Tetrahedron Letters,Vol.30,No.19,pp 2575-2576,1989
Printed in Great Britain

0040-4039/89 $3.00 + .00
Pergamon Press plc

ASYMMETRIC OXIDATION OF THIOETHERS.[1]
OPTICAL RESOLUTION OF [1,1'-BINAPHTHALENE]-2,2'-DITHIOL

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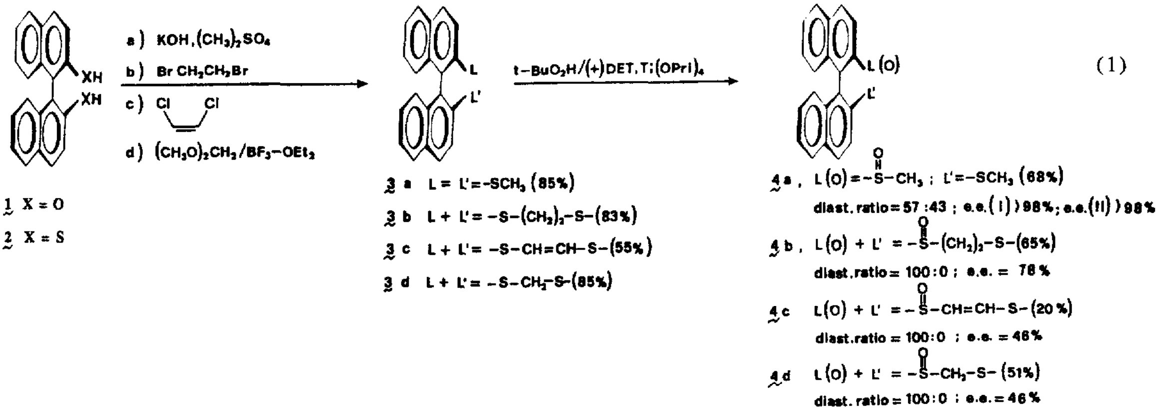
Summary: Almost optically pure (e.e. > 98%) [1,1'-binaphthalene]-2,2'-dithiol (**2**) is obtained by resolution of racemic **2** *via* the transformation of the sulfidryl functions into the corresponding thioethers **3** which are asymmetrically oxidized to diastereomeric chiral monosulfoxides **4** and then reconverted into **2**. The diastereo and enantioselectivity *is dependent on the structure of the thioether; i.e. the dimethylthioether 3a gives two* diastereomeric sulfoxides **4a** in *ca.* 1:1 ratio, each of them in >98% e.e., while cyclic dithioethers **3b-d** afford a single diastereomeric sulfoxide **4b-d** in 46-78% e.e..

Macrocyclic host compounds, *e.g.* polyethers and polysulfides,[2] have been synthesized from [1,1'-binaphthalene]-2,2'-diol (1), and from [1,1'-binaphthalene]-2,2'-dithiol (2), respectively.[3] Chiral macrocyclic polyethers derived from optically pure **1** are capable of chiral recognition towards suitable guest compounds.[3] By contrast little or no information is available on chiral reagents and/or macrocyclic polysulfides derived from [1,1'-binaphthalene]-2,2'-dithiol **2**, presumably because of lack of satisfactory resolution procedures.[4]

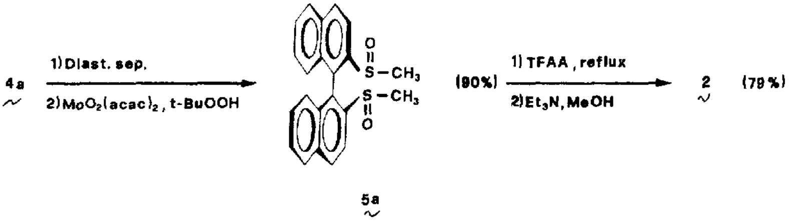
In this paper we illustrate a route for resolving **2** characterized by acceptable chemical *yields and fairly high, more than 98%, enantiomeric yields. Racemic* **2** *is obtained from* commercially available (±) **1** by a reported procedure[3] (73% yield). The series of reactions involved in its resolution is shown in equation 1. The sulfidryl groups of **2** are converted into thioethers **3a-d** by standard procedures.[5] The asymmetric oxidation of thioethers **3** to the monosulfoxides **4a-d**[6] by means of the reagent developed in our laboratory[7] is the key step of the



(1)

resolution. As previously observed,[8-11] the stereochemical outcome of thioethers asymmetric oxidations markedly depends on the structure of the substrate. The oxidation of the methylarylthioether **3a** is highly enantioselective, e.e. > 98%, but shows almost no diastereoselectivity, whereas, when the sulfur atom is fused into a ring system, as in **3b-d**, the oxidation is diastereospecific, but the enantioselectivity is less satisfactory (e.e. up to 78%).

After chromatographic separation of the diastereoisomers, a Pummerer reaction[12] on the bis-sulfoxide **5a**, obtained from **4a** by oxidation with *t*-$BuO_2H/MoO_2(acac)_2$,[13] directly furnishes **2** in > 98% e.e.[14] (equation 2). Alternatively, bithionaphthol **2** of comparable optical purity, can be obtained by reduction, with sodium in liquid ammonia, of **4b** (one diastereoisomer only) which is easily upgraded to e.e. > 98% by crystallization (dichloromethane/pentane). The latter procedure is advantageous in large scale preparations. It is worth noting that the reduction of the methyl derivative **4a** under the same reaction conditions leads partially to hydrogenation of the naphthyl residues and that the Pummerer reaction applied to the cyclic bis-sulfoxide derived from **4b** gives mostly dinaphthothiophene.



(2)

The availability of optically pure bithionaphthol and derivatives is likely to be exploited in a wide variety of asymmetric reactions. Some of them are examined in our laboratories.

ACKNOWLEDGEMENT: We are grateful to Dr. Vanna Delogu (Istituto per l'Applicazione delle Tecniche Chimiche Avanzate ai Problemi Agrobiologici del CNR, Sassari) for preliminary preparations of the substrates.

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5. **3a**: obtained from dimethylsulfate methylation, 85% yield, mp 185-6°C; **3b** and **3c**: from reaction of the anion of **2** with 1,2-dibromoethane or (Z)-1,2-dichloroethylene in 83 and 55% yield respectively, mp 254-6 and 209-210°C; **3d**: from dimethoxymethane acetalization under BF_3 catalysis, 89% yield, mp 158-160°C.
6. Correct elemental analysis and spectral data in accord with the proposed structures were obtained for all new reported compounds.
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14. From the major diastereoisomer of **4a**, (-)-**2** is obtained, whereas, the other diastereoisomer provides (+)-**2**. Attempts to evaluate directly the e.e. value of **2** either by NMR or by HPLC separation of the enantiomers were unsuccessful. Thus, the e.e. value of **2** has been estimated from the e.e. value (> 98%) of the corresponding disulfide by HPLC on a Pirkle covalent phenyl-glycine (Regis Chemical Company) chiral column.

(Received in UK 30 March 1989)