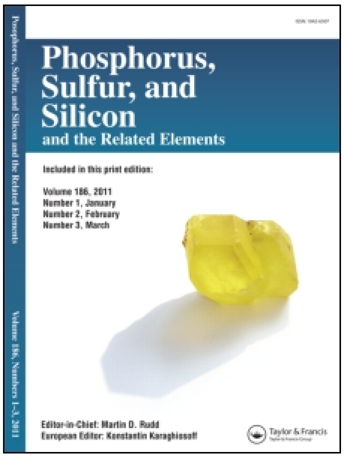

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Enantioselective Oxidation of Thioethers. An Improved Route to the Resolution of [1,1'-Binaphthalene]-2,2'-Dithiol

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ENANTIOSELECTIVE OXIDATION OF THIOETHERS.[1] AN IMPROVED ROUTE TO THE RESOLUTION OF [1,1'-BINAPHTHALENE]-2,2'-DITHIOL

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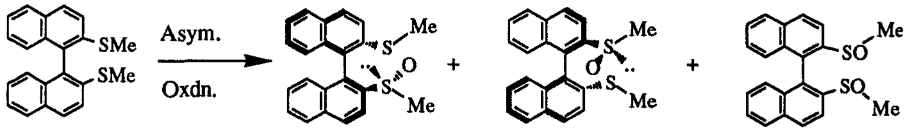
Abstract (±)-[1,1'-Binaphthalene]-2,2'-*bis*-methylthioether (±)-**1** was oxidized with high enantioselectivity by using our asymmetric reagent [Ti(IV) : (+)-DET : TBHP = 1 : 4 : 2]. An appropriate substrate/oxidant ratio afforded such a product distribution that allowed us to obtain, after chromatographic separation and chemical transformations, optically pure [1,1'-binaphthalene]-2,2'-dithiol in ca. 80% yield based on the racemic starting material.

In the course of our studies on the thioethers enantioselective oxidation obtained by our modified Sharpless reagent[2] [Ti(IV) : (+)-diethyltartrate : *t*-butylhydroperoxide = 1 : 4 : 2][3] we noticed that our system is extremely efficient in the oxidation of (±)-[1,1'-binaphthalene]-2,2'-*bis*-methylthioether (±)-**1**.[4]

When the reaction is performed with an excess of substrate over the oxidant [(±)-**1**: Ti(IV):(+)-DET: TBHP = 4: 1: 4: 2] two diastereomeric *mono*-sulfoxides (+)-**2a** (C_S, S_R) and (+)-**2b** (C_R, S_R) in very high enantiomeric excesses values (>98%) and reasonable chemical yields (25% on the starting material) are obtained, together with a 10% mixture of the three diastereomeric *bis*-sulfoxides **3** (Scheme 1).

SCHEME 1. Asymmetric oxidation of (±)-**1** [Substrate:Ti(IV):(+)-DET: TBHP = 4: 1: 4: 2].

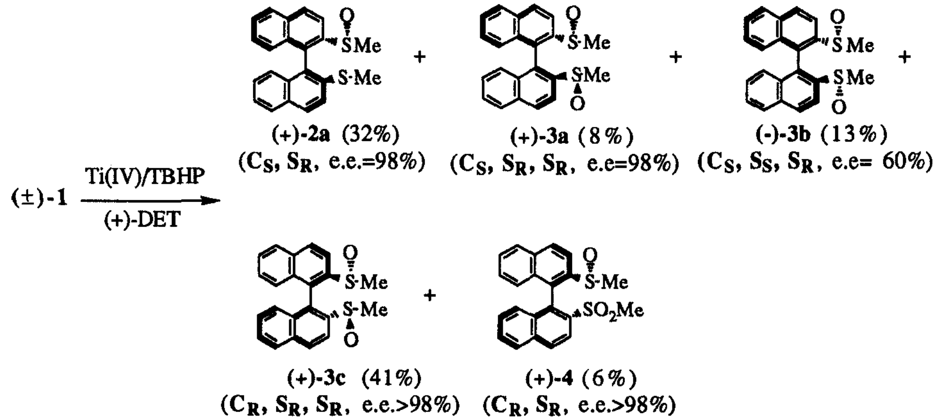


(±)-**1** (+)-**2a** (e.e>98%) (+)-**2b** (e.e.>98%) **3a** + **3b** + **3c**

The two *mono*-*S*-oxides (+)-**2a** and (+)-**2b** , after chromatographic separation, further oxidation to the *bis*-*S*-oxides and Pummerer reaction, afforded the (+)-(S)- and (-)-(R)-[1,1'-binaphthalene]-2,2'-dithiol respectively with an e.e.>98%.

A careful evaluation of the results reported above suggested that the method might be improved by carrying on further the oxidation. This was confirmed by the data reported below which were obtained by using a larger amount of the oxidant, *i.e.* (±)-**1** : TBHP = 1 : 1.8 ratio. In fact a quite interesting products distribution was observed (Scheme 2).

SCHEME 2. Asymmetric oxidation of (±)-**1** [Substrate:Ti(IV):(+)-DET: TBHP = 1: 0.9: 3.6: 1.8].



(+)-**2a** (32%) (C_S, S_R, e.e.=98%)

(+)-**3a** (8%) (C_S, S_R, S_R, e.e=98%)

(-)-**3b** (13%) (C_S, S_S, S_R, e.e= 60%)

(+)-**3c** (41%) (C_R, S_R, S_R, e.e.>98%)

(+)-**4** (6%) (C_R, S_R, e.e.>98%)

Under these conditions we were able to recover the *mono*-sulfoxide (+)-**2a** (C_S, S_R) (e.e.=98%, 32%) as the only *mono-S*-oxide and the *bis*-sulfoxide (+)-**3a** (C_S, S_R, S_R) (e.e.=98%, 8%), both having the S absolute configuration at the binaphthyl moiety, together with the *bis*-sulfoxide (+)-**3c** (C_R, S_R, S_R) (e.e>98%, 41%) which has opposite configuration at the binaphthyl residue. Consequently, we reached a 81% net recover of resolved products (40% of the S form and 41% of the R one) based on the racemic starting material (±)-[1,1'-binaphthalene]-2,2'-*bis*-methylthioether (±)-**1**. Moreover, it is worthy of mention that the two products present in larger amounts, the (+)-**2a** and (+)-**3c**, having opposite absolute configuration at the binaphthyl moiety are not diastereomers, as commonly obtained in resolution procedures. Rather they are completely different compounds, *i.e.* a *mono*-sulfoxide the first and a *bis*-sulfoxide the second one, thus making particularly easy their chromatografic separation. Studies aimed at an optimization of the substrate/oxidant ratio and at a complete rationalization of the processes involved are now under investigation.

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