Induction of Axial Dissymmetry into the 1,1′-Binaphthyl Bond *via* an Intramolecular Ullmann Coupling Reaction

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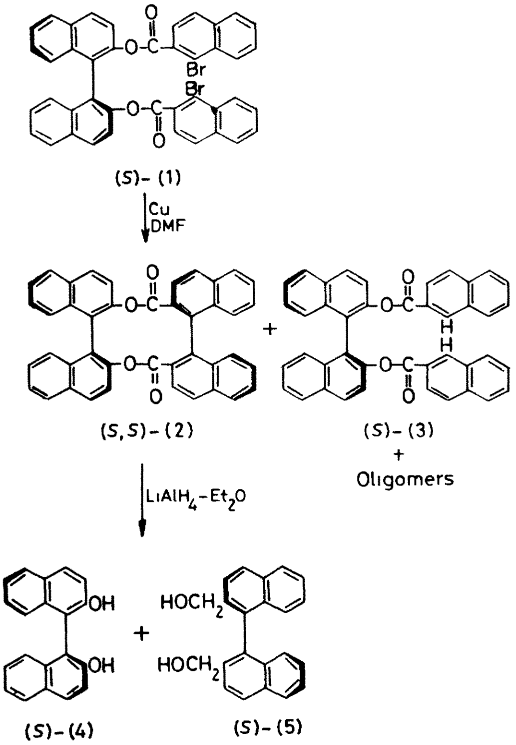
Summary Intramolecular Ullmann coupling of (*S*)-2,2′-bis-(1-bromo-2-naphthylcarbonyloxy)-1,1′-binaphthyl [(*S*)-(**1**)] induced axial dissymmetry of the *S*-configuration into the newly formed 1,1′-binaphthyl linkage affording (*SS*)-tetranaphtho[2,1-*b*; 1,2-*d*; 2,1-*h*; 1,2-*j*][1,6]dioxacyclododecene-11,26-dione [(*SS*)-(**2**)] with virtually complete diastereoselectivity.

RECENTLY, much attention has been centred on asymmetric reactions using an axially dissymmetric biaryl component as the chirality-inducing source[1] Although there are a number of methods currently available for the synthesis of biaryls,[2] direct routes to their atropisomers are limited [3]

We report here the induction of axial dissymmetry, with virtually complete diastereoselectivity, into the newly formed 1,1′-binaphthyl linkage *via* the intramolecular Ullmann coupling of a chiral substrate, (*S*)-2 2′-bis-(1-bromo-2-naphthylcarbonyloxy)-1,1′-binaphthyl {(*S*)-(**1**) m p 180—182 °C $[\alpha]_D^{22}$ +34 7° (*c* 0 922, acetone)†} (Scheme) In a representative reaction, (*S*)-(**1**) (2 05 mmol) was added slowly (1 h) under nitrogen to a well stirred, gently refluxing suspension of freshly activated copper powder[4] (3 g) in *NN*-dimethylformamide (DMF) (50 ml), the debromination reaction of the substrate was completed within 5 h heating at reflux The pale yellow organic residue {1 21 g, $[\alpha]_D^{24}$ −196 5° (*c* 1 11, benzene)} obtained after the usual work-up was chromatographed on a silica-gel column using chloroform (1% ethanol) as eluant to give a 36% isolated yield of the intramolecularly coupled product (*SS*)-(**2**), as a white powder, *m/e* 592 (M^+), $[\alpha]_D^{23}$ −457 6° (*c* 0 507 benzene), m p >350 °C, i r (KBr) ν 1752 cm^{-1} (C=O) The *SS*-configuration for the two binaphthyl units in the cyclic diester was unambiguously established as follows Reductive cleavage of the ester linkage by treatment with lithium aluminium hydride in boiling ether gave enantiomerically pure (*S*)-2,2′-dihydroxy-1,1′-binaphthyl [(*S*) (**4**)] and (*S*)-2,2′-bis(hydroxymethyl)-1,1′-binapththyl [(*S*)-(**5**)],as judged by optical rotations and by n m r spectral study of their (*R*)-α-methoxy-α-trifluoromethylphenyl acetic esters[5] (*S*)-(**4**), $[\alpha]_D^{24}$ −35 5° [*c* 1 03, tetrahydrofuran (THF)] {*cf* lit[6] $[\alpha]_D^{25}$ −33 3° (*c* 1 1, THF)}, (*S*)-(**5**), $[\alpha]_{546}^{23}$ −86 0° (*c* 1 43, acetone) {*cf* lit[7] $[\alpha]_{546}^{23}$ −83 0° (*c* 0 9815, acetone)}



SCHEME

Although the Ullmann reaction of (*S*)-(**1**) was accompanied by the formation of the reduction product, (*S*)-(**3**), as well as other oligomeric compounds, careful liquid chromatography did not suggest the presence of detectable amounts of the (*SR*)-isomer of (**2**), showing that the intramolecular coupling proceeded with remarkably high diastereoselectivity.

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† Satisfactory elemental analyses and spectroscopic data were obtained for all new compounds

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