CHEMISTRY LETTERS, pp. 1135-1136, 1989.

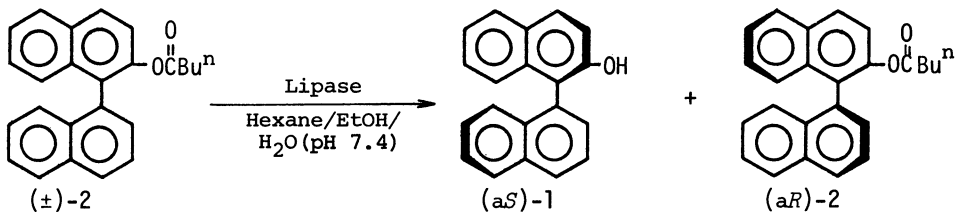
Reinvestigation of the Addition of Methylmagnesium Iodide to the Benzoylformate of Enantiomerically Pure 1,1'-Binaphthyl-2-ol Prepared by Enzymatic Kinetic Resolution[1)]

Yasufumi TAMAI, Tomoyuki NAKANO, Sinji KOIKE, Kan KAWAHARA, and Sotaro MIYANO*
Department of Biochemistry and Engineering, Faculty of Engineering,
Tohoku University, Aramaki-Aoba, Sendai 980

A lipase from pseudomonas was found to catalyze almost completely enantioselective hydrolysis of the valerate of racemic 1,1'-binaphthyl-2-ol (**1**). The Prelog's atrolactic acid synthesis by use of (a*R*)-**1** induced *S*-chirality with much lower levels of optical yields (3–17%) than that reported previously (85%).

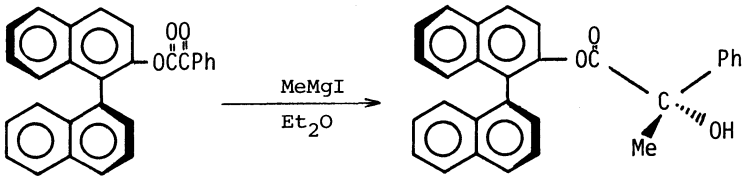
Although the stereochemistry of Grignard addition to α-keto acid esters of C-centro-chiral alcohols can correctly be predicted by the Prelog's rule, optical yields of the 1,4-asymmetric induction are generally less than 20%.[2)] Exceptionally high levels of optical yields (>90%) have been reported by Berson and Greenbaum for the reaction of MeMgI with benzoylformates of axially chiral 1,1'-biphenyl-2-ols derived from phenyldihydrotebaine, and a steric model was devised to explain the stereochemistry.[3)] Based on the model, they tentatively assigned (a*R*)-configuration to the dextro-rotatory 1,1'-binaphthyl-2-ol in methanol ((+)-**1**).[4)] In 1981, however, Kabuto and his coworkers revised that the (+)-**1** should be (a*S*) by chemically correlating it to binaphthyls of established configuration.[5,6)] None the less, the reported optical yield as high as 85% in the atrolactic acid synthesis was still fascinating, but difficulties in obtaining enantiomerically pure **1** in substantial quantities have retarded us to use it as highly efficient chiral auxiliary.

Herein we wish to report that both enantiomers of **1** can easily be obtained by a lipase-catalyzed, almost completely enantioselective hydrolysis of the valeric ester (**2**) of racemic **1**,[7)] which enabled us to reinvestigate the reaction of MeMgI with enantiomerically pure benzoylformate of **1**: A solution of 4.0 g of (±)-**2** (11.3 mmol) in ethanol (16 ml) and hexane (2 ml) was added dropwise to a vigorously stirred solution of 0.1 M phosphate buffer (120 ml, pH 7.4) and 15 ml of 2 wt% PVA to form an emulsion, to which was added portionwise 11.2 g (3.7×10^5 units) of



(±)-**2** (a*S*)-**1** (a*R*)-**2**

Scheme 1.



(a*R*)-3 (a*R*,*S*)-4

Scheme 2.

a lipase preparation (Lipase P AMANO from Amano Pharmaceutical Co.) (Scheme 1). After the mixture was stirred at room temperature for 24 h and then worked up as usual, products were chromatographed on silica-gel column (ethyl acetate–hexane (1/20)) to afford 1.25 g of (a*S*)-**1** (40% yield, 99% ee by HPLC on Pirkle column) and 1.97 g of (a*R*)-**2** (49% yield, >99% ee). Enantiomerically pure sample of (a*R*)-**1** ($[\alpha]_D^{20}$ -3.8° (c 1.14, MeOH)) was obtained from the (a*R*)-2 via reductive cleavage with $LiAlH_4$, and then converted into (a*R*)-1,1'-binaphthyl-2-yl benzoylformate (a*R*)-**3** by treatment with benzoylformyl chloride without loss of enantiomeric purity.

In a typical Grignard reaction (Scheme 2), 1.0 M solution of MeMgI in Et_2O (0.62 ml, 0.62 mmol) was allowed to react with 200 mg of (a*R*)-**3** (0.500 mmol) in Et_2O (3 ml) under the conditions similar to those of the literature except the scale of the reaction.[4] The atrolactic acid ester **4** was obtained in high yield (85%) by preparative TLC. Its diastereomeric composition, and thus the optical yield of the reaction, were determined by ^1H NMR. It has been found that (a*R*)-chirality in the binaphthyl axis induced (*S*)-centro-chirality on the atrolactic acid residue. This is in agreement with the result of Berson and Greenbaum in the sense that they obtained (*R*)-(-)-atrolactic acid from (+)-**1**. At our hand, however, the optical yield (16%) was much lower than that reported (85%). Several efforts, which included variation of the temperature, concentration of the reagents, and so on, did not improve the optical yield (3–17%). Thus, we regret to conclude that **1** is not so good a chiral-inducer in the classical asymmetric atrolactic acid synthesis at least under our reaction conditions, and that the steric model derived from the esters of the 1,1'-biphenyl-2-ols[4] can not be applied to that of 1,1'-binaphthyl-2-ol.

References

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(Received March 23, 1989)