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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

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To cite this Article Allenmark, Stig , Claeson, Sofia , Löwendahl, Christina and Widell, Petra(1999) 'Routes to Endocyclic Sulfoximides Via Electrophilic Amination Reactions', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 153: 1, 359 – 360

To link to this Article: DOI: 10.1080/10426509908546470

URL: <http://dx.doi.org/10.1080/10426509908546470>

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Routes to Endocyclic Sulfoximides Via Electrophilic Amination Reactions

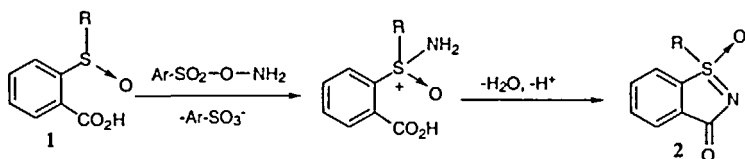
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Reaction of a 2-carboxyphenyl sulfide with non-anhydrous O-(mesityl-enesulfonyl)-hydroxylamine (MSH) in excess gives the corresponding endocyclic sulfoximides, while reaction with anhydrous MSH leads to the respective sulfimides.

Keywords: 2-carboxyphenyl sulfides; MSH; sulfoximides; resolution

We have previously found that amination of an optically active sulfoxide (**1**) by MSH gives essentially complete formation of enantiopure sulfoximide (**2**, >94% ee), while the use of hydrazoic acid (HN_3) yields a partially racemized product^[1].



Further, the two aminating reagents give products having opposite signs of rotation, shown by enantioselective LC to correspond to the two opposite enantiomers^[2]. The difference in stereochemistry is likely to be caused by a neighbouring carboxyl group participation taking place in the strongly acid medium used in the reaction with HN_3 . An X-ray

crystallographic determination of the absolute configuration of the product obtained from the MSH reaction, showed the latter to give overall retention of the configuration at sulfur^[3].

When the same amination was carried out with the sulfide corresponding to **1** ($R = C_8H_{17}$), two racemates were observed from the reaction with MSH when the reaction product was analyzed by LC (Fig. 1).

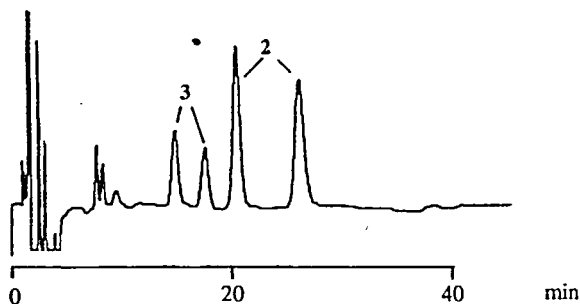
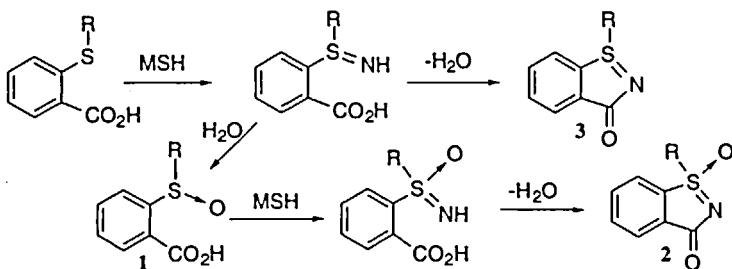


FIGURE 1 The two racemates **2** and **3** present after the reaction

The yield of the first eluted racemate increased with decreased water content of the MSH used. Scheme 1 shows the reaction path suggested.



SCHEME 1. The role of water in the amination reaction

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- [2] S. Allenmark, S. Claeson and C. Löwendahl, *Tetrahedron: Asymmetry* **7**, 361 (1996).
- [3] S. Allenmark, S. Claeson and S. Sundell, *Enantiomer* **2**, 113 (1997).