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Generation of Sulfonyl Radicals from Sodium Sulfinates by Oxidation with Metallic Oxidants and Their Addition Reaction with Olefins

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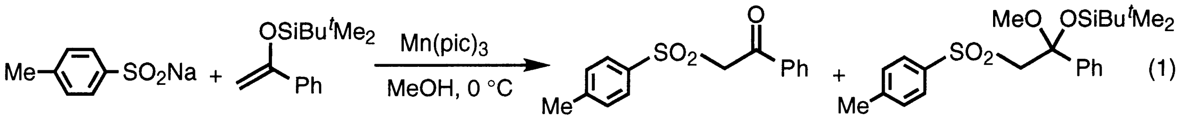
Sodium arylsulfinates are treated with manganese(III) 2-pyridinecarboxylate or cerium(IV) tetrabutylammonium nitrate to generate sulfonyl radicals, which react with various olefins giving the addition products.

Sulfonylation of olefins has been widely studied since organosulfones are of importance as synthetic intermediates. Utilization of sulfonyl radicals is an effective method for the sulfonylation of olefins because the addition reaction proceeds under almost neutral conditions.[1]

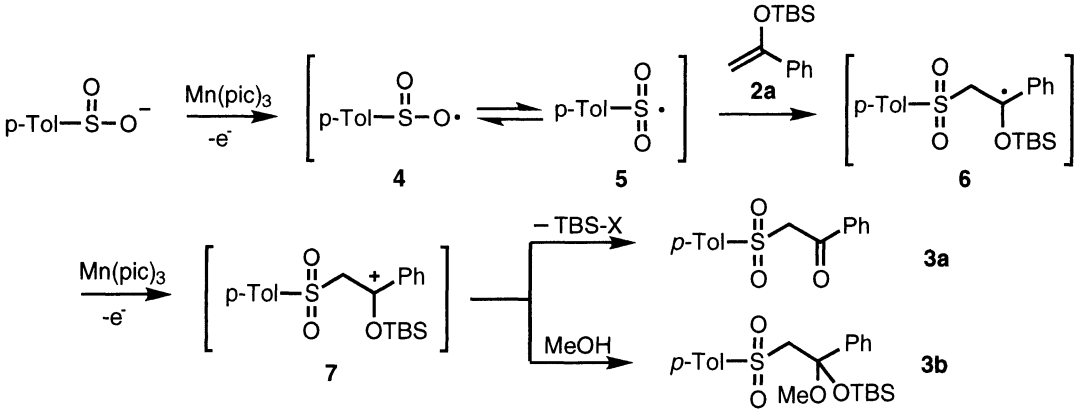
Previously, we reported the generation of α-keto radicals[2] and β-keto radicals[3] from β-keto carboxylic acids and cyclopropanols, respectively, by treatment with manganese(III) 2-pyridinecarboxylate ($\mathrm{Mn(pic)_3}$) as an oxidant and their addition reactions with various olefins. $\mathrm{Mn(pic)_3}$ was also found to be effective for the generation of alkyl radicals from pentacarbonyl(1-oxidoalkylidene)chromium(0) complexes.[4] These results prompted us to attempt the oxidation of sulfinates to generate sulfonyl radicals.

Sodium *p*-toluenesulfinate (**1a**) was treated with 2.2 molar amounts of $\mathrm{Mn(pic)_3}$ in methanol at 0 °C in the presence of α-(*t*-butyldimethylsiloxy)styrene (**2a**) as a radical trapping agent to afford a β-ketosulfone **3a** (14%) and its silylacetal **3b** (74%).[5] (Eq.1) The reaction was also tried in an aprotic solvent, dimethylformamide or dimethylsulfoxide, but the yield of **3a** decreased considerably.



1a **2a** **3a** 14% **3b** 74%

The reaction is supposed to proceed as depicted in Scheme 1. An oxygen-centered radical **4** generated by the oxidation of **1a** with $\mathrm{Mn(pic)_3}$ equilibrates with a sulfonyl radical **5**. This radical adds to the olefin **2a** to give a radical intermediate **6**, which is smoothly oxidized by $\mathrm{Mn(pic)_3}$ to a cation intermediate **7**. Finally, by elimination of the *t*-butyldimethylsilyl (TBS) group or by nucleophilic attack of methanol, the β-ketosulfone **3a** and the silylacetal **3b** are yielded.

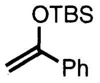
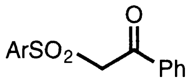
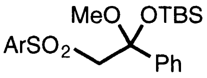
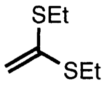
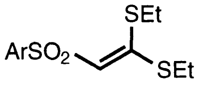
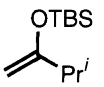
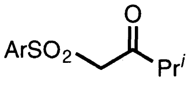
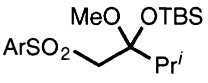
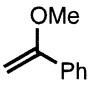
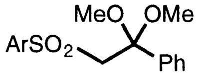
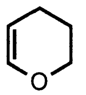


Scheme 1.

The sulfonylation of various electron rich olefins was examined and the results are shown in Table 1. Sodium 2-naphthalenesulfinate (**1b**) is also utilized as a sulfonylation reagent (entry 2, 4, 6 and 8). Aryl substituted silyl or methyl enol ethers and a ketene dithioacetal reacted with the arylsulfinates, giving the products in good yield (entry 1, 2, 3, 4, 7 and 8). However, an alkyl-substituted silyl enol ether **2c** afforded the

Table 1. Sulfonylation of Various Olefins with Mn(pic)$_3$

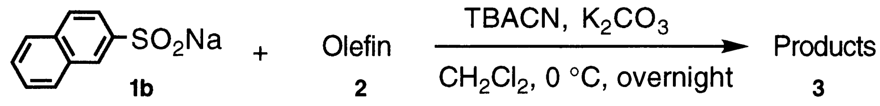
$$\underset{\mathbf{1}}{ArSO_2Na} + \underset{\mathbf{2}}{\text{Olefin}} \xrightarrow[\text{MeOH, 0 °C, overnight}]{Mn(pic)_3} \underset{\mathbf{3}}{\text{Products}}$$

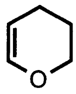
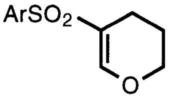
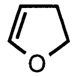
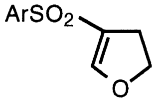
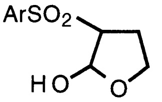
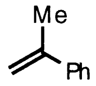
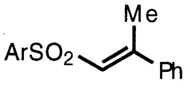
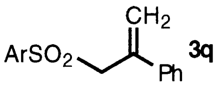
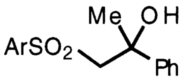
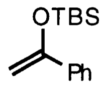
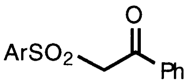
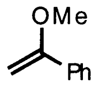
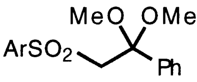
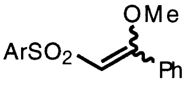
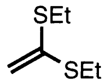
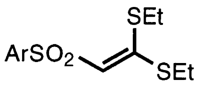
Entry	Ar	Olefin		Products (Yield / %)	
1	*p*-Tolyl		**2a**	 **3a** (14)	 **3b** (74)
2	2-Naphthyl			**3c** (14)	**3d** (72)
3	*p*-Tolyl		**2b**	 **3e** (87)	
4	2-Naphthyl			**3f** (84)	
5	*p*-Tolyl		**2c**	 **3g** (11)	 **3h** (13)
6	2-Naphthyl			**3i** (20)	**3j** (30)
7	*p*-Tolyl		**2d**	 **3k**(quant)	
8	2-Naphthyl			**3l** (89)	
9	*p*-Tolyl		**2e**	no adduct	

corresponding sulfones **3g**, **i** in poor yield (entry 5 and 6). In addition, dihydropyran (**2e**) was found unsuitable as an radical acceptor (entry 9), because **2e** reacted with methanol to give methyl 2-tetrahydropyranyl ether.

Accordingly, the reaction was investigated by the use of other oxidants in an aprotic solvent. When **1b** was treated with cerium(IV) tetrabutylammonium nitrate (TBACN) in the presence of K_2CO_3 and dihydropyran (**2e**) in dichloromethane at 0 °C, the sulfonylated dihydropyran **3m** was obtained in 81% yield.[6] This procedure is also effective for the reaction with α-methylstyrene (**2g**) (Table 2, entry 3). However, when the aromatic enol ethers **2a**,**d** and the ketene dithioacetal **2b** were used as olefins, the product yields were lower than those in the previous method, because these olefins were gradually oxidized with TBACN (Table 1, entry 2 and 4, Table 2, entry 4 and 6).

Table 2. Sulfonylation of Various Olefins with TBACN



Entry	Olefin		Products (Yield / %)
1		**2e**	 **3m**(86)
2		**2f**	 **3n**(20)  **3o**(42)
3		**2g**	 **3p** (5)  **3q** (41)  **3r** (32)
4		**2a**	 **3c**(30)
5		**2d**	 **3t** (47)  **3s**(19)
6		**2b**	 **3f**(50)

As mentioned above, oxidative sulfonylation proceeds by the use of sodium arylsulfinates and manganese(III) or cerium(IV) compounds. These two methods enable the generation of sulfonyl radicals under very mild reaction conditions, and the radicals thus generated add to various electron rich olefins.

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References

1) Sulfonyl halides add to olefins through the sulfonyl radicals, see; induced by light or peroxide: W. E. Truce and G. C. Wolf, *J. Org. Chem.*, **36**, 1727 (1971); induced by copper catalyst: L. K. Liu, Y. Chi, and K. -Y. Jen, *J. Org. Chem.*, **45**, 406 (1980); induced by ruthenium catalyst: N. Kamigata, J. Ozaki, and M. Kobayashi, *J. Org. Chem.*, **50**, 5045 (1985), and references cited therein.

2) K. Narasaka, N. Miyoshi, K. Iwakura, and T. Okauchi, *Chem. Lett.*, **1989**, 2169.

3) N. Iwasawa, S. Hayakawa, K. Isobe, and K. Narasaka, *Chem. Lett.*, **1991**, 1193; N. Iwasawa, M. Funahashi, S. Hayakawa, and K. Narasaka, *ibid.*, **1993**, 545; N. Iwasawa, S. Hayakawa, M. Funahashi, K. Isobe, and K. Narasaka, *Bull. Chem. Soc. Jpn.*, **66**, 819 (1993).

4) K. Narasaka and H. Sakurai, *Chem. Lett.*, **1993**, 1269.

5) The typical procedure using Mn(pic)$_3$ is as follows: A solution of sodium *p*-toluenesulfinate (**1a**, 182 mg, 1.0 mmol) and a-(*t*-butyldimethylsiloxy)styrene (**2a**, 520 mg, 2.2 mmol) in methanol (15 ml) is added to a suspension of Mn(pic)$_3$ (931 mg, 2.2 mmol) in methanol (5 ml) at 0 ^{o}C. After the mixture was stirred overnight, pH 7 buffer solution was added to the reaction mixture, and the resulting precipitates were filtered off through Celite. Then the filtrate was extracted with ethyl acetate and dried over Na_2SO_4. The crude product was purified by silica gel column chromatography to afford the b-ketosulfone **3a** (40 mg, 14%) and the silylacetal **3b** (315 mg, 74%) .

6) The typical procedure using TBACN is as follows: To a dichloromethane (30 ml) suspension of TBACN (9.4 g, 9.4 mmol) and K_2CO_3 (3.0 g, 22 mmol) was added a dichloromethane (30 ml) solution of dihydropyran (**2e**, 840 mg, 9.9 mmol) and then, dichloromethane (30 ml) suspension of sodium 2-naphthalenesulfinate (**1b**, 930 mg, 4.3 mmol) at 0 ^{o}C under an argon atmosphere. After the mixture was stirred overnight, pH 7 buffer solution was added to the reaction mixture, and the mixture was filtered through Celite, extracted with ethyl acetate. The extract was dried over Na_2SO_4. The crude product was purified by silica gel column chromatography to afford the vinylsulfone **3m** (1.00 g, 86%).

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