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Cu(I)-Catalyzed Sulfoximination

Jürgen F. K. Müller*, Patrick Vogt

Institute of Inorganic Chemistry, University of Basel, Spitalstrasse 51, CH-4056 Basel

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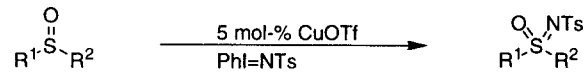
Abstract:

The reaction of PhI=NTs with sulfoxides in the presence of catalytic amounts of CuOTf afforded the corresponding N-tosylsulfoximines in high yield. The use of enantiomerically pure sulfoxides allowed stereoselective access to N-tosylsulfoximines with complete retention of configuration at sulfur.

Keywords: Catalysis; Copper; Sulfoximines

Sulfoximines contain a configurationally stable chiral sulfur moiety which is attracting increasing attention in asymmetric synthesis [1-3]. Several strategies for their preparation are known [4,5], but for enantiopure sulfoximines only a limited number of methods are available. One route involves oxathiazole-2-oxides which react with Grignard reagents to yield enantiopure sulfoximines [6]. The resolution of S-methyl-S-phenylsulfoximine with camphorsulfonic acid [7] along with the imination of optically active sulfoxides with O-mesitylenesulfonylhydroxylamine [8] are additional methods. So far, no catalytic method for the synthesis of sulfoximines is available. Recently, it was demonstrated, that PhI=NTs acts as a nitrene source for the N-functionalisation of alkenes and sulfides [9, 10]. It is our aim to apply this reagent for the imination of racemic and enantiopure sulfoxides.



1a-f **2a-f**

Upon treatment of racemic S-methyl-S-phenylsulfoxide **1a** with 1.1 equivalents of PhI=NTs and catalytic amounts of Cu(I) triflate in toluene, the desired product **2a** was obtained in 84% yield. The imination of various racemic sulfoxides **1a-1f** gave the related N-

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tosylsulfoximines **2a-f** in generally high yields (see Table 1).[1]

Table 1: Catalytic synthesis of sulfoximines **2a-g**.

entry	R^1	R^2	t (°C)	Product **2**	isolated yield (%)
1	Ph	Me	25	**a**	84
2	Ph	Et	25	**b**	86
3	Ph	*i*-Pr	25	**c**	81
4	Ph	Vinyl	40	**d**	79
5	Ph	Allyl	40	**e**	93
6	Ph	Benzyl	40	**f**	89
7	Tol	Me	25	**g**	82

Sulfoxides containing a C=C double bond such as **1d,e** reacted exclusively to give the N-tosylsulfoximines **2d** and **2e** in excellent yields. The stereoselective imination of enantiopure (-)-*R*-tolylmethylsulfoxide **1g** to (-)-*R*-**2g** was achieved in high yield (82%) under retention of configuration (≥98% ee) [11]. As optically active sulfoxides are easily accessible [12], we can now offer a simple and mild method to the stereoselective imination to give the related N-tosylsulfoximines.

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[1] Typical procedure: To a solution of 0.5 g (3.2 mmol) (-)-*R*-**1g** and 0.040 g CuOTf (0.16 mmol) in 10 ml dry toluene, 1.3 g (3.5 mmol) of PhI=NTs were added at 0 °C under argon. The reaction mixture was stirred for 12 h at 25 °C, filtrated over celite and the solvent removed in *vacuo*. The resulting brown oil was purified by column chromatography (ethyl acetate/hexane = 1:1), which afforded (-)-*R*-**2g** as colourless crystals (0.84 g, 82%). Experimental data for **2g**: R_f = 0.34 (ethyl acetate/hexane = 1:1).^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.39 (s, 3H), 2.47 (s, 3H), 3.41 (s, 3H), 7.25 (dm, 2H, arom.-H), 7.38 (dm, 2H, arom.-H), 7.82-7.87 (m, 4H, arom.-H).^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.55, 21.68, 46.84, 126.68, 127.54, 129.28, 130.34, 135.7, 140.9, 142.81, 145.9. MS (EI, 70eV) m/z (%) = 323 [M^+] (6), 216 (16), 155 (22). $[\alpha]_D^{25}$ = -138° (c 1.06, acetone) [11].