic acid. The optical purity of (S) (+) cryptostyline I (23.5% ee) was not better compared to the one got using (S)-N-benzyloxycarbonylproline. The results obtained by the use of other optically active dicarboxylic acids such as (2S, 3S)-(–) tartaric acid and (1R, 3S)-(+) camphoric acid in place of binaphthic acid were inferior (<7% ee of **1**).

After completion of this work, Cho and Han[10] reported the asymmetric reduction of **6**, **11** and **12** using potassium glucoride, Itsuno's reagent and Mosher's reagent to obtain optically active **1**, **2** and **3** in 6–43% ee.

Disheartened by our results, we reinvestigated the asymmetric reduction of **5** using sodium tris [(S)-N-benzyloxycarbonyl-prolyloxy] borohydride[4]. However, we obtained laevorotatory norcryptostyline I (**4**) only in 41.5% ee and not 85% as reported earlier.

Table I

Reduction of dihydroisoquinolines with sodium tris-acyloxyborohydrides

Substrate	*Product*[a]	*Chiral acid used*	*mp(°C)*	*Yield %*	*Optical rotation*[b] $[\alpha]_D^{25}$	*ee*
6	**1**	S-N-Carbobenzyloxyproline	111–113	78.4	+14.08	25.1
6	**1**	S(+)-Naproxen	115–116	59.2	–3.35	5.8
6	**1**	S-Pyroglutamic acid	115–116	80.4	+1.7	3.0
6	**1**	S-N-(α-Phenethyl) oxamic acid	113–114	35.1	+4.36	7.7
6	**1**	(+) 2,2'-Binaphthic acid (2 eq)+acetic acid (1 eq)	112–113	42.8	+13.2	23.5
6	**1**	(+) Camphoric acid (2 eq)+acetic acid (1 eq)	113–114	32.5	+1.27	2.3
6	**1**	(-) Tartaric acid (2 eq)+acetic acid (1 eq)	115–116	45.8	+3.6	6.4
11	**2**	S-N-Carbobenzyloxyproline	106–108	65.5	+11.9	20.0
12	**3**	S-N-Carbobenzyloxyproline	138–140	59.6	+14.75	18.9
9	**10**	S-N-Carbobenzyloxyproline	oil	83.3	+2.92	11.9
5	**4**	S-N-Carbobenzyloxyproline	129–130	68.1	–9.6	30.7 (41.5 based on ref. 3)

a. All products had correct elemental analyses and were characterised by UV, IR, NMR and mass spectra.
b. Rotations were measured for approximately 1% solution in $CHCl_3$ and at about 25°C.

Further, we discovered *(vide infra)* that the optical rotation of pure **4** upon which ees were based was much higher than the one reported by Brossi and Teitel[3].

In a final effort we attempted an asymmetric hydrogenation of **6** using the homogeneous chiral catalyst, R, R-DIPAMP[11] which was available to us in the form of its cyclooctadiene complex [Rh, (R,R-DIPAMP) COD] BF_4, an excellent asymmetric hydrogenation catalyst for olefins. However, **6** was recovered unchanged in spite of the use of increasingly larger amounts of the catalyst and higher temperature.

4. Kinetic resolutions

In the last approach to our objective, we investigated possiblities of the synthesis of optically active 1-aryl-1,2,3,4-tetrahydroisoquinolines by a kinetic resolution through a two-pronged strategy, one involving a Pictet–Spengler reaction[12] of the N(S)-camphorsulphonyl derivative **13** of homoveratryl amine with piperonal which may lead to the (1S), (1O'S) tetrahydroisoquinoline [(1S) norcryptostyline I **14**] derivative **15** or its (1R) (1O'S) diastereomer **16** [related to the

(1R) enantiomeric norcryptostyline I **17**] or a mixture thereof. In the second route, (±) norcryptostyline I (**4**) was to be treated with (S) camphorsulphonyl chloride in the expectation that one enantiomer may react faster than the other to afford **15** or **16** in excess.

Evaluation of both routes required access to pure diastereomers **15** and **16**, which should become available from **14** and **17**, respectively. Resolution of (±) **4** with (–) tartaric acid through the crystalline salt led to the isolation of (–) (S) **14** with $[\alpha]_D$ –31.6°, which was considerably higher than the value –23.0° reported in literature[3]. The optical purity of **14** was checked by conversion to (+) (S) cryptostyline I (**18**), $[\alpha]_D$ +57.4°. Use of (+) tartaric acid in the resolution of (±) **4** gave pure (+) (R) **17**, $[\alpha]_D$ +30.9°, higher than the reported value of +23.0°[3]. Hence, the ees published by Yamada *et al*[4] based on rotations of 23° for **14** and **17** need to be appropriately discounted.

Reactions of **14** and **17** with (+) (S) camphorsulphonyl chloride gave, respectively, the diastereomeric sulphonamides (1S) (10'S) **15**, $[\alpha]_D$ +106.6° and (1R) (10'S) **16**, $[\alpha]_D$ –80.2°. The pair could not be separated on silica TLC plates in several solvent systems.

However, they were easily distinguished in their 200 MHz ^{1}HNMR spectra in the aromatic region and more so by the signals of one of the two camphor methyl groups: δ for **15**, 0.78 ppm and for **16**, 0.71 ppm.

The Pictet–Spengler reaction was now performed on the sulphonamide **13** using piperonal as the aldehyde component. The product obtained in 47% yield had $[\alpha]_D$ –0.94° and was a mixture of **15** and **16** in the ratio of 3:4 (200 MHz ^{1}HNMR spectrum) indicating nominal enantioselectivity in favour of the (1R)-diastereomer.

On the other hand, when (±) **4** was treated with (+) (S) camphorsulphonyl chloride, the product obtained in 26% yield had $[\alpha]_D$ –46.3° and was determined to be a mixture of **15** and **16** in the ratio of 1:4 (200 MHz ^{1}HNMR), the reaction exhibiting superior diastereoselectivity over the Pictet–Spengler synthesis. A byproduct of the reaction was **5**, presumably arising from the sulphonamide, by the elimination of camphorsulphenic acid.

5. Conclusion

Although yeast failed to reduce the 3,4-dihydroisoquinolines, chemical reagents brought about the desired reactions, but with poor enantioselectivity. Kinetic resolution was observed in the cyclization of the camphorsulphonamide **13** and in the camphorsulphonylation of (±) **4**. The latter reaction occurred with 60% diastereoselectivity, the best obtained in our studies.

6. Experimental

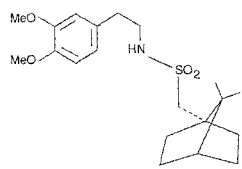
General

The dihydroisoquinolines **5** and **7** and methiodides **6**, **9**, **11** and **12** were made by standard procedures:

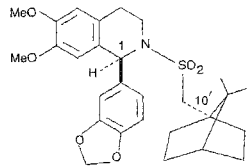
5, mp 108–110°[1]; **7**, mp 105–106°[13]

6, mp 207–209°[1]; **9**, mp 240–241°[13]

11, mp 194–196°[14]; **12**, mp 176–178°[1]



13



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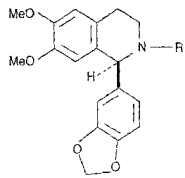
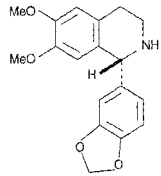


14 R = H

18 R = Me



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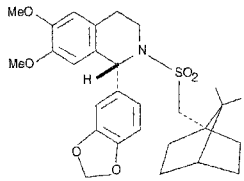

16

Attempted reduction with fermenting baker's yeast

To a fermenting mixture[8] of tap water (20 ml), sugar (6.5 g) and yeast (4.5 g) (CO_2 evolution starts after 1 h) was added a filtered solution of methiodide **6** (0.3 g) in tap water (50 ml). The mixture was stirred overnight when evolution of CO_2 had ceased. This restarted when a warm (40°) solution of sugar (4.5 g) in water (20 ml) was added. After 1 h, another lot of the methiodide (0.3 g) in tap water (50 ml) was introduced. The mixture was then stirred occasionally and monitored by TLC over 4 days. TLC (silica; $CHCl_3$–MeOH, 9:1) showed only starting material and no trace of **1**. Extraction with chloroform afforded unreduced **6** (0.5 g).

Similar reaction of **9** also did not yield the tetrahydroisoquinoline **10** although **9** could not be recovered due to hydrolytic destruction of the iminium bond. **5** and **7** were dissolved in alcohol for exposure to yeast, but were recovered unreacted.

(S)-N-(α-Phenethyl) oxamic acid

S-α-Phenethyl amine (7.5 g) was dissolved in absolute ethanol (75 ml). To the stirred solution, diethyl oxalate (19 ml) was added over 1 h. After the addition was over, the mixture was left standing overnight. It was then filtered and the filtrate evaporated to give ethyl N-(α-phenethyl) oxamate as a semisolid.

This was hydrolysed by heating under reflux in methanol (50 ml) containing potassium hydroxide (2.5 g) for 1 h. Water (75 ml) was then added and the solution extracted with CH_2Cl_2. The aqueous layer was acidified with conc. HCl to give the oxamic acid (4.6 g, 38.6%), white crystals from benzene–hexane, mp 142–144°, $[\alpha]_D$ +120.9° (c=1.03, $CHCl_3$). (Found: C, 62.04; H, 5.36; N, 7.18. $C_{10}H_{11}NO_3$ requires C, 62.16; H, 5.74; N, 7.25%).

*Asymmetric reduction of iminium salts **6**, **9**, **11** and **12** and imine **5** with sodium tris-acyloxy borohydrides–general procedure*

To a vigorously stirred suspension of sodium borohydride (6 mmole; Fluka, 97.8% assay) and dry THF was added, at 0° and in a nitrogen atmosphere, a solution of (S)-N-benzyloxycarbonylproline (18 mmole) in dry THF (15 ml) dropwise during 1 h. The mixture was stirred at 25° for 2 h and cooled again to 0°. A solution of the iminium iodide or imine (2 mmole) in CH_2Cl_2 (30 ml) was added to the borohydride complex at 0° over 1 h. The mixture was stirred at 25° for 2 h and left standing overnight. THF and CH_2Cl_2 were then distilled off *in vacuo* and the residue heated with dil. HCl (5%, 75 ml) at 60° for 1/2 h. The mixture was cooled and extracted with EtOAc (5×25 ml) to recover (S)-benzyloxycarbonylproline nearly quantitatively. The aqueous layer was made alkaline with 20% aq. Na_2CO_3 and extracted with EtOAc (5×25 ml). The combined extracts were dried (Na_2SO_4) and evaporated *in vacuo* to give the tetrahydroisoquinolines (Table I).

*Resolution of (±)1-(3,4-methylenedioxyphenyl)-1,2,3,4-tetrahydro-6,7-dimethoxyisoquinoline **(4)***

A solution of **4** (5 g, 16 mmole, prepared from **5** by reduction with sodium borohydride in aq. MeOH[3]) in hot MeOH (60 ml) was added to (–) tartaric acid (2.4 g, 16 mmole) in MeOH (10 ml). The solution was heated, filtered and cooled overnight. The precipitate (2. 2 g) was filtered off and crystallised from MeOH to give the crystalline tartrate (1.2 g). This was suspended in CH_2Cl_2 (30 ml) and washed with dil. aq. NaOH (5%; 4×10ml). The CH_2Cl_2 layer was dried (Na_2SO_4) and evaporated to give (–) (S) **14** (0.88 g, 35.2%) as white crystals from aq. MeOH; mp 122–123°, $[\alpha]_D$–31.6° (c=1, $CHCl_3$) [lit[3]. mp 122–123°, $[\alpha]_D$ –23.0° ($CHCl_3$)]. (Found: C, 68.81; H, 6.18; N, 4.59. $C_{18}H_{19}NO_4$ requires C, 68.99; H_1, 6.11; N, 4.47%).

A similar resolution of **4** with (+) tartaric acid gave (+) (R) **17** in 30.4% yield; white crystals from aq. MeOH, mp 123–124°, $[\alpha]_D$ +30.9° (c=0.95, $CHCl_3$) [lit.[3] mp 123–124°; $(\alpha)_D$ +23.0° ($CHCl_3$)]. (Found: C, 68.73; H, 6.08; N, 4.29. $C_{18}H_{19}NO_4$ requires C, 68.99; H, 6.11; N, 4.47%).

*Conversion of (–) (S) **14** to (+) cryptostyline I **(18)***

A solution of **14** (0.2 g) in formic acid (85%, 2 ml) containing aq. formaldehyde (37%; 2 ml) was heated at 100° for 3 h. The solution was cooled and basified with aq. NaOH (10%).

Extraction with CH_2Cl_2 and evaporation of the extract afforded **18** (0.17 g, 85%) as white crystals from Et_2O; mp 101–102°, $[\alpha]_D$ + 57.4° (c=0.42, $CHCl_3$) [lit[3]. mp 101–102°; $(\alpha)_D$ +56 0° (c = 2.7, $CHCl_3$)]. (Found: C, 69.59; H, 6.32; N, 4.26. $C_{19}H_{21}NO_4$ requires C, 69.70; H, 6.47; N, 4.28%).

*N-(S) Camphorsulphonyltetrahydroisoquinolines (**15** and **16**)*

A mixture of **14** (0.47 g), S-10-camphorsulphonyl chloride (0.4 g) and dry pyridine (2 ml) was heated under reflux for 1 h. A second instalment of sulphonyl chloride (0.4 g) and pyridine (1 ml) were added and reflux continued for one more hour. The next day, the mixture was poured over ice; the product was extracted with CH_2Cl_2 and purified by chromatography over silica (30 g) in $CHCl_3$. Elution with $CHCl_3$ gave the (1S) (10'S) derivative **15** as yellow crystals, 0.2 g (25.3%), mp 94–96°, $[\alpha]_D$ + 106.6° (c=1, $CHCl_3$). (Found: C, 63.47; H, 6.31; N, 2.57. $C_{28}H_{33}NO_7S$ requires C, 63.75; H, 6.26; N, 2.65%).

Similarly, the (1R) tetrahydroisoquinoline **17** gave the (1R) (10'S) camphorsulphonyl derivative **16**; yield 24.4%; mp 94–96°; $[\alpha]_D$ –80.17° (c=1.0, $CHCl_3$). (Found:C, 63.71; H, 6.13; N, 2.71. $C_{28}H_{33}NO_7S$ requires C, 63.75; H, 6.26; N, 2.65%).

*Camphorsulphonylation of (±) **4***

The reaction was carried out on **4** (3.13 g) and the sulphonyl chloride (2.65 g) as earlier. The crude product was obtained as a brown powder (3.4 g) showing three spots on a TLC plate (silica, $CHCl_3$: MeOH, 9%). This was chromatographed in $CHCl_3$ over a silica column (90 g). Elution with chloroform gave unreacted sulphonyl chloride (0.5 g). $CHCl_3$–1%, MeOH eluted the camphorsulphonyl derivative, 1.4 g (26.5%), mp 93°, $[\alpha]_D$ - 46.3° (c=1.04, $CHCl_3$) consisting of **15** and **16** in the ratio of 1:4 (Found : C, 63.49; H, 6.31; N, 2.61. $C_{28}H_{33}NO_7S$ requires C; 63.75; H, 6.26; N, 2.65%). Further elution of the column with $CHCl_3$: MeOH, 93:7 yielded unreacted **4**, 0.21 g, mp 132°, $[\alpha]_D$–2.62°(c=1.07, $CHCl_3$), showing a slight excess of the S component.

*N-(S) 10-Camphorsulphonylhomoveratrylamine (**13**)*

To a stirred mixture of aq. NaOH (10%, 3 ml) and homoveratrylamine (0.9 g) in CH_2Cl_2 (5 ml) was added at 0°, camphorsulphonyl chloride (1.32 g) in CH_2Cl_2 (10 ml). The mixture was stirred at 0° for 1 h and left to stand overnight. The CH_2Cl_2 layer was then separated, dried and evaporated. The product was crystallised from $CHCl_3$–MeOH to afford **13** (1.5 g, 79%), mp 110–111° $[\alpha]_D$ + 25.50 (c=1, $CHCl_3$). (Found : C, 60.37; H, 7.12; N, 3.61; M+ 395. $C_{20}H_{29}NO_5S$ requires C, 60.75; H, 7.34; N, 3.54; M 395).

*Condensation of **13** with piperonal*

A mixture of **13** (0.4 g), piperonal (0.23 g) and $POCl_3$ (1 ml) in toluene (20 ml) was heated under reflux for 1 h. The mixture was cooled, treated with water (10 ml) and excess aq. ammonia. The toluene layer was separated and evaporated *in vacuo* to give a gum (0.4 g) consisting of piperonal and product (TLC:silica, benzene: acetone 9:1). This was dissolved in benzene and chromatographed over silica (20 g). Elution with the same solvent gave piperonal (0.1 g). Benzene-1% acetone yielded the cyclized product, 0,25 g (47.4%); white crystals from MeOH, mp 122–124°; $[\alpha]_D$ –0.94° (c=0.95, $CHCl_3$) consisting of **15** and **16** in

the ratio 3:4. (Found: C, 63.66; H_7, 6.13; N,2.77. $C_{28}H_{33}NO_7S$ requires C, 63.75; H, 6.26; N, 2.65%).

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