Mg-Promoted Stereoselective Desulfonation of *β*-Arylvinyl Sulfone Derivatives

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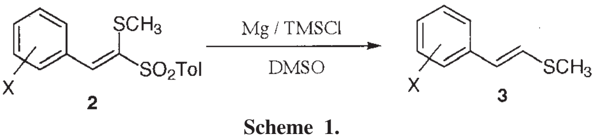
β-Arylvinyl *p*-tolylsulfones, easily prepared from base-catalyzed condensation of aromatic aldehydes with a variety of *p*-tolylsulfones, were efficiently transformed to the corresponding (*E*)-*β*-substituted aromatic olefins in a stereoselective manner through Mg-promoted reduction. The reaction may be initiated through electron transfer from Mg metal to the vinyl sulfones to give the corresponding anionic species followed by stereoselective elimination of a sulfonyl group.

Stereoselective synthesis of olefins are one of the most important and challenging subjects in organic synthesis.[1–3] In this study, we wish to report a novel stereoselective method for formation of (*E*)-*β*-substituted aromatic olefins (**3**, **6**) through Mg-promoted desulfonation of *β*-arylvinyl *p*-tolylsulfones (**2**, **4**, **5**), easily prepared from base-catalyzed condensation of aromatic aldehydes with a variety of *p*-tolylsulfones.

As one of the typical starting sulfones, *β*-aryl-*α*-(methylthio)-vinyl *p*-tolylsulfones (**2**) were prepared from various aromatic aldehydes and (methylthio)methyl *p*-tolylsulfone (MT-sulfone)[4] (**1**) in 85–96% yields according to the modified method reported by Ogura and coworkers.[5] These sulfones exclusively consisted of one stereoisomers(>99%) and characterized them as the (*E*)-isomers based on NMR analysis.[6,7] UV-irradiation of (*E*)-*β*-phenyl-*α*-(methylthio)vinyl *p*-tolylsulfone (**2a**) led to photochemical isomerzation[8] to form the stereoisomeric mixture ((*E*)/(*Z*) = 95/5), which was treated by column chromatography to give the new stereoisomeric mixture ((*E*)/(*Z*) = 7/3). Treatment of either of **2a** ((*E*)-isomer) or the 7/3 mixture with Mg turnings[9] (3 equiv) in dimethyl sulfoxide (DMSO)[10] containing trimethylsilyl chloride (5 equiv: TMSCl)[11] at room temperature for 1 day brought about stereoselective desulfonation to give (*E*)-*β*-(methylthio)styrene (**3a**) as a sole product in 68 and 69% yields, respectively. Under the same reaction conditions, Mg-promoted reduction of a variety of *β*-aryl-*α*-(methylthio)vinyl *p*-tolylsulfones (**2a-g**) afforded the corresponding (E)-*α*-aryl-*β*-(methylthio)ethylenes (**3a-g**) in 57–73% yields in a stereoselective manner, as shown in Scheme 1 and Table 1.



Scheme 1.

Cyclic voltammetry of **2a**, **2b**, **2c**, and **2g** showed that they were readily accessible to electron transfer type of reduction at −1.62–−1.68 V vs Ag/AgCl,[12] and the substrates possessing more positive reduction potential were transformed to the corresponding products more efficiently than those with more negative potential although the differences among the yield of the products (**3a**, **3b**, **3c**, **3g**) were relatively small (Table 1). Also cyclic voltammetry of **2a** indicated that the anion species generated by electron transfer, possibly the anion radical, is so easy to lose *p*-toluenesulfinate anion that only a little of its reverse oxidation peak was observed, as shown in Figure 1. It was also clarified that the product (**3a**) could be hardly reduced in this reaction since reduction potential of **3a** was much more negative (−2.5 V vs Ag/AgCl). These electrochemical results as well as our recent study[13–15] on Mg-promoted reductive cross-coupling reactions of aryl-substituted active olefins may suggest that the present desulfonation proceeded through electron transfer reaction promoted by Mg metal.

Table 1. Mg-Promoted desulfonation of *β*-aryl-*α*-(methylthio)vinyl tolylsulfones

X	Yield **3**/%	$E_p{}^a$/V (**2**)
H (**2a**)	68 (**3a**)	−1.63
p-F (**2b**)	72 (**3b**)	−1.62
p-MeO (**2c**)	57 (**3c**)	−1.68
p-Cl (**2d**)	71 (**3d**)	—
m-Cl (**2e**)	73 (**3e**)	—
o-Cl (**2f**)	63 (**3f**)	—
p-Me (**2g**)	67 (**3g**)	−1.63

[a] Reduction potential (V vs Ag/AgCl), Conditions; Solvent DMSO, Supporting Electrolyte n-Bu_4NClO_4, Electrodes Pt, Sweep Rate 200 mV/s.

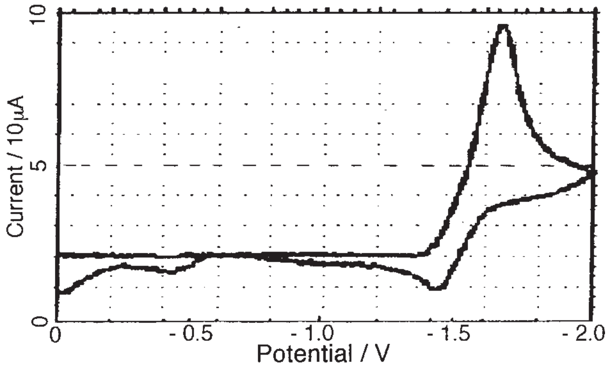
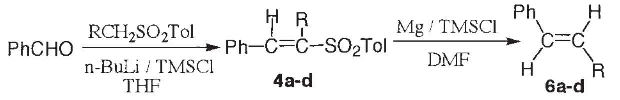


Figure 1. Cyclic voltammetry of **2a**. Working electrode(Pt), Counter electrode(Pt), Reference electrode(Ag/AgCl), in DMSO/n-Bu_4NClO_4, Sweep rate: 200 mV/s.

Furthermore, the present stereoselective desulfonation was found to proceed smoothly for other aromatic vinyl sulfones (**4a-d**), and (*E*)- and (*Z*)-*α*-(methylthio)styryl methyl sulfoxides (**5a,b**). For example, similar Mg-promoted reduction in DMF of stereoisomeric mixtures of *β*-phenyl-*α*-alkylvinyl *p*-tolylsulfones (**4a-d**),[16,17] readily prepared from base-catalyzed condensation of benzaldehyde and alkyl *p*-tolylsulfones in 77–88% yields, led to efficient and stereoselective desulfonation to afford the corresponding (*E*)-*β*-alkylstyrenes (**6a-d**) exclusively in 72–85% yields, as shown in Scheme 2 and Table 2.

(*E*)- and (*Z*)-*α*-(methylthio)styryl methyl sulfoxides (**5a,b**)[8,18] were also reduced by Mg turnings in DMF or DMSO containing TMSCl and a small amount of phenol as a proton donor to give (*E*)-

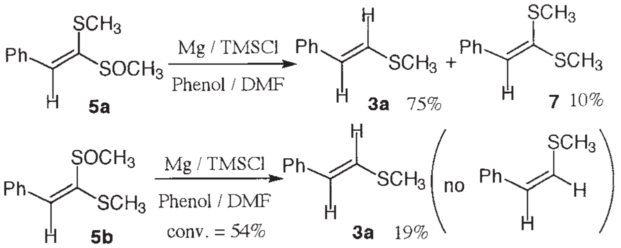


Scheme 2.

Table 2. Synthesis and Mg-promoted stereoselective desulfonation of *β*-phenyl-*α*-alkylvinyl tolylsulfones **4**

R	**4a-d** E/Z	**4a-d** Yield/%	**6a-d** E/Z	**6a-d** Yield/%
CH_3	55/45	77	>99 (E)	72
CH_2CH_3	68/32	88	>99 (E)	81
$CH_2CH_2CH_3$	69/31	88	98/2	75
$CH_2C_6H_5$	90/10	87	99/1	85

β-(methylthio)styrene (**3a**) in a stereoselective manner accompanying the formation of a small amount of *β*, *β*-bis(methylthio)styrene (**7**), as shown in Scheme 3.[19,20]



Scheme 3.

Although a detailed reaction mechanism for the present stereoselective desulfonation is ambiguous as yet, the following scheme may be proposed as one of the most plausible mechanisms, as shown in Scheme 4. The first electron transfer from Mg metal to the starting substrate **2**, **4** or **5** generates the corresponding anion radical (**8**), whose carbanion center and an oxygen atom of the sulfonyl or sulfinyl group may be coordinated by Mg^{2+} cation, causing one conformation (**9A**) more favorable than the other (**9B**). Subsequent stereoselective elimination of the sulfonyl or sulfinyl group from the favorable conformation (**9A**) followed by the second electron transfer from Mg metal may give a (*E*)-vinyl anion (**10**), which is protonated by a proton donor such as solvent,[21] phenol or moisture in solvent.

As a conclusion, Mg-promoted reduction of *β*-arylvinyl *p*-tolylsulfones, easily prepared from aromatic aldehydes with various *p*-tolylsulfones, brought about efficient and stereoselective formation of the corresponding (*E*)-*β*-substituted aromatic olefins. The reaction may be characterized by simple procedure, mild conditions, high stereoselectivity, easy availability of the starting compounds, satisfactory yield, non-polluted feature of Mg metal, and may therefore provide one of specific methods for stereoselective synthesis of (*E*)-*β*-substituted aryl olefins.

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References and Notes

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6 Chemical shift (*δ* value) of an olefinic proton of **2a** was observed at 8.26 ppm (in $CDCl_3$) while calculated ones[6] for its (*E*) and (*Z*)-isomers were 7.66 and 7.27 ppm, respectively. Since some deshielding (0.6 ppm) can be elucidated by hydrogen bonding of the olefinic proton with an oxygen atom of the sulfonyl group, **2a** was identified as the (*E*)-isomer. An olefinic proton of the other isomer came out at $\delta = 7.18$ ppm.

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9 Mg turnings for Grignard reaction was used without any pre-treatment.

10 The reaction of **2a** in DMSO was found to give the optimum yield (68%) among those in other aprotic polar solvents such as DMF (45%), sulforane (40%), DMAC (23%), THF (20%), and acetonitrile (14%).

11 Although the detailed role of TMSCl is still unclear, two main roles may be postulated, i.e., activation of the surface of Mg metal and stabilization of anionic intermediates generated by electron transfer from Mg metal.

12 Mg metal is thought to be able to reduce readily compounds possessing less negative reduction potential than −1.80 V vs Ag/AgCl under these conditions. See Ref. 11.

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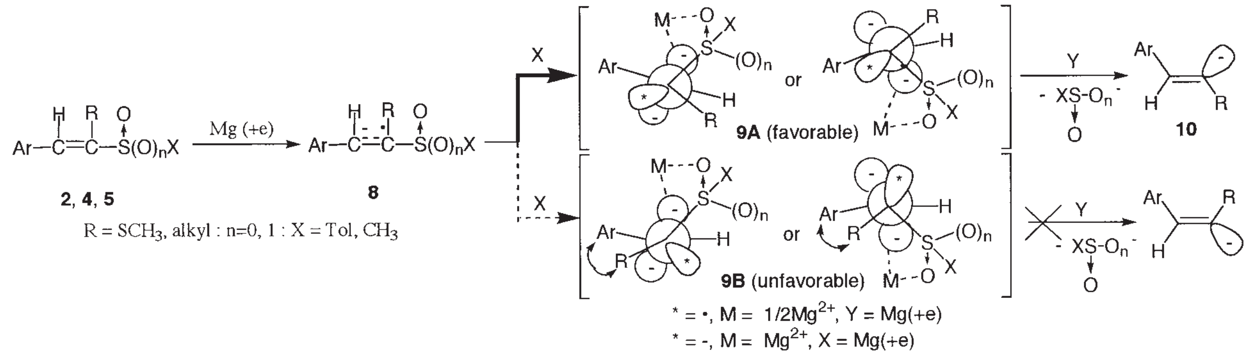
21 Use of DMSO-d_6 as a solvent and addition of 5 equiv of D_2O in the solvent of DMSO in the reaction of **2a** led to the formation of a mixture of **3a**-D and **3a**-H in the ratios of 1 : 1 and 9 : 1, respectively while addition of 5 equiv of D_2O after the reaction in DMSO resulted in no formation of **3a**-D to give **3a**-H as the sole product.



Scheme 4.