C_2-Symmetric Ligands for Asymmetric Catalysis based on Feist's Acid

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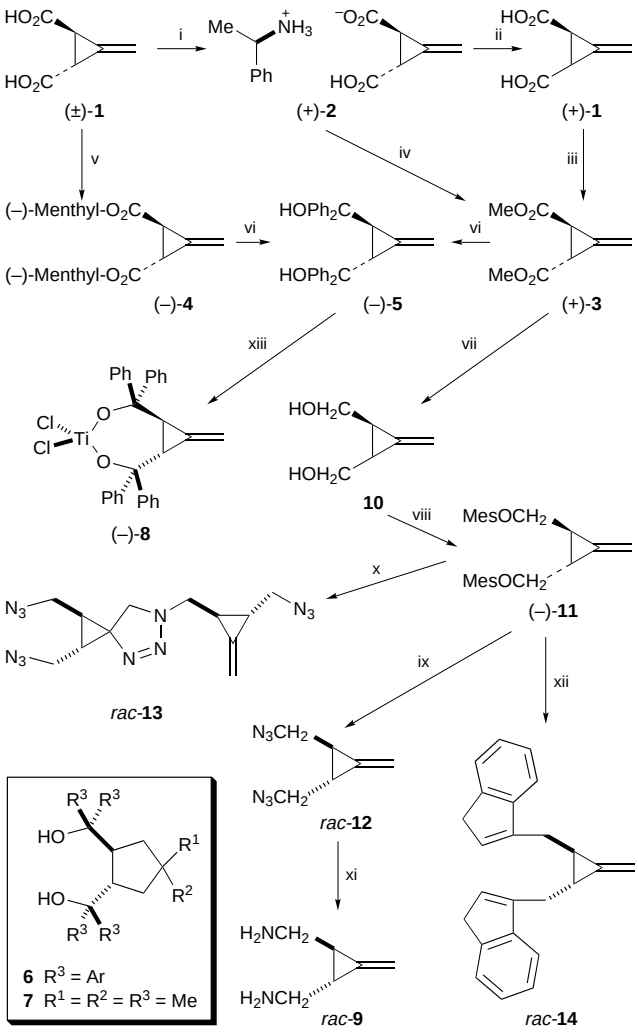
We describe a study of some of the chemistry of Feist's acid and attempts to prepare new diol and diamine ligands as well as a bis(indene) derivative.

There have been several reports on the resolution of Feist's acid. The earliest of these was by von Doering and Roth[4] using L-(−)-quinine as the resolving agent, while a recent patent[5] uses (*R*)-(+)-α-methylbenzylamine. As resolution is a critical issue if Feist's acid is to be a useful precursor to asymmetric ligands we carried out an investigation to compare the two different methods. In our hands reaction between (±)-Feist's acid and L-(−)-quinine in refluxing ethanol over 20 min gave a 43% yield of the L-quinine salt of (2*R*,3*R*)-(+)-1-methylidenecyclopropane-2,3-dicarboxylic acid {mp 183–184 °C, $[\alpha]_{546}^{23}$−145° {*c* 0.4, EtOH} [lit.,[9] mp 146–147 °C, $[\alpha]_{546}^{23}$−139.7° (*c* 0.7, EtOH)]} after fractional crystallisation from dry ethanol. Clearly, the mp of our salt was at variance with that reported by von Doering, although the specific rotation values were in agreement within experimental error. Hydrolysis of the salt with 10% sulfuric acid gave (2*R*,3*R*)-(+)-Feist's acid, (+)-**1** {mp 207 °C, $[\alpha]_{546}^{23}$+116° (*c* 0.4, EtOH) [lit.,[4] mp 203–205 °C, $[\alpha]_{546}^{23}$+176° (c 0.7, EtOH)]} in 84% yield. This suggested that either our sample was impure, despite the agreement in the mps, or that the quoted specific rotation values were inaccurate.

In an effort to resolve this issue the reaction between (±)-Feist's acid and 1 mol equivalent of (*R*)-(+)-α-methylbenzylamine was carried out in aqueous isopropyl alcohol to give a mixture of diastereomeric salts in 89% yield. Fractional crystallisation from isopropyl alcohol–water (3:1) gave the pure (+)-α-methylbenzylammonium salt of (2*R*,3*R*)-(+)-1-methylidenecyclopropane-2,3-dicarboxylic acid (+)-**2** in 73% of the theoretical yield; the mp and specific rotation values agreed well with those reported[5] Hydrolysis of this salt using 1 M HCl in ethyl acetate gave (2*R*,3*R*)-(+)-Feist's acid in 92% yield (mp 204–205 °C, $[\alpha]_{546}^{23}$+155.5° (*c* 0.70, EtOH}). Hydrolysis of the mother liquor gave impure (2*S*,3*S*)-(−)-Feist's acid {mp 199.2–199.7 °C, $[\alpha]_{546}^{23}$−95.3° (*c* 0.81, EtOH)}. This last method of resolution is more convenient practically and gives superior yields to the previous method described by von Doering. Our results indicate that the specific rotation value for the pure enantiomers is somewhat lower than that reported. As a further indication of purity, a sample of (+)-**1** prepared by the last method was esterified to give the known dimethyl ester (*R*,*R*)-**3** as a single enantiomer {mp 33–34 °C, $[\alpha]_{D}^{23}$+123.3° (*c* 0.76, CCl_4) [lit.,[5] mp 32–33 °C, $[\alpha]_{D}^{23}$+124.8° (*c* 0.76, CCl_4)]} in 89% yield. The optically pure ester could also be obtained directly from the salt (+)-**2** in 71% yield under rather more forcing conditions (see Scheme 2).

Furuta *et al.*[6] have previously described a procedure for the synthesis of (+)-(1*S*,2*S*)-cyclopropane-1,2-dicarboxylic acid by the condensation of (−)-dimenthyl succinate dianion with bromochloromethane followed by alkaline hydrolysis of the dimenthyl ester. This suggested a new alternative method of resolution for Feist's acid *via* the dimenthyl esters. Consequently, treatment of (+)-Feist's acid with two equivalents of L-(−)-menthol in refluxing toluene for 48 h gave the expected mixture of diastereomers in 73% yield. Repeated separation by column chromatography followed by recrystallization from dry methanol gave pure (−)-dimenthyl (2*R*,3*R*)-(−)-1-methylidenecyclopropane-2,3-dicarboxylate **4** {$[\alpha]_{D}^{23}$−122° (*c* 0.47, $CHCl_3$)} in 59% of the theoretical yield (Scheme 2). Attempts to hydrolyse the diester using the procedure applied successfully by Furuta *et al.*[3] (10% KOH solution in 9:1 methanol–water at 60 °C for 4 h) resulted in total racemization in our hands. Various



Scheme 2 *Reagents and conditions*: (i) (*R*)-(α)-PhCHMeNH$_2$, Pr^{i}OH–H$_2$O (9:1), 80 °C; ii, 1 M HCl, EtOAc; iii, MeOH, conc. H$_2$SO$_4$ (cat), 35 °C, 24 h; iv, MeOH, conc. H$_2$SO$_4$ (cat), 35 °C, 48 h; v, L-(−)-menthol, *p*-TsOH (cat.), toluene, reflux, 48 h; vi, (*a*) PhMgBr, THF, reflux, 2.5 h; (*b*) NH$_4$Cl; vii, LiAlH$_4$,THF, −78 °C to room temp., 24 h; viii, MeSO$_2$Cl, CH$_2$Cl$_2$, Et$_3$N, 0 °C, 2 h; ix, NaN$_3$, DMF, 60 °C, 6 h; x, NaN$_3$, DMF, 100 °C, 10 h; xi, 5% Pd–CaCO$_3$, EtOH, H$_2$, room temp., 24 h; xii, indeneMgBr,THF, reflux, 30 min, xiii, (*a*) BuLi, Et$_2$O, 0 °C; (*b*) TiCl$_4$, CH$_2$Cl$_2$ room temp

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attempts at hydrolysis under acidic conditions [CF_3CO_2H, CH_2Cl_2 at 0 °C, Me_3SiCl, NaI in CH_3CN] were equally unsuccessful.

The optically pure dimethyl ester (*R*,*R*)-**3** reacted with 2 mol equiv. of phenylmagnesium bromide in THF to give a single enantiomer of the diol (2*R*,3*R*)-(−)-**5** {$[\alpha]_D^{23}$ −276 ° (*c* 0.25, CCl_4)} in 58% isolated yield (Scheme 2). The same compound could also be obtained directly from the dimenthyl ester **4** under similar conditions, but the yield was poor (10%), presumably owing to steric hindrance from the menthyl chiral auxiliary. Diol **5** has a superficial similarity to the tetraaryldioxolanedimethanol (TADDOL, **6**) and hexamethyldioxolanemethanol (HMDDOL, **7**) ligands, which, as their titanium derivatives, have been used successfully by Seebach and others for asymmetric alkylation[9] and allylation[10] of aldehydes and for Diels–Alder reactions.[11–13] Work is currently in progress to assess the efficiency of the titanium complexes of diol **5** in similar reactions. Preliminary results indicate that the titanium complex **8** has activity for the addition of dialkylzinc to aldehydes, but as yet the yields and ee values have not been optimised.

The diamine **9** has not been described previously and an initial attempt at synthesis was by conversion of (*R*,*R*)-**3** to the known (*R*,*R*)-diol **10**[17] followed by treatment under Mitsonobu conditions with diphenylphosphoryl azide. Although all of the starting material was consumed, this reaction was not clean and the desired diazide could not easily be separated from the impurities. More success was achieved using the classical conversion of **10** into its dimesylate **11** followed by reaction with sodium azide in DMF at 60 °C for 6 h to give the diazide **12** in 84% isolated yield. The conditions of this reaction are critical and if a higher temperature (100 °C) is emplyed then the spirotriazoline **13** is the major product, formed by the 1,3-dipolar addition of **12** to the C=C bond of a second molecule. Hydrogenation of **12** gave the desired diamine **9** in 60% yield (Scheme 2). The diamine is an oil, which is difficult to purify as it is very sensitive to oxidation.

The *rac*-dimesylate **11** proved to be a useful precursor to the C_2-symmetric bis(indene) derivative *rac*-**14** formed in 69% yield by reaction with 2 mol equiv. of indenylmagnesium bromide. Work is in progress to synthesise *ansa*-titanium and -zirconium complexes of this ligand and its separate enantiomers to explore their efficiency as catalysts for asymmetric alkylation, hydrogenation and Ziegler–Natta polymerization of α-olefins.

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Techniques used: ^1H and ^{13}C NMR

References: 17

Schemes: 2

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