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Stereoselective synthesis of 1-methylcarbapenem precursors: studies on the diastereoselective hydroformylation of 4-vinyl β-lactam with aminophosphonite–phosphinite and aminophosphine–phosphite rhodium(I) complexes

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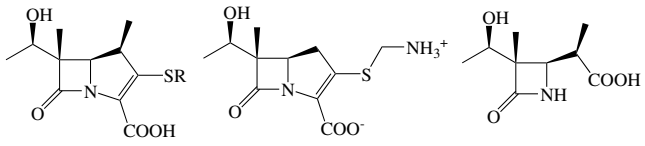
Abstract—The asymmetric hydroformylation of variously *N*-substituted 4-vinyl β-lactams catalyzed by rhodium aminophosphonite–phosphinite and rhodium aminophosphine–phosphite complexes was studied. These products are valuable intermediates in the preparation of 1-methylcarbapenem antibiotics; the stereoselectivity to the desired β-isomer is related to the presence of a substituent at the N atom of the β-lactam ring. The regioselectivity (branched/linear) but not the stereoselectivity (β/α) was found to be dependent on the substrate to catalyst ratio.

1. Introduction

1β-Methylcarbapenem **1** and the other homologous β-lactams are unnatural antibiotics[1] that have stimulated considerable interest due to their dehydropeptidase stability and to the improved chemical stability compared to that of the founder of the family, the potent broad spectrum antibiotic thyenamicin **2**, a fungal metabolite discovered in the late 70s[2] (Scheme 1).



1 **2** **3**

Scheme 1.

Due to the lack of practical biotechnological methods of preparation,[3] many efforts have been made in developing synthetic routes to the 1β-methylcarbapenem **1**, in particular, to the key intermediate, monocyclic β-lactam **3**.

An elegant way to obtain **3** is based on the highly regioselective and diastereoselective hydroformylation of the 4-vinyl β-lactam, (3*S*,4*R*)-3-[(*R*)-1-(*tert*-butyldimethylsilyloxy)ethyl-4-vinyl-2-azetidinone] **4a** to give **5aβ** followed by the oxidation of the branched β-aldehyde; the reaction was first reported by Nozaki et al.[4] using $Rh(acac)(CO)_2$ and the chiral bidentate phosphorus ligand BINAPHOS[5] (Scheme 2).

Alper et al.,[6] in 1999, obtained a higher diastereo- and regioselectivity using the catalyst derived from the zwitterionic rhodium complex, $(NBD)Rh^+B(Ph)_4$ and the chiral phosphine (*S*,*S*)-2,4-bis(diphenylphosphino)pentane, (*S*,*S*)-BDPP, a ligand originally prepared by Bosnich in the 80s and successfully used in asymmetric hydrogenations.[7]

Recently we have prepared new electron deficient aminophosphonite–phosphinite and aminophosphine–phosphite ligands, which gave satisfactory Rh(I)-catalysts for asymmetric hydrogenations of the dehydroaminoacids.[8] These ligands, as described in Scheme 3, combine the chirality of one stereogenic sp^3 carbon

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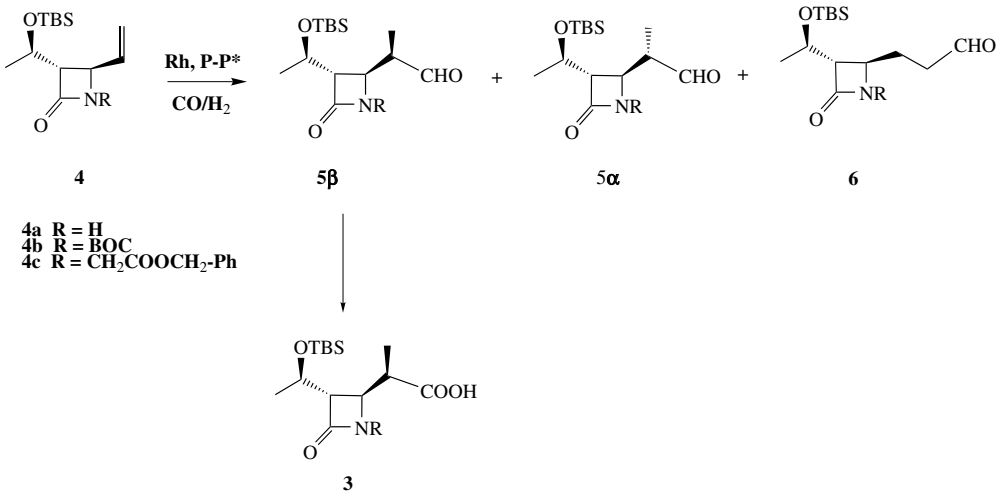
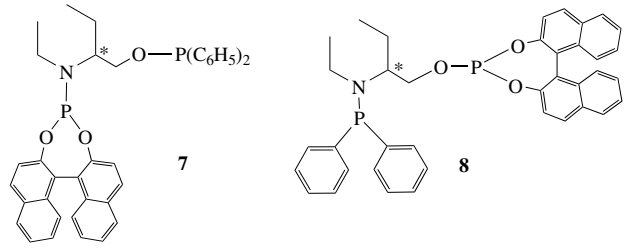


Scheme 2.



7 = (*SS, RR, SR, RS*) Aminophosphonite-phosphinite

8 = (*SS, RR, SR, RS*) Aminophosphine-phosphite

Scheme 3.

atom on the aminoalcohol backbone with the stereogenic axis of the 1,1′-binaphthyl moiety.

The $Rh(acac)(CO)_2$ complexes with these ligands gave very high regioselectivities and satisfactory enantioselectivities in the asymmetric hydroformylation of vinylacetate.[8] The stereodifferentiating ability of the catalyst derived from these ligands and the structural similarities to binaphthols or to the other bisphosphites, which seem to be the ligands of choice for the asymmetric hydroformylation,[9] prompted us to investigate aminophosphonite–phosphinite and aminophosphine–phosphite ligands in the preparation of 1β-methylcarbapenem by the asymmetric hydroformylation of different *N*-substituted azetidinones, **4a**–**c**.

2. Results and discussion

The asymmetric hydroformylation of enantiomerically pure azetidinones **4a**–**c** are summarized in Table 1. Due to the fact that in our preliminary investigations[8] we did not find any remarkably different activities between $Rh(acac)(CO)_2$ and the zwitterionic (NBD)-$Rh^+B(Ph)_4$ complex, we concentrated our efforts only on the catalytic system generated 'in situ' by mixing the zwitterionic Rh(I) complex with the appropriate ligand in a 1:2 ratio. The reaction conditions, that is, solvent (benzene, 30 mL), pressure (60 atm), temperature (60 °C), CO/H_2 ratio (1:1) and substrate concentration (0.017 M) were kept constant. The Rh(I) concentration was adjusted to obtain the proper substrate/catalyst ratio; with all our ligands we always obtained homogeneous solutions; no precipitation of the catalyst was observed. When the aminophosphonite–phosphinites **7** were used, no appreciable differences were seen when the chirality of the binaphthol changed from *S* to *R* (entries 1 and 2) and when the chirality of the backbone changed from *S* to *R* (entries 2 and 3); the branched aldehydes prevailed but the diastereoselectivity was disappointingly low, to predominantly give the undesired **5α** isomer. The only difference was that **7**-(*SS*) gives a more efficient catalyst with a catalyst activity (TOF) of at least 15 times higher than the other ligands of the same type (entry 2). Analogous results were obtained when aminophosphine–phosphites **8** were used (entries 4, 5 and 6); also in this case the (*S*,*S*) stereochemistry of the ligand gave rise to a very efficient catalyst (entry 6). When the substrate/catalyst ratio was increased to 1000/1, the diastereoselectivity remained unchanged, although the regioselectivity and catalyst activity were strongly reduced. These results indicate that aminophosphonite–phosphinites and aminophosphine–phosphites closely resemble the behaviour shown by (*R*)- and (*S*)-Binap.[6] Contrary to all expectations we found that also the regio- and diastereoselectivity of (*S*,*S*)-BDPP-(NBD)$Rh^+B(Ph)_4$ are strongly dependent on the substrate/catalyst ratio; in fact changing the ratio from a 20/1 (5 mol%) to 1000/1 meant that the regioselectivity of the (*S*,*S*)-BDPP-(NBD)$Rh^+B(Ph)_4$ catalyst dropped from 97/3 to 61/39 (branched/linear) while the diastereoselectivity was dramatically reversed, changing from 91/9 to 41/59 (**5β/5α**) (entries 8, 9 and 10).

The introduction of the bulky electron deficient *t*-Boc group reduces dramatically the regioselectivity in the hydroformylation of **4b**; linear aldehyde **6b** became predominant whatever ligand was used; this behaviour closely resembles that of (*S*,*S*)-BDPP-(NBD)$Rh^+B(Ph)_4$ (entries 11–18 and entry 19). The presence of the *t*-Boc

Table 1. Asymmetric hydroformylation of **4a–c**

Entry	Substrate	Catalyst	Sub/cat	Yield (%)	Time (h)	**5α+5β/6**	**5β/5α**
1	**4a**	**7**-*RR*/Rh(NBD)B(Ph)$_4$	20/1	100	60	68/32	39/61
2	**4a**	**7**-*SS*/Rh(NBD)B(Ph)$_4$	20/1	93	4	62/38	40/60
3	**4a**	**7**-*RS*/Rh(NBD)B(Ph)$_4$	20/1	100	60	64/36	40/60
4	**4a**	**8**-*SR*/Rh(NBD)B(Ph)$_4$	20/1	100	64	69/31	40/60
5	**4a**	**8**-*RR*/Rh(NBD)B(Ph)$_4$	20/1	100	17	58/42	39/61
6	**4a**	**8**-*SS*/Rh(NBD)B(Ph)$_4$	100/1	100	17	63/37	38/62
7	**4a**	**8**-*SS*/Rh(NBD)B(Ph)$_4$	1000/1	94	167	52/48	39/61
8	**4a**	(*SS*)BDPP/Rh(NBD)B(Ph)$_4$	20/1	100	24	97/3	91/9
9	**4a**	(*SS*)BDPP/Rh(NBD)B(Ph)$_4$	80/1	90	88	81/19	37/63
10	**4a**	(*SS*)BDPP/Rh(NBD)B(Ph)$_4$	1000/1	93	114	61/39	41/59
11	**4b**	**7**-*RR*/Rh(NBD)B(Ph)$_4$	20/1	100	17	52/48	38/62
12	**4b**	**7**-*RS*/Rh(NBD)B(Ph)$_4$	20/1	100	60	26/74	40/60
13	**4b**	**7**-*SS*/Rh(NBD)B(Ph)$_4$	20/1	100	78	48/52	66/34
14	**4b**	**7**-*SR*/Rh(NBD)B(Ph)$_4$	20/1	100	78	12/88	61/39
15	**4b**	**8**-*RR*/Rh(NBD)B(Ph)$_4$	20/1	95	17	24/76	78/22
16	**4b**	**8**-*SS*/Rh(NBD)B(Ph)$_4$	20/1	100	17	44/56	75/25
17	**4b**	**8**-*SR*/Rh(NBD)B(Ph)$_4$	20/1	100	40	27/73	78/22
18	**4b**	**8**-*SS*/Rh(NBD)B(Ph)$_4$	500/1	50	168	7/93	n.d.
19	**4b**	(*SS*)BDPP/Rh(NBD)B(Ph)$_4$	20/1	100	24	13/87	>99/1
20	**4c**	**7**-*SR*/Rh(NBD)B(Ph)$_4$	20/1	100	90	30/70	60/40
21	**4c**	**7**-*RS*/Rh(NBD)B(Ph)$_4$	20/1	100	90	1/>99	n.d.
22	**4c**	**8**-*SR*/Rh(NBD)B(Ph)$_4$	20/1	100	48	14/86	62/38
23	**4c**	**8**-*RS*/Rh(NBD)B(Ph)$_4$	20/1	100	168	21/79	60/40
24	**4c**	(*SS*)BDPP/Rh(NBD)B(Ph)$_4$	20/1	0	48	—	—

Reactions were carried out under 60 atmos of a 1/1 mixture of CO/H_2, at 60 °C, with a ligand/catalyst ratio = 2/1 and a substrate concentration 0.017 M. The % conversion and the ratio are determined by ^{1}H NMR spectroscopy and by GC–MS.

group at nitrogen implies a great change in the diastereoselectivity; the aminophosphine–phosphite ligands **8** always gave the desired β-isomer with diastereoselectivities up to 78/22 (entries 15, 16 and 17). With aminophosphonite–phosphinites **7**, **7**-(*SS*) and **7**-(*SR*) gave the β-isomer (entries 13 and 14) while the **7**-(*RR*) and **7**-(*RS*) ligands gave the α-isomer (entries 11 and 12). When the substrate/catalyst ratio was increased to 500/1, the only product obtained was the linear aldehyde **6b** (entry 18). The introduction at the nitrogen of the less electron deficient group $–CH_2COOCH_2Ph$ implies that the regioselectivity is reduced and the linear aldehyde **6c** is always the prevailing product; both aminophosphonite–phosphinite ligands **7** and aminophosphine–phosphite ligands **8** however, give the desired **5cβ**-isomer prevailing on the **5cα**-isomer (entries 20–23). The chiralities of the ligands seem to only affect the overall productivities of the catalysts (entry 23 compared to entries 20–22). It is noteworthy that (*S*,*S*)-BDPP-(NBD)Rh$^+$B(Ph)$_4$ is completely inactive on substrate **4c** (entry 22).

3. Conclusions

Aminophosphonite–phosphite and aminophosphonite–phosphinite–Rh(I) complexes catalyze the asymmetric hydroformylation of 4-vinyl azetidin-2-one to (3*S*,4*R*)-4-[(*R*)-1′-formylethyl]azetidin-2-one, a pivotal intermediate for the synthesis of 1β-methylcarbapenem. A bulky group must be present on the nitrogen to drive the reaction with good diastereoselectivity towards the derived β-isomer, even if this implies a reduction in the regioselectivity to the branched aldehyde. Unlike the behaviour of other active and successful Rh(I) complexes, the diastereoselectivity of aminophosphonite–phosphite and aminophosphonite–phosphinite–Rh(I) complexes seems to be independent from the substrate/catalyst ratio.

4. Experimental

The aminophosphonite–phosphite and aminophosphonite–phosphinite ligands and catalysts were prepared according to the literature procedure,[8] under an inert atmosphere (argon) using standard Schlenk techniques. Catalytic reactions were performed in a 200 mL stainless steel autoclave equipped with temperature control and magnetic stirrer. Unless otherwise stated, the other materials were obtained from commercial suppliers and used without further purification. The rhodium zwitterionic catalyst, (NBD)Rh$^+$B(Ph)$_4$, was prepared according to the literature procedure[10] as well as the 4-vinyl β-lactam **5a**.[11]

^{1}H NMR spectra are recorded on a Bruker AC300 equipped with a non-reverse probe and also or on a Bruker DRX300 Avance. GC–MS spectra are recorded on Thermo Finningan MD 800 equipped with GC Trace (SE 52 column: length 25 m, ϕ int. 0.32 mm, film 0.4–0.45 μm).

4.1. Preparation of 4b

Triethylamine (140 μL, 1.1 mmol) was added to a mixture of di-(*tert*-butyl)dicarbonate (436 mg, 1.1 mmol), **4a** (255 mg, 1 mmol) and DMAP (123.4 mg, 1.1 mmol) in methyl chloride (10 mL). The reaction mixture was stirred for 6 h at room temperature and then quenched with saturated NH_4Cl and extracted with ethyl acetate (20 mL). The combined organic layers were dried over

anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the residue by flash chromatography on silica gel, with hexane/ether (1:10) as eluants, gave 302 mg (85%) of **4b** as a yellow oil. ^{1}H NMR: δ 0.054 (s, 3H), 0.061 (s, 3H), 0.85 (s, 9H), 1.18–1.21 (dd, 3H), 1.48 (s, 9H), 2.86–2.90 (m, 1H), 4.27–4.32 (m, 1H), 4.50–4.54 (m, 1H), 5.24–5.44 (dd, 2H), 5.88–6.00 (m, 1H); $C_{18}H_{33}NO_4Si$ calcd 355.55, found 298.2 (M^+-57, $-C_4H_9$); IR (CH_2Cl_2): 1722.59 (C=O, lactam), 1805.53 (C=O, carbamate) cm^{-1}.

4.2. Preparation of 4c

Compound **4a** (510 mg, 2 mmol) in THF (3 mL) was added to a solution of NaH (55 mg, 2.2 mmol) in THF (10 mL) at 0 °C. The reaction mixture was stirred for 30 min, and then benzyl bromoacetate (458 mg, 2 mmol) in THF (3 mL) added at −78 °C. The reaction mixture was stirred for 6 h while the temperature of the reaction was allowed to run to room temperature, then treated with saturated NH_4Cl and the aqueous solution further extracted with ether (40 mL) and then with methylene chloride (20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the residue by flash chromatography on silica gel, with hexane/ether (1:9) as eluants, gave 334.5 mg (83%) of **5c** as a yellow oil. ^{1}H NMR: δ 0.025 (s, 3H), 0.059 (s, 3H), 0.87 (s, 9H), 1.22–1.24 (d, 3H), 2.91–2.94 (dd, 1H), 3.81–3.86 (m, 2H), 4.05–4.22 (m, 2H), 4.68–4.70 (m, 2H) 5.10–5.33 (m, 2H), 5.82–5.84 (m, 1H), 7.20–7.37 (m, 5H); $C_{22}H_{33}NO_4Si$ calcd 403.59, found 346.3 (M^+-57, $-C_4H_9$); IR (CH_2Cl_2): 1730.70 (C=O, lactam), 1825.42 (C=O, carbamate) cm^{-1}.

4.3. General procedure for hydroformylation of 4

In a typical run, the 4-vinyl β-lactam **4** (0.5 mmol), the (NBD)Rh$^+$B(Ph)$_4$ complex (5 mmol% to the substrate), and phosphorus ligand (10 mmol% to the substrate) were placed in a Schlenk tube, at which point benzene (30 mL) was added, the resulting solution stirred for 20 min and then transferred to a stainless steel autoclave previously purged five times with a H_2/CO mixture. The autoclave was pressured and heated in an oil bath. At the end of the reaction, the autoclave was vented and the solvent distilled. The branched/linear ratio **5/6**, the conversion and the diastereomeric excess of **5** were determined by ^{1}H NMR and GC–MS.

Compound **5aα**: ^{1}H NMR: δ 0.01 (s, 3H), 0.03 (s, 3H), 0.81 (s, 6H), 1.21–1.27 (d, 6H), 2.45–2.63 (m, 1H), 2.73–2.85 (dd, 1H), 3.60–3.62 (d, 2H), 4.10–4.17 (m, 2H), 6.2 (br, 1H), 9.68 (s, 1H); $C_{14}H_{27}NO_3Si$ calcd 285.18, found 228.2 (M^+-57, $-C_4H_9$).

Compound **5aβ**: ^{1}H NMR: δ 0.01 (s, 3H), 0.02 (s, 3H), 0.87 (s, 6H), 1.16–1.19 (d, 6H), 2.53–2.69 (m, 1H), 2.94–3.01 (dd, 1H), 3.86–3.93 (d, 2H), 4.13–4.20 (m, 2H), 6.1 (br, 1H), 9.73 (s, 1H); $C_{14}H_{27}NO_3Si$ calcd 285.18, found 228.2 (M^+-57, $-C_4H_9$).

Compound **6a**: ^{1}H NMR: δ 0.01 (s, 3H), 0.04 (s, 3H), 0.85 (s, 6H), 1.19–1.23 (d, 6H), 2.43–2.62 (m, 1H), 2.71–2.80 (dd, 1H), 3.59–3.63 (d, 2H), 4.10–4.20 (m, 2H), 6.1 (br, 1H), 9.77 (s, 1H); $C_{14}H_{27}NO_3Si$ calcd 285.18, found 228.2 (M^+-57, $-C_4H_9$).

Compound **5bα**: ^{1}H NMR: δ 0.02 (s, 3H), 0.03 (s, 3H), 0.85 (s, 6H), 1.12–1.15 (d, 6H), 1.49 (s, 9H) 2.73–2.87 (m, 1H), 3.98–4.32 (m, 1H), 4.33–4.48 (m, 1H), 5.26–5.45 (m, 2H), 5.96–6.00 (m, 1H), 6.8 (br, 1H), 9.69 (s, 1H); $C_{19}H_{35}NO_5Si$ calcd 385.58, found 328.5 (M^+-57, $-C_4H_9$).

Compound **5bβ**: ^{1}H NMR: δ 0.02 (s, 3H), 0.03 (s, 3H), 0.85 (s, 6H), 1.12–1.15 (d, 6H), 1.49 (s, 9H) 2.73–2.87 (m, 1H), 3.98–4.32 (m, 1H), 4.33–4.48 (m, 1H), 5.26–5.45 (m, 2H), 5.96–6.00 (m, 1H), 6.8 (br, 1H), 9.69 (s, 1H); $C_{19}H_{35}NO_5Si$ calcd 385.58, found 328.5 (M^+-57, $-C_4H_9$).

Compound **6b**: ^{1}H NMR: δ 0.03 (s, 3H), 0.059 (s, 3H), 0.87 (s, 6H), 1.13–1.17 (d, 6H), 1.54 (s, 9H) 2.73–2.87 (m, 1H), 3.86–4.25 (m, 1H), 4.35–4.49 (m, 1H), 5.31–5.47 (m, 2H), 5.93–5.99 (m, 1H), 6.5 (br, 1H), 9.73 (s, 1H); $C_{19}H_{35}NO_5Si$ calcd 385.58, found 328.5 (M^+-57, $-C_4H_9$).

Compound **5cα**: ^{1}H NMR: δ 0.01 (s, 3H), 0.02 (s, 3H), 0.9 (s, 9H), 1.20–1.22 (d, 6H), 1.70–1.82 (m, 1H), 2.0–2.2 (m, 1H), 2.4–2.65 (m, 2H), 2.85–2.95 (m, 1H), 3.76–4.2 (m, 2H), 5.1–5.3 (m, 1H), 7.3–7.6 (m, 5H), 9.73 (s, 1H); $C_{23}H_{35}NO_5Si$ calcd 433.62, found 376.2 (M^+-57, $-C_4H_9$).

Compound **5cβ**: ^{1}H NMR: δ 0.01 (s, 3H), 0.02 (s, 3H), 0.9 (s, 9H), 1.20–1.22 (d, 6H), 1.70–1.82 (m, 1H), 2.0–2.2 (m, 1H), 2.4–2.65 (m, 2H), 2.85–2.95 (m, 1H), 3.76–4.2 (m, 2H), 5.1–5.3 (m, 1H), 7.3–7.6 (m, 5H), 9.73 (s, 1H); $C_{23}H_{35}NO_5Si$ calcd 433.62, found 376.2 (M^+-57, $-C_4H_9$).

Compound **6c**: ^{1}H NMR: δ 0.01 (s, 3H), 0.02 (s, 3H), 0.9 (s, 9H), 1.20–1.22 (d, 6H), 1.70–1.82 (m, 1H), 2.0–2.2 (m, 1H), 2.4–2.65 (m, 2H), 2.70–2.72 (m, 1H), 3.76–4.2 (m, 2H), 5.1–5.3 (m, 1H), 7.3–7.6 (m, 5H), 9.73 (s, 1H); $C_{23}H_{35}NO_5Si$ calcd 433.62, found 376.2 (M^+-57, $-C_4H_9$).

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