Asymmetric Destruction of (±)-2,3-Bis(phenylsulphonyl)butane

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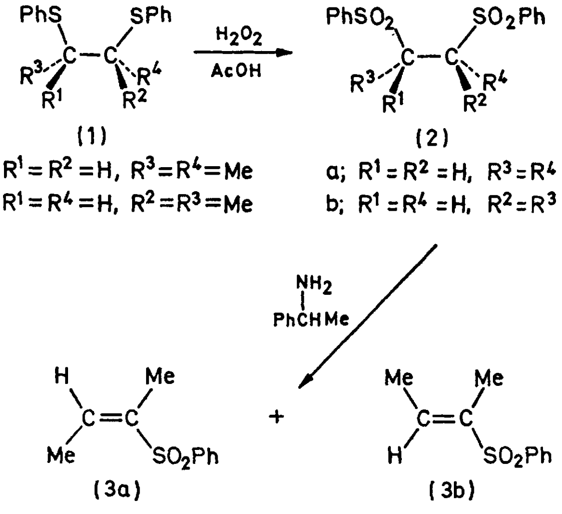
Summary *meso*- and (±)-2,3-Bis(phenylsulphonyl)butane (**2a**) and (**2b**) have been synthesized; when (**2b**) was allowed to react incompletely with chiral α-phenylethylamine, recovered (**2b**) was partially resolved.

In a study of the pyrolysis of the diastereomeric 2,3-bis(phenylthio)butanes (**1**),[1] it became necessary to assign the structures of the diastereoisomers. A mixture of (**1a**) and (**1b**) was prepared by reaction of sodium thiophenoxide with a solution of *meso*- and (±)-2,3-dichlorobutane in dimethylformamide. Hydrogen peroxide oxidation of (**1a**) and (**1b**) in glacial acetic acid gave the corresponding disulphones *meso*- and (±)-2,3-bis(phenylsulphonyl)butane, (**2a**) and (**2b**). The diastereoisomers of (**1**) and (**2**) may be separated by column chromatography on silica gel. In both (**1**) and (**2**) the material which was eluted first from the column was subsequently shown to have the (±) structure.†

The disulphones were expected to undergo base-catalysed elimination of phenylsulphinic acid. Base-catalysed eliminations on β-substituted sulphones have been shown to involve proton removal in the rate-determining step.[2] If a suitable chiral base is chosen to effect elimination, loss of phenylsulphinic acid from one enantiomer may occur more rapidly than from its mirror image. In this case, recovered (**2b**) should be partially resolved; recovered (**2a**) is incapable of resolution. If resolution occurs, a simple assignment of structure to (**2a**) and (**2b**) will be possible. Such kinetic resolutions have been observed in dehydrohalogenations with the chiral base brucine.[3,4]

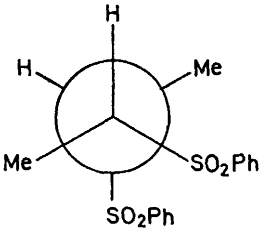
Equimolar quantities of (**2b**) and (*R*)-α-phenylethylamine were refluxed in xylene until t.l.c. showed destruction of *ca.* 50% of starting material. After removal of solvent,



(1)
a; $R^1 = R^2 = H$, $R^3 = R^4 = Me$
b; $R^1 = R^4 = H$, $R^2 = R^3 = Me$

(2)
a; $R^1 = R^2 = H$, $R^3 = R^4 = Me$
b; $R^1 = R^4 = H$, $R^2 = R^3 = Me$

(3a) (3b)



(4)

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† Satisfactory elemental analysis as well as i.r. and n.m.r. spectra were obtained for diastereoisomers of (**1**) and (**2**).

the unchanged (**2b**), recrystallized from ethanol, showed optical activity {$[\alpha]^{25}_D$ −109·5° (2·5% in CH_2Cl_2)}. A similar experiment with (*S*)-α-phenylethylamine and (**2b**) gave recovered (**2b**) with $[\alpha]^{25}_D$ +36° (2·5% in CH_2Cl_2). When (**2a**) was treated with (*R*)-α-phenylethylamine, the recovered (**2a**) showed no optical activity. The results of these kinetic resolutions allow assignment of structure to (**2a**) and (**2b**) and to their precursers, (**1a**) and (**1b**).

The elimination products, characterized by their i.r. and n.m.r. spectra, were the expected *cis*- and *trans*-2-(phenylsulphonyl)but-2-enes (**3a**) and (**3b**). Elimination of phenylsulphinic acid from (**2b**) yields exclusively (**3a**) while (**2a**) gives (**3a**) and (**3b**) in the ratio 1·6 : 1. The *cis*- and *trans*-vinyl sulphones were differentiated by the chemical shift of their vinyl protons; δ 6·90 for (**3a**) and δ 6·05 p.p.m. for (**3b**). In analogy with other vinyl sulphones,[5,6] the proton *cis* to the sulphonyl group is expected to be more deshielded than the *trans*-proton.

Thus, (**2b**) undergoes *syn*-elimination, while (**2a**) gives products resulting from both *syn*- and *anti*-elimination. An *anti*-elimination on (**2b**) is probably precluded by the unfavourable steric interactions in the conformation (**4**) leading to *anti*-elimination. Other β-substituted sulphones in which steric consideration favour *syn*-elimination have been reported.[7,8]

Examination of recovered (**2a**) and (**2b**) showed that no interconversion of diastereisomers occurred under the reaction conditions. This is consistent with the fact that the inversion of α-sulphonyl carbanions is slow compared to other competing processes.[9,10]

This kinetic asymmetric destruction appears to represent a general method for partially resolving vicinal disulphones.[11] It may be possible to extend this procedure to other β-substituted sulphones with bulky β-substituents which are good leaving groups.

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