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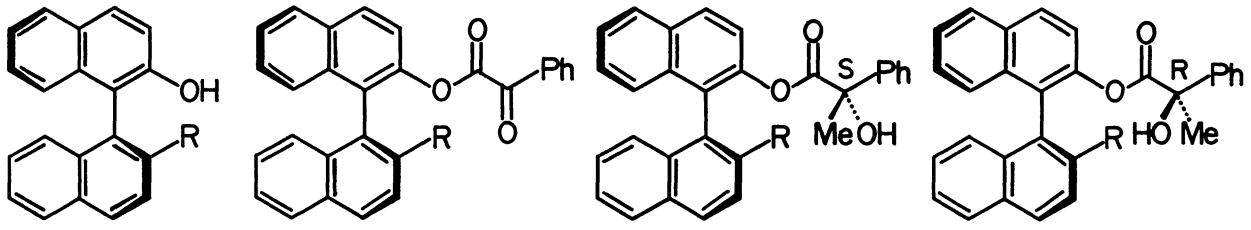
# An Investigation of the Inherent Chiral Induction Ability of Axially Chiral 1,1'-Binaphthalene Framework in the Prelog's Atrolactic Acid Synthesis

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

In the Prelog's atrolactic acid synthesis using 2'-substituted 1,1'-binaphthalen-2-ols as the chiral auxiliaries, the sense of the diastereoselection could not solely be determined by the helicity of the 1,1'-binaphthalene framework. A revised steric model is proposed to explain the selectivity.

Recently axially chiral 1,1'-binaphthalene derivatives have attracted much attention as highly efficient chiral inducers for a wide range of asymmetric reaction. In the course of our study on the remote asymmetric induction using 2'-substituted 1,1'-binaphthalen-2-ols (**1**) as the chiral auxiliary, [1] we recently reported that the Prelog's atrolactic acid synthesis [2] using 1,1'-binaphthalen-2-ol (**1a**) as the chiral alcohol resulted in a poor diastereoselectivity [ <20% diastereoisomeric excess (d.e.)], [3] in contrast to the high value (85% d.e.) reported previously. [4] Furthermore, it has been shown that the proposed steric model could not explain the observed sense of diastereoselection. [3,5] These discrepancies prompted us to investigate the inherent chiral induction ability of the axially chiral 1,1'-binaphthalene framework. In this letter, we wish to report the Prelog's atrolactic acid synthesis by use of **1** and a steric model to explain the effect of the 2'-substituent.

Homochiral 2'-substituted 1,1'-binaphthalen-2-yl benzoylformates (**2a-2f**), having respectively the same helicity as depicted below, were synthesized in 80 - 90% yields by treatment of the corresponding hydroxyl compounds **1a-1f** [3,6] with benzoylformyl chloride. The nucleophilic addition of MeMgI (1.0 mol $dm^{-3}$ in ether) to **2a-2f** in ether at -78 °C afforded the corresponding atrolactic acid esters **3a-3f** and **4a-4f** in high yields with moderate diastereoselectivity (Table 1). The ratio between **3** and **4** was determined by 250 MHz $^1H$ NMR analysis. The absolute configuration of the newly formed chiral center was determined from the specific rotation of the corresponding atrolactic acid after the complete hydrolysis of the diastereomer mixture.




**1a-f** **2a-f** **3a-f** **4a-f**

a: R = H, b: R = OMe, c: R = Me, d: R = $OPr^i$, e: R = $OSiMe_2Bu^t$, f: R = $OSiPh_2Bu^t$

Table 1. Addition of MeMgI to **2a-2f**

| Ester | R | Yield[a]/% | Ratio (**3** : **4**) [b] |
|---|---|---|---|
| **2a** | H | 95 | 52 : 48 |
| **2b** | OMe | 76 | 53 : 47 |
| **2c** | Me | 74 | 42 : 58 |
| **2d** | $OPr^i$ | 91 | 37 : 63 |
| **2e** | $OSiMe_2Bu^t$ | 98 | 25 : 75 |
| **2f** | $OSiPh_2Bu^t$ | 98 | 24 : 76 |

a) Isolated yields were based on the consumed **2**.

b) Ratios were determined by 250 MHz $^1H$ NMR.

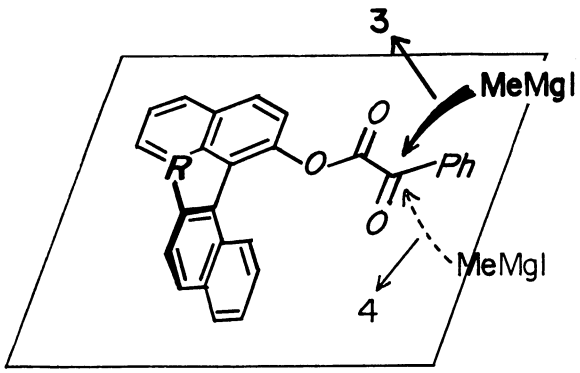



Fig. 1. A revised steric model.

The reaction of **2a** and **2b** preferentially induced (*S*)-centro-chirality on the atrolactic acid residue, while (*R*)-centro-chirality was preferred in the reaction of **2c-2f**. Moreover, the content of **4** increased with increasing the bulkiness of the 2'-substituent. Since the dihedral angle of the two naphthalene plains seems to be around 90°,[7] and the α-keto ester moiety of **2a-2f** should exist as *s*-trans conformer due to the dipole-dipole repulsion of the two carbonyl groups in the transition state, a steric model depicted in Fig. 1 may explain the diastereoselectivity. Thus, the steric hindrance imposed by C2'-R is smaller than that of the C5'-C8' moiety when the 2'-substituent is H or OMe; MeMgI attacks the keto carbonyl group preferentially from the less hindered upper side to give the diastereomer **3**. On the other hand, less hindered site is reversed when 2'-substituent is Me or a bulkier group to give **4** preferentially.

In conclusion, in the Prelog's atrolactic acid synthesis using 2'-substituted 1,1'-binaphthalen-2-ols, the sense of the diastereoselection could not solely be determined by the helicity of the 1,1'-binaphthalene skeleton. It should be noted that the low selectivity observed in the reaction of **2a** suggests that the difference of the actual bulkiness between the C2'-R and C5'-C8' moieties of the 1,1'-binaphthalene skeleton is rather smaller than might be expected.

References

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6) Compound **1b** was prepared from 2'-methoxy-1,1'-binaphthalene-2-carboxylic acid by the following reactions. i, $LiAlH_4$ /THF; ii, HBr/AcOH; iii, $LiAlH_4$/ether; iv, $BBr_3/CH_2Cl_2$. Synthesis of **1c** and **1d**, see: W. H. Pirkle and J. L. Schreiner, *J. Org. Chem.*, **46**, 4988 (1981). Synthesis of **1e** and **1f**, see: A. Aigner, F. Vögtle, S. Franken, and H. Puff, *Chem. Ber.*, **118**, 3643 (1985).

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