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## Embedding an Allylmetal Dimer in a Chiral Cavity: The Unprecedented Stereoselectivity of a Twofold Wittig [1,2]-Rearrangement

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1,1'-Binaphthyl-2,2'-bis(diphenylphosphine) ("BINAP") is arguably the most popular ligand for the catalysis of asymmetric hydrogenation and isomerization reactions. The bisphosphine was originally prepared starting from 1,1'-binaphthalene-2,2'-diol ("BINOL"), a cornerstone of atropisomeric chemistry, through 2,2'dibromonaphthalene<sup>1</sup> until an improved procedure based on the palladium-mediated condensation of the BINOL-derived 1.1'binaphth-2,2'-diyl bis(trifluoromethane sulfonate) with diphenylphosphine was disclosed.<sup>2</sup> This triflate was also found to be amenable to a palladium-catalyzed methoxycarbonylation, providing dimethyl 1,1'-binaphthyl-2,2'-dicarboxylate in high yield.<sup>3</sup> This switch from oxygen to carbon functionality intrigued us. We wondered whether it could not be brought about in a different manner featuring a Wittig rearrangement as the key step. In fact, when a solution of 2,2'-di(2-propenoxy)-1,1'-binaphthyl in tetrahydrofuran was treated at -75 °C with the LIC-KOR mixture<sup>4</sup> (butyllithium + potassium *tert*-butoxide) before being neutralized at +25 °C, 1,1-(1,1'-binaphth-2,2'-diyl)bis(2-propen-1-ol) (1a; see Scheme 1) was isolated indeed in high yield (72% after recrystallization). The mother liquors contained not even trace amounts of a 3-(1,1'-binaphthyl)-substituted propanal. This would have resulted from a [1,4]- rather than [1,2]-migration, the former process being the predominant mode when alkyl allyl ethers, as opposed to aryl allyl ethers, are subjected to the rearrangement.<sup>5</sup>

The diol **1a** was converted into 1,1-(1,1'-binaphthyl-2,2'-bis(3-chloro-1-propene) (**2**). Consecutive*vic*-dihydroxylation of the olefinic double bonds using sodium periodate and osmium tetroxide-promoted glycol cleavage gave 1,1-dinaphthyl-2,2'-dicarbaldehyde (**3**, 63%; Scheme 2).<sup>6</sup> The dialdehyde**3**could be reduced with sodium borohydride to 1,1'-dinaphthyl-2,2'-bismethanol<sup>7</sup> and was oxidized with sodium chlorite to give 1,1'-dinaphthyl-2,2'-dicarboxylic acid<sup>8</sup> (**4**, 91%; Scheme 2). Repetition of the entire reaction sequence employing optically active BINOL<sup>9</sup> produced of course the enantiomerically pure diacid**4**.<sup>10</sup>

Due to its two exocyclic stereocenters, the diol **1** exhibits both axial and tetrahedral chirality. High crystallinity and a narrow melting range suggested immediately that *a single diastereoisomer was formed* in the course of the Wittig rearrangement. This was confirmed by X-ray crystallography of the 4-bromobenzoate **1b** (see Scheme 1). The axial chirality  $(M)^{11}$  was found to be associated with the (S) configuration of the oxygen-bearing side chain and the  $(P)^{11}$  helicity with the (R) configuration (see Scheme 3).

In the allyl alcohol family, diastereoselectivity can be readily traded in for enantioselectivity by applying the Sharpless–Katsuki epoxidation protocol<sup>12</sup> for kinetic racemate resolution. In fact, when the racemic mixture of (*M*)-(*S*,*S*)-**1a** and (*P*)-(*R*,*R*)-**1a** was exposed at -25 °C for 20 h to *tert*-butyl hydroperoxide, titanium tetraisopropoxide, and (+)-diisopropyl (*R*,*R*)-tartrate (DIPT) in dichloromethane and in the presence of molecular sieves, the (*P*)-(*R*,*R*)-**1** component was completely consumed, with the supposed (*R*,*R*)-

**Scheme 1.** Witting Rearrangement of 2,2'-Di(2-propenoxy)-1,1'-binaphthyl To Afford 1,1-(1,1'-Binaphth-2,2'-diyl)bis(2-propen-1-ol) (**1**; 72%)<sup>a</sup>



<sup>*a*</sup> Conditions: (a)  $\text{LiC}_4\text{H}_9 + \text{KOC}(\text{CH}_3)_3$  in tetrahydrofuran at -75 °C; (b) temperature increased to +25 °C; (c) H<sub>2</sub>O.

**Scheme 2.** Transformation of the Diol **1** to the Bis(allyl chloride) **2** (90%) and Oxidation of the Latter to the Dialdehyde **3** (82%) and the Dicarboxylic acid **4** (91%)<sup>a</sup>



 $^a$  Conditions: (a) Ethanolic hydrogen chloride; (b) OsO4 (1%) + excess NaIO4 in aqueous THF at 25 °C; (c) NaClO<sub>2</sub> + H<sub>2</sub>O<sub>2</sub> in NaH<sub>2</sub>PO<sub>4</sub>-buffered aqueous acetonitrile at +40 °C.





48 % recov'd (*ee* ≥ 99 %) consumed

 $^a$  Conditions: (a) (H\_3C)\_3COOH + Ti(O^iC\_3H\_7)\_4 + (+)-DIPT in CH\_2Cl\_2 at 25 °C.

bisepoxide **5** (27%) being isolated as the main product (Scheme 4). Enantiomerically pure (M)-(S,S)-**1a** was recovered almost quantitatively (Scheme 3).

Irrespective of its practical potential, we need to rationalize the origin of this unprecedented diastereoselectivity. The phenomenon must have to do with intramolecular organometallic aggregation as the monoallyl ether **6** underwent stereochemically random rearrangement giving rise to a 1:1 mixture of (*R*) and (*S*) alcohols **7** (see Scheme 4). In contrast, the Wittig rearrangement of doubly metalated 2,2'-di(2-methyl-2-propenoxy)-1,1'-binaphthyl **8** proved again perfectly diastereoselective, affording the presumed (*M*)-(*S*,*S*)-**9** and (*P*)-(*R*,*R*)-**9** structures (Scheme 4).

Scheme 4. Diastereochemically Unselective and Selective Rearrangement of Metalated

2-(Propenyloxy)-2'-propyloxy-1,1'-binaphthyl and Dimetalated 2,2'-Bis(2-methyl-2-propenyloxy)-1,1'-binaphthyl To Afford Products 7 (70%) and 9 (82%), Respectively<sup>a</sup>



<sup>*a*</sup> Conditions: (a) LiC<sub>4</sub>H<sub>9</sub> + KOC(CH<sub>3</sub>)<sub>3</sub> in tetrahydrofuran at -75 °C; (b) temperature increased to +25 °C; (c) H<sub>2</sub>O.

Scheme 5. Metamorphosis of the Internal Bisallylmetal Aggregate 10 through the Meisenheimer Complex 11 to the Mixed Aggregate 12, The Intermediate Formed in the First Rearrangement Step



[OR = OC(CH<sub>3</sub>)<sub>3</sub>; Sv = solvent (i.e. THF)]

Our detailed analysis of the rearrangement process relies on plausible assumptions. In view of the immense difference in O-M and C-M bond strength<sup>13</sup> (M = alkali metals), it is safe to surmise that allylpotassium species and lithium tert-butoxide prevail as soon as metallomeric equilibrium has been attained. With allyl-allyl distances of approximately 4.5 Å at a 45° aryl-aryl twist, the allyl units can readily assemble one on top of the other (constructing the internal aggregate 10; see Scheme 5) to accommodate one or two lithium atoms in the pocket thus formed (average C-Li distance 2.3  $Å^{14}$ ). On the other hand, no potassium atom (average C-K distance 3.2 Å<sup>14</sup>) fits into this gap, not even if the torsion angle were compressed to unrealistically small 25°. Thus, potassium has to occupy the outside allyl faces (Scheme 5, species 10). In agreement with substituent effects on the rearrangement rates,<sup>15</sup> we believe the aryl [1,2]-migration occurs by intramolecular nucleophilic substitution (passing through a spiro-6-oxa[5,2]octa-3,5dienide Meisenheimer complex 11; see Scheme 5) rather than by the radical cleavage/recombination sequence<sup>16</sup> governing the alkyl [1,2]-migration and postulated<sup>17</sup> for the mono-rearrangement of a structurally related allyl naphthyl ether. If the carbon-carbon linking obeys the inversion mode with respect to the location of the potassium atom (and the retention mode with respect to lithium),

the first new stereocenter should have the (S) configuration when accompanied by (M) helicity and the (R) configuration when associated with a (P) axis. The second rearrangement must follow instantaneously, before any structural reorganization can take place. The conversion of the dimetalated species 10 into the monorearranged species 12 (see Scheme 5) should weaken the intraaggregate stabilization and hence provide an extra driving force for further transformation. Moreover, metal $-\pi$  interactions<sup>18</sup> may well be operative in the new intermediate 12 (as shown in Scheme 5) and help to prevent a premature structural collapse of this mixed aggregate. Consequently, also the second rearrangement step will proceed under  $(M) \rightarrow (S)$  and  $(P) \rightarrow (R)$  stereocontrol.

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Supporting Information Available: Working procedures and complete characterization data for compounds 1a, 1b, and 2-9 and full crystallographic details of compound 1b (including the associated CIF tables) are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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