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REDUCTIONS WITH NADH MODELS II: ASYMMETRIC INDUCTION WITH SUGAR SUBSTITUTED HANTZSCH ESTERS OR WITH CHIRAL LEWIS ACIDS

SADEK ZEHANI, JIAN LIN and GEORGES GELBARD*

Laboratoire des Matériaux Organiques - C.N.R.S.
B.P. n° 24, F-69390 Lyon-Vernaison, France.

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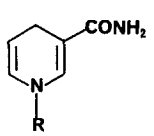
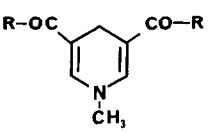
Abstract: Hantzsch esters 3 and 4 have been used as NADH models instead of the well documented nicotinamides 1 for the sake of greater flexibility in the preparation and chemical modifications. Compounds 3 and 4, bearing monosaccharide-derived substituents in the 4- or in both the 3- and 5-positions were examined in the asymmetric reduction of several prochiral ketones: namely methyl phenylglyoxylate, trifluoroacetophenone and 2-acetyl pyridine. The e.e.'s obtained are discussed in terms of the structure of the sugar residue and its position on the dihydropyridine ring. The effects of Mg^{2+} catalysis is discussed and the possibility of using others Lewis acids - especially chiral ones - is examined.

Performing organic reactions in a similar manner to that which occurs in living cells is a facinating challenge to organic chemists. It may lead to a better understanding of biochemical mechanism and it may also assist to the design of new synthetic methods of increased efficiency in terms of enhanced kinetics reactivity and selectivity (chemo- regio- and stereoselection).

Biomimetic chemistry attempts to "mimic" the action of natural enzymatic systems using chemical models (1). As oxidation and reduction reactions are important biological processes, models of the relevant coenzymes have been studied. Those related to the NAD^+ / NADH system have been the most extensively investigated for the reduction of unsaturated systems (2). All the models contain as a common feature the 1,4-dihydropyridine ring of the nicotinamide part of the coenzyme and most of them have one of three fundamental stuctures: viz. a dihydronicotinamide 1, a 3,5-disubstituted dihydropyridine 2 or a Hantzsch ester (HEH) 3 (Scheme I).



1



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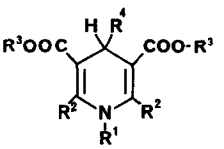

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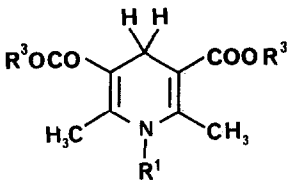
Scheme I

All the NADH models reported so far are able only to reduce the carbonyl groups of activated aldehydes and ketones to the corresponding alcohols; non-conjugated carbonyls are not reduced at a practically useful rate.

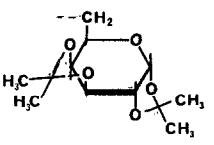
Most of the work on NADH models have been with models of type 1, which exhibit the closest similarity to the active part of the coenzyme and which have good reactivity. The Hantzsch esters 3 were examined for mechanistic studies (3), for the reduction of imminium salts (4) and in the

1,4 reduction of Michael receptor type substrates (5). Though they exhibit a lower reactivity than models 1, the Hantzsch esters 3 or 4 were chosen for further studies because of their easy preparation by a one-pot cyclisation reaction and because it is possible to introduce chiral substituents on the dihydropyridine ring by a proper choice of chiral aldehydes or alcohols as starting materials. Sugar derivatives were generally used as the source of chirality.

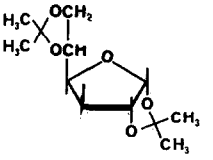


3

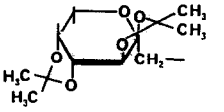
a: $R^1 = H$ $R^3 = CH_3$
b: $R^1 = CH_3$ $R^3 = CH_3$
c: $R^1 = H$ R^3 = D-galacto
d: $R^1 = CH_3$ R^3 = D-galacto
e: $R^1 = H$ R^3 = D-gluco
f: $R^1 = CH_3$ R^3 = D-gluco
g: $R^1 = H$ R^3 = D-fructo
h: $R^1 = CH_3$ R^3 = D-fructo



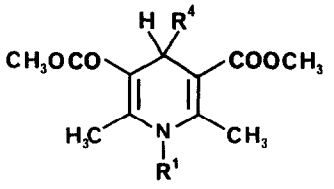
D-galacto



D-gluco

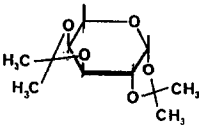


D-fructo

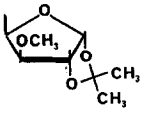


4

a: $R^1 = CH_3$ R^4 = cyclohexyl
b: $R^1 = H$ R^4 = L-arabino
c: $R^1 = CH_3$ R^4 = L-arabino
d: $R^1 = H$ R^4 = L-threo
e: $R^1 = H$ R^4 = (4S)-2,2-dimethyl-1,3 dioxolyl



L-arabino

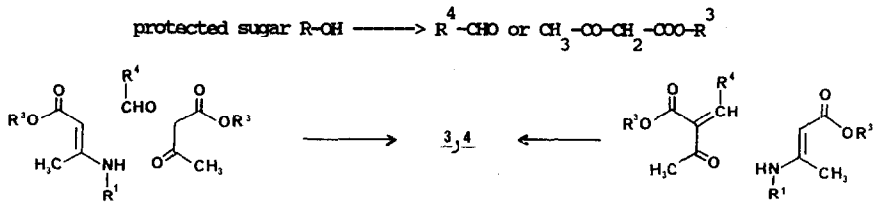


L-threo

(4S)-2,2-dimethyl-1,3 dioxolyl

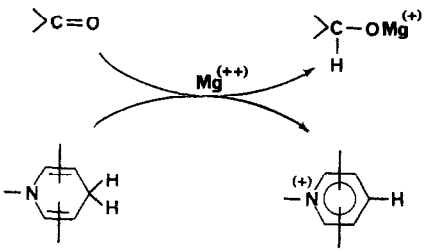
Scheme III

The Hantzsch esters (HEH) investigated contain either one sugar residue in the 4-position (HEH 4) or two sugar residues in the both 3- and 5- positions of the dihydro-pyridine ring (HEH 3). These chiral HEH, described in detail elsewhere (6), were prepared as outlined in scheme II. The structures of the products 3 and 4 are summarised in Scheme III.



Scheme II

This is the first report of the use of monosaccharides as chiral substituents for asymmetric induction in NADH models of types 3 or 4; only one example has been reported of glucose N-sustituted nicotinamides 1 (7). In the present work methyl phenylglyoxylate 5, trifluoroacetophenone 6 and 2-acetylpyridine 7 were subjected to reduction with several models of types 3 and 4 in the presence of magnesium perchlorate as catalyst. The reduction of ketones (and aldehydes) to the corresponding alcohols results in the neat transfer of a hydrogen from position -4 to the carbon of the carbonyl. This may occur either as a direct hydride transfer or through a $e^-/H^+/e^-$ sequential process (8); depending on the nature of the substituent R^1, the oxidized form of the dihydropyridine ring is either a pyridine (R^1=H) or a pyridinium (R^1=alkyl) (Scheme IV).



Scheme IV

It was expected that the extent of the asymmetric induction would be closely related to the distance between the reducing H-4 and the chiral substituent. It can be seen that in HEH 3 the sugar residues (as esters in the 3- and 5- positions) are 5 bonds away, where as in HEH 4 the first chiral atom is only two bonds away (Scheme III): higher e.e.'s would be expected with the latter.

Since the presence of a bulky substituent at that place might make HEH 4 less reactive than HEH 3, this point was examined in a preliminary experiment with the model 4a bearing a cyclohexyl group (to mimic roughly the bulk of a cyclic monosaccharide).

In the initial reductions methyl phenylglyoxylate 5 was treated with the achiral models 3a or 4a with stoechiometric amounts of magnesium perchlorate in acetonitrile at 70°C. The results (Table I) show that here HEH are less reactive than the nicotinamide models 1 (R^1 = $PhCH_2$) (entries 1 and 2); the presence of the bulky cyclohexyl group in the vicinity of the H-4 decreases the reactivity of model 4a (entry 4) though it still remains in an operatively useful range. Accordingly chiral HEH 4b-e were examined. A particularly interesting feature is the enhanced reactivity of the N-substituted model 3b vs. 3a; this will be discussed below. Reduction of the other activated ketones 6 and 7 gave less satisfactory results.

In the model 3 series, the e.e.'s of methyl mandelate were low when the nitrogen was unsubstituted (entries 7, 9 and 11); substantial rises in the reactivity and in the e.e.'s were obtained with the corresponding N-CH_3 models (entries 8 and 10). Glucose was a better inductor than galactose, fructose or D-glyceraldehyde, but the most striking fact is the inversion of the configuration of the major enantiomer after N-alkylation model 3e to the N-CH_3 model 3f (entries 9-10).

When the chiral substituents were in the 4 position (models 4b-e), the reaction times remained important but significant e.e.'s were obtained (entries 17, 19 and 20).

Table I: Reduction[a] of Prochiral Ketones with HEH Models of Type 3 and 4.

Entry	Model	Substrate	Yield% (time)	$[\alpha]_D$[b]	e.e.%[c] (Config.)
1	1	5	95 (7h)		
2	3a	5	99 (17h)		
3	3b	5	89 (2h)		
4	4a	5	55 (10d)		
5	3a	6	60 (12d)		
6	3a	7	50 (7d)		
7	3c	5	93 (4d)	-5,9	4 (R)
8	3d	5	44 (2.5d)	(d)	18 (R)
9	3e	5	84 (12d)	-5,9	4 (S)
10	3f	5	68 (2.5d)	(d)	79 (R)
11	3g	5	96 (4d)	+17,3	13 (S)
12	3h	5	74 (1d)	(d)	1 (S)
13	3c	6	51 (28d)	+0,625(e)	4,6 (S)
14	3e	6	36 (16d)	+0,8(e)	6 (S)
15	3g	6	59 (28d)	+0,38(e)	3 (S)
16	3g	7	53 (15d)	-3,80	6,7 (S)
17	4b	5	45 (15d)	+58,70	44 (S)
18	4c	5	66 (20d)	+103,15	77 (S)
19	4d	5	60 (20d)	+52,43	34 (S)
20	4e	5	86 (20d)	+17,40	13 (S)

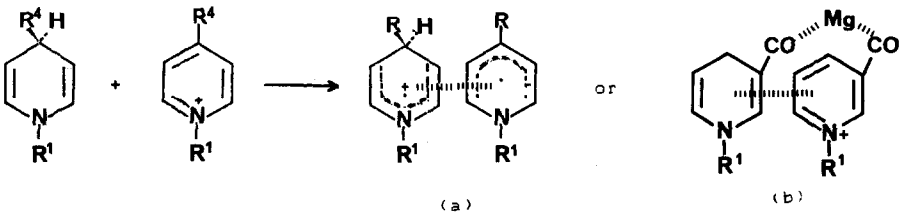
(a) in acetonitrile at 70°C with 1 eq. of $Mg(ClO_4)_2$. (b) in EtOH.
(c) from the maximum reported value for the optical rotation of pure 8-(S): $[\alpha]_D$+133.9 (c 1.0 95% aq.EtOH) (9); 9-(R) $[\alpha]_{578}$-13,5(benzene) (10); 10-(S): $[\alpha]_D$-56,7(EtOH) (11). (d) by ^{19}F NMR spectroscopy of the diastereomeric MTPA esters according to the procedure described in ref. 12.
(e) in C_6H_6.

The high value given by model 4c (entry 18) is in part due to the presence of the $N-CH_3$, as with model 3f (entry 10). The expected effect of higher e.e.'s when the chiral substituent is in the 4-position is attested in the N-H series.

Interestingly, both antipodes of methyl mandelate can thus be obtained in optical purities approaching 80% using either glucose or galactose derivatives.

The high reactivities and the high asymmetric inductions obtained simultaneously with N-methyl sustituted HEH are not very surprising and can be accounted for by the inductive effect of the methyl group which increases the negative redox potential of the ring as shown by indirect measurements on models of types 1 and 2 (13). However, the main reason is undoubtfully related to the fact that in the latter case, the oxidation product is a pyridinium ion instead of a pyridine (see Scheme IV). In the transition state complexation between the consumed dihydropy-ridine and the appearing pyridinium ion may occur and this may well be a favorable kinetic and stereoselective factor (14) (Scheme Va). More interesting was the assumption made on the formation of a ternary complex between the dihydropyridine, the Mg^{2+} cation and the pyridinium: this species is supposed to be the most reactive reducing agent present in the medium and respo sible for the high e.e. obtained (15)(Scheme Vb).

To gain some insight into this complexation, NMR experiments were carried out with the model 4c and substate 5 only in the presence of magnesium perchlorate. No alteration in the ^1H- and ^{13}C-NMR of the substrate was detected but this does not preclude any kind of electrophilic activation since this may occur at a low level.



Scheme V

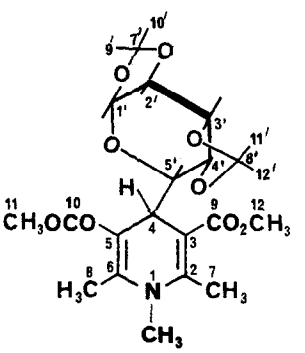
Alterations in the ^{1}H- and ^{13}C-NMR spectra of 4c were found and are reported in Table II.

As expected from earlier work on model of type 1 (1f)(2a)(16), complexation of the carbonyl oxygens is evidenced from the $\Delta\nu$ of C-9 and C-10 and, to a lesser extent, of C-11 and C-12. Complexation at the nitrogen is suggested from the $\Delta\nu$ of CH_3-N, though C-2,C-6 and C-7, C-8 do not shift significantly. This may be due to a complexation at the carbonyl followed by resonance effects through the β-aminocrotonate system (17). One of the most largest shifts is that of H-4 to higher field. This suggest that this reacting hydrogen will have an enhanced "hydride character". In the ^{13}C spectrum C-4 shows a positive induced shift, but this does not reflect the electron density change. It may, however, represent a change in the mean exitation energy or through-bound inductive and through-space electric field effects. The opposite shifts observed for H-4 and C-4 could also be explained in this way (18). The oxygen atoms of the sugar part, especially those of the 3'-4' isopropylidene group, are also involved in the complexation. This means that the magnesium ion keeps the chiral group in a rigid conformation through the 4-5' bond relative to the pyridine ring. The high e.e. observed with this model may result from the rigididity of the chiral substituent. This should occur similarly with model 3f which also gives very high chiral induction.

Table II: Alteration of the Chemical Shifts[(a)] of Model 4c in the Presence of 1 Eq. of Magnesium Perchlorate[(b)].

atom number	^{1}H $\Delta\nu$(Hz)	^{13}C $\Delta\nu$(Hz)
1	+6.65	+4.82
2		+0.28
6		+14.5
3		-15.01
5		+0.52
4	-50.75	+1.61
7	0	+7.5
8	+1.05	+4.82
9		+20.9
10		+16.63
11		+18.23
12		+15.54
1'	+7.175	-1.146
2'	+5.95	0
3'	+12.25	+5.89
4'	+15.4	-3.22
5'	+7	+2.67
7'		+1.09
8'		+3.76
9'	+3.85	-4.82
10'	+1.4	-2.15
11'	+2.45	-1.61
12'	+2.8	-2.15

(a) in CD_3CN for ^{1}H and ^{13}C at 350 and 20.1 MHz. respectively.
(b) [model]=[Mg]=$5.38.10^{-2}$ m.l^{-1}.



4c

In order to improve both the reactivity and the asymmetric induction, other Lewis acids were examined in place of magnesium perchlorate with the aim of using such chiral catalysts with achiral NADH models 1 or 3 and to check a possible double asymmetric induction with both chiral models and catalysts. Achiral models 1 and 3a were used in this study together with several fluoro β-diketonates of the lanthanide series (19)(20) and the results were compared with those obtained using magnesium perchlorate (see entries 1 and 2 -Table III).

The activities of the europium (entries 7-8) and neodymium (entries 5-6) salts are greater than those of the lanthanum (entries 3-4) but they are all less reactive than the usual magnesium perchlorate. However the opportunity arises for the use of the chiral fluoro β-diketonates known as NMR shift reagents (entries 9-14). The catalytic activity is still high at room temperature (entries 9-10), but an significant degree of asymmetric induction did occur.

The NADH models 1 and 3a behaved similarly. The most important feature is the nature of the chiral ligand. The trifluoromethyl ligands gave higher induction than the heptafluoromethyl ones and in all cases, the ligands derived from (+)-camphor and its complexes led to methyl mandelate with an excess of the (S)-enantiomer.

The asymmetric induction should result from a template effect which brings the model, substrate and the metal together in a ternary complex. In this, both the substrate and model should be complexed through the carbonyls (23)(24). Thus a electrophilic assistance in the transfer of H to the carbonyl group of the substrate appears more likely than with magnesium salts. The aforementioned ternary complex (15) would involve the metal, the model and the substrate in an arrangement where the prochiral side of the carbonyl group faces one of the two equivalent H-4 hydrogens of the model 3. In model 1, the H-4 hydrogens become enantiotopic after complexation (as when NADH is associated with the apoenzyme) and the asymmetric induction

Table III: Reductions[(a)] Catalysed by Lanthanide β-diketonates.

Entry	NADH model	Catalyst[(b)]	Solvent (t°C)	% Yield (time/day)	% e.e.[(c)] (config.)
1	1	$Mg(ClO_4)_2$ (d)	CH_3CN (70)	>98 (7 h)	
2	3a	$Mg(ClO_4)_2$ (d)	CH_3CN (50)	84 (7 h)	
3	1	$La(F_6acac)_3$ (e)	CH_3CN (70)	50 (5)	
4	3a	$La(F_6acac)_3$	CH_3CN (70)	16 (2)	
5	1	$Nd(F_6acac)_3$ (f)	CH_3CN (70)	68 (6)	
6	3a	$Nd(F_6acac)_3$	CH_3CN (70)	69 (6)	
7	1	$Eu(fod)_3$ (g)	CH_3CN (70)	90 (7)	
8	3a	$Eu(fod)_3$	CH_3CN (70)	39 (7)	
9	1	$Eu(tfc)_3$ (h)	CH_2Cl_2 (r.t.)	30 (8)	44 (S)
10	3a	$Eu(tfc)_3$	CH_2Cl_2 (r.t.)	28 (8)	55 (S)
11	3a	$Eu(tfc)_3$	CH_3CN (70)	>98 (3)	25 (S)
12	1	$Eu(hfc)_3$ (i)	CH_2Cl_2 (r.t.)	20 (20)	31 (S)
13	3a	$Eu(hfc)_3$	CH_2Cl_2 (r.t.)	12 (14)	22 (S)
14	3a	$Eu(hfc)_3$	CH_3CN (70)	75 (6)	25 (S)

(a) of methyl phenylglyoxylate 5 in 1/1 ratio of model/substrate
(b) 0.1 eq. vs. both substrate and model, otherwise stated.
(c) from the maximum reported value (9) for the optical rotation of pure (S)-8 $[\alpha]_D$ +133.9 (c 1.0 95% aq.EtOH).
(d) 1 eq. vs. substrate and model.
(e) Tris-(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)lanthanum (21).
(f) Tris-(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)neodymium (22).
(g) Tris-(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-octane-3,5-dionato)europium
(h) Tris-[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]europium.
(i) Tris-[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium.

results from the transfer of one of these two hydrogens to one of the faces of the keto group. This scheme is also suggested in the asymmetric reduction with chiral nicotinamide derivatives 1 (25)(26).

Attempts to obtain double asymmetric induction with chiral models 3 or 4 and $Eu(tfc)_3$ gave no reduction reaction. The size of the chiral models probably hinders the formation of the ternary complex.

Chiral shift reagents heve been previously used successfully in organic synthesis (27) (28). These last results are, however, the first examples of organic reductions catalyzed with this type of reagents. We first show here the effectiveness of the asymmetric reduction of prochiral ketones with a new types of NADH models of the Hantzsch esters series where the chiral part derived from a sugar.

Experimental part:

Chiral NADH models 3 and 4 were prepared as reported elsewhere (6b) and were stored under nitrogen at 5°C. Methyl phenylglyoxylate 5, trifluoroacetophenone 6 and 2-acetyl pyridine 7 are commercial products and were distilled prior to use. The corresponding tertiary alcohols are commercially available (methyl mandelate , 1-phenyl 2,2,2-trifluoro ethanol) or were prepared by conventional reduction methods (29). Neodymium and lanthanum β-diketonates were prepared by known methods (21) (22). Analytical grade acetonitrile was dried by percolation through W-200 basic alumina (activity I), degassed by bubbling a nitrogen stream during a 20 min. sonication sequence and used immediately.

Reductions were performed on a 2 mmole scale with a 1/1/1 ratio of model/substrate/ Mg catalyst or a 1/1/.1 ratio of model/substrate/Ln catalyst. The reagent, the substate and the catalyst were weighted in a 50ml inactinic glass flask fitted with a serum cap; the flask was purged several time, filled with nitrogen using a vacuum line. Acetonitrile (20ml) was then introduced by syringe.

The reductions were monitored by GLC on a Carlo Erba Fractovap 2150 apparatus connected to a Spectraphysic Minigrator integrator. The operating conditions were the following (substrate, column, oven temperature, internal standard given): methyl phenyl-glyoxylate, Carbowax 20M 10% 2.5 m, 180° C, neroline; acetylpyridine, Carboxax 20M 10% 2.5m, 140°C, diphenylether; trifluoro-acetophenone, SE 30 15% 2.5m, 120°C, n-hexadecane. After the appropriate heating time, 2ml of methanol were introduced and then the reaction mixture was evaporated to dryness. The residue was extracted several times with ether, the extracts filtered and the concentrate purified by preparative layer chromatography on silica gel Merck plates n°5717 with a $CHCl_3/Et_2O$ 95/5 solvent system; 2-(1-hydroxy-ethyl)pyridine required a 80/20 CH_2Cl_2/hexane solvent system.

The optical rotations were mesured at room temperature with a Perkin-Elmer 141 polarimeter; the e.e.'s are calculated from the values given for the optically pure compounds (9)(10)(11). Some e.e.'s were determined on an AC-200 Brucker by ^{19}F NMR integration of the signals of the diastereomeric esters of methyl mandelate with (S)-(+)α-methoxy-α-trifluoromethyl phenylacetic acid (MTPA) according to the improved procedure given by Meyers (12).

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