Synthesis of tetracoordinated rhodium(I) complexes with chiral Shiff bases prepared from dehydroabietic acid

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New optically active Shiff bases **16**–**19** have been prepared from dehydroabietic acid **1** and have been used as ligands to synthesize tetracoordinated rhodium(I) complexes **20**–**27**.

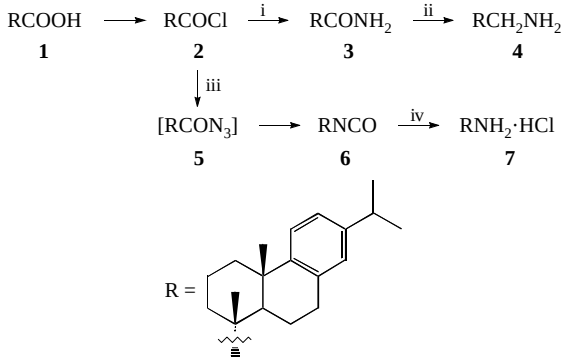
Synthesis of numerous pharmacologically valuable compounds is based on catalytic enantioselective reduction of prochiral ketones to optically active carbinols. Apart from direct hydrogenation, reactions of hydrosilylation and hydrogen transfer promoted by transition metal complexes with chiral P,N-donor ligands can be used to achieve the transformation under discussion.[1–3] The use of tetra- and pentacoordinated rhodium(I)- and iridium(I)-complexes with Shiff bases, prepared by interaction between optically active amines and heteroaromatic aldehydes, provided high chemical and optical yields of the products of reduction of acetophenone and its homologues.[4,5]

Having defined the synthesis of chiral ligands as the key objective in the concept we are developing for the various uses of natural higher terpenoids, we notice that resin acids have been studied only slightly in this respect. The adducts of levopimaric acid with maleic anhydride and *p*-quinone were shown to be promising starting compounds for the synthesis of optically active phosphorus-containing ligands.[6,7]

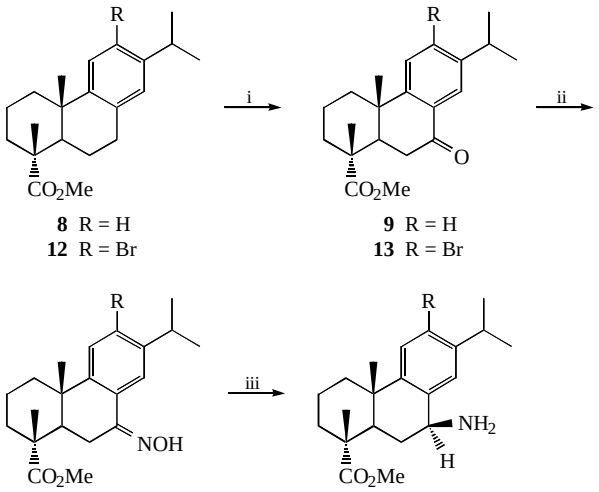
The purpose of the present work was to synthesize tetracoordinated rhodium(I) complexes with chiral Shiff bases prepared from dehydroabietic acid **1**.[8] The treatment of its acyl chloride **2**[9] with a saturated NH_3 solution in methanol at 0 °C produced amide **3** (92%), which was then reduced using a three-fold excess of $LiAlH_4$ to dehydroabietylamine **4** (75%). The latter compound is the same as that described in refs. 10 and 11.

The interaction of acyl chloride **2** with NaN_3 and thermal rearrangement of the intermediate azide **5** resulted in dehydroabietyl isocyanate **6**,[9] which was heated with concentrated hydrogen chloride in benzene to obtain amine hydrochloride **7** (65%).

Amine **11** was synthesized according to the following procedure (Scheme 2). Methyl dehydroabietate **8** was oxidized by $KMnO_4$ immobilized on Al_2O_3 to produce methyl-7-ketodehydroabietate **9**,[12] which was readily transformed to the corresponding oxime **10** (75%) under the action of



Scheme 1 *Reagents and conditions*: i, NH_3, MeOH, 0 °C, 2 h; ii, $LiAlH_4$, Et_2O, 35 °C, 8 h; iii, NaN_3, Me_2CO, 0 °C, 1 h, then MePh, 100 °C, 1.5 h; iv, HCl, C_6H_6, 80 °C, 5 h.



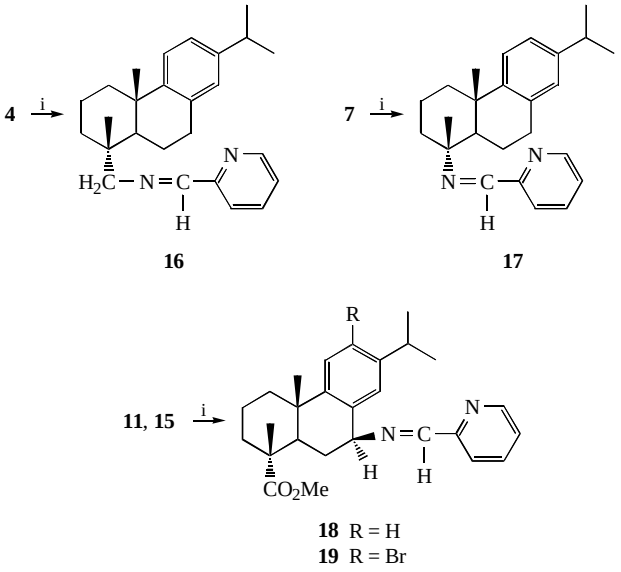
Scheme 2 *Reagents and conditions*: i, $KMnO_4/Al_2O_3$, Me_2CO, 20 °C, 12 h; ii, $NH_2OH·HCl$, AcONa, EtOH, 78 °C, 3 h; iii, H_2, PtO_2, MeOH/HCl, 20 °C, 1.5 h, then Et_3N, Et_2O, 20 °C.

$NH_2OH·HCl$. This compound was hydrogenated over a PtO_2 catalyst in the presence of an equimolar quantity of HCl in methanol to produce a mixture of products, from which the target compound, methyl 7-aminodehydroabietate **11** (80%) was isolated after neutralization using column chromatography on SiO_2. A comparative analysis of ^1H and ^{13}C NMR spectra recorded for hydrochloride **7** and amines **4**, **11**† suggested that the β-configuration of the NH_2 group in compound **11** was favoured. A similar example of the selective reduction of oximes is the preferential formation of β-amines in the catalytic (PtO_2) hydrogenation of some oximino-derivatives of monoterpenes and steroids.[13,14] Oxidation of methyl 12-bromodehydroabietate **12** with $KMnO_4/Al_2O_3$ in acetone gave methyl 12-bromo-7-ketodehydroabietate **13** (85%). Oxime **14** synthesized from this was hydrogenated over PtO_2 under the same conditions as oxime **10**. A mixture of products was obtained, among which methyl 7(β)-amino-12-bromodehydroabietate **15** (56%) was isolated.

The reaction between pyridine-2-carboxaldehyde and amine **4** was conducted in benzene in the presence of anhydrous Na_2SO_4 and gave azomethine **16** (67%).‡ Chiral Shiff bases **17** (52%), **18** (60%) and **19** (54%) were synthesized in the same way from amines **7**, **11** and **15**, respectively.

Chiral rhodium(I) complexes **20**–**27** were prepared through interaction of ligands **16**–**19** with di-μ-chlorobis(cyclooctadiene)dirhodium and $NaClO_4$ or $NaBF_4$ in methanol.

Reduction of acetophenone to phenethyl alcohol by means of a hydrogen transfer reaction under the conditions given elsewhere[4] was used as an example for the preliminary



Scheme 3 *Reagents and conditions*: i, pyridine-2-carboxaldehyde, Na_2SO_4, C_6H_6, 20 °C, 2 h.

estimation of the catalytic activity and enantioselectivity of the new complexes. For example, at [cat.] = 1.6×10^{-4} M and ratios of [sub.]/[cat.] = 1000, [propan-2-ol]/[sub.] = 80, the transformation of acetophenone in boiling propan-2-ol catalysed by complex **20**‡ produced (+)-(*R*)-phenethyl alcohol at 50% conversion and a moderate optical yield (12%) {$[\alpha]_D^{20}$ +5.1° (neat), lit.,[4] $[\alpha]_D^{20}$ +43.6° (neat)}.

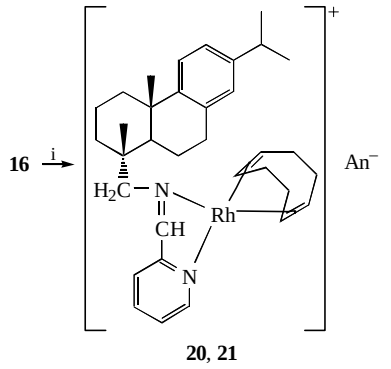
† A Bruker DRX 500 spectrometer was used to record ^{1}H and ^{13}C NMR spectra for compounds **7** and **11**, and a Bruker AC-200 for compounds **16** and **20**.

7: mp 250 °C (decomp.), $[\alpha]_D^{20}$ +49.6° (c 0.74, in $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 1.19 (s, 3H, 18-H_3), 1.22 (d, 6H, 16-H_3, 17-H_3, J = 7 Hz), 1.46 (s, 3H, 19-H_3), 1.52 (m, 1H, 1-H_a, J_{hem} = 13 Hz, J = 13 Hz, J = 4 Hz), 1.73 (m, 1H, 3-H_a), 1.76–1.87 (m, 3H, 2-H_2, 6-H_a), 1.99 (d, 1H, 5-H, J = 13 Hz), 2.19–2.30 (m, 3H, 3-H_b, 6-H_b, 1-H_b), 2.81 (septet, 1H, 15-H, J = 7 Hz), 2.93 (m, 1H, 7-H_a, J_{hem} = 17 Hz, J = 7 Hz), 3.00 (m, 1H, 7-H_b, J_{hem} = 17 Hz, J = 11.5 Hz, J = 6.5 Hz), 6.88 (d, 1H, 14-H, J = 1.5 Hz), 6.98 (dd, 1H, 12-H, J = 8 Hz, J = 1.5 Hz), 7.13 (d, 1H, 11-H, J = 8 Hz), 8.4 (br. s, 3H, NH_2·HCl); ^{13}C NMR ($CDCl_3$) δ: 18.72, 18.77 (C-2, C-6), 19.89 (C-19), 23.83 (C-16, C-17), 24.74 (C-18), 29.74 (C-7), 33.38 (C-15), 37.18 (C-1), 37.86 (C-10), 37.89 (C-3), 48.49 (C-5), 58.44 (C-4), 124.01 (C-12), 124.35 (C-11), 126.77 (C-14), 134.10 (C-8), 145.05 (C-9), 145.87 (C-13).

11: oil, $[\alpha]_D^{18}$ +13.9° (c 1.50, in $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 1.21 (d, 6H, 16-H_3, 17-H_3, J = 7 Hz), 1.24 and 1.26 (s, 6H, 18-H_3, 19-H_3), 1.31–1.93 (m, 8H, 1-H_2, 2-H_2, 3-H_2, 6-H_2), 2.25 (dd, 1H, 5-H, J = 12 Hz, J = 2 Hz), 2.84 (septet, 1H, 15-H, J = 7 Hz), 3.64 (s, 3H, OCH_3), 4.01 (dd, 1H, 7-H_2, J = 10.5 Hz, J = 7.2 Hz), 7.03 (dd, 1H, 12-H, J = 8.0 Hz, J = 2.0 Hz), 7.13 (d, 1H, 11-H, J = 8.0 Hz), 7.28 (d, 1H, 14-H, J = 2.0 Hz); ^{13}C NMR ($CDCl_3$) δ: 16.24 (C-19), 18.27 (C-2), 23.69, 23.84 (C-16, C-17), 25.41 (C-18), 33.21 (C-6), 33.47 (C-15), 36.32 (C-1)*, 37.31 (C-10), 37.90 (C-3)*, 43.77 (C-5), 47.12 (C-4), 51.47 (C-7), 51.77 (OCH_3), 123.98 (C-12)*, 124.92 (C-11), 125.14 (C-14)*, 138.24 (C-8), 146.14 (C-13), 146.55 (C-9), 178.54 (CO_2CH_3). Signal assignments follow the assumed formula.

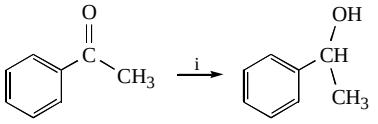
‡ **16**: mp 107–108 °C (C_2H_5OH), $[\alpha]_D^{24}$ +29.1° (c 0.48, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 1.07 (s, 3H, 18-H_3), 1.24 (d, 6H, 16-H_3, 17-H_3, J = 7 Hz), 1.26 (s, 3H, 19-H_3), 1.32–2.05 (m, 8H, 1-H_2, 2-H_2, 3-H_2, 6-H_2), 2.30 (d, 1H, 5-H, J = 13 Hz), 2.85 (m, 3H, 7-H_2, 15-H), 3.45 (d, 1H, 20-H_a, J = 12 Hz), 3.55 (d, 1H, 20-H_b, J = 12 Hz), 6.88 (s, 1H, 14-H), 7.01 (d, 1H, 12-H, J = 8 Hz), 7.19 (d, 1H, 11-H, J = 8 Hz), 7.30 (m, 1H, 5′-H, J = 8.5 Hz, J = 2 Hz), 7.70 (t, 1H, 4′-H, J = 8 Hz), 8.02 (d, 1H, 3′-H, J = 8 Hz), 8.36 (s, 1H, 1′-H), 8.60 (d, 1H, 6′-H, J = 5 Hz).

20: mp 210–220 °C (decomp.); ^{1}H NMR ($CDCl_3$) δ: 1.15 (d, 6H, 16-H_3, 17-H_3, J = 7 Hz), 1.19 (s, 3H, 18-H_3), 1.21 (s, 3H, 19-H_3), 1.31–2.15 [m, 8H, 1-H_2, 2-H_2, 3-H_2, 6-H_2, 4H (1,5-COD)], 2.27 (m, 1H, 5-H), 2.38–2.62 [m, 4H (1,5-COD)], 2.72–3.05 (m, 3H, 7-H_2, 15-H), 3.15 (d, 1H, 20-H_a, J = 11 Hz), 3.41 (d, 1H, 20-H_b, J = 11 Hz), 4.45 [m, 4H (1,5-COD)], 6.88 (s, 1H, 14-H), 6.94 (d, 1H, 12-H, J = 8 Hz), 7.11 (d, 1H, 11-H, J = 8 Hz), 7.68 (m, 1H, 5′-H), 7.85 (d, 1H, 6′-H, J = 5 Hz), 8.09 (m, 1H, 4′-H), 8.20 (d, 1H, 3′-H, J = 7.5 Hz), 8.55 (s, 1H, 1′-H).



Scheme 4 *Reagents and conditions*: i, $[Rh(C_8H_{12})Cl]_2$, $NaClO_4$ or $NaBF_4$, MeOH, 20 °C, 0.5 h.

A further communication concerned with a detailed study of the catalytic activity and enantioselectivity of new rhodium(I)-complexes in hydrogen transfer reactions will follow.



Scheme 5 *Reagents and conditions*: i, Pr^iOH, **20**, 83 °C, 24 h.

This work was supported by the Russian Foundation for Basic Research (grant no. 96-15-97013).

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Received: Moscow, 27th November 1997
Cambridge, 8th January 1998; Com. 7/08971J