

A Convenient Method for the Synthesis of β,γ -Unsaturated Sulfones through Zinc-Mediated C—S Coupling Reaction

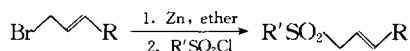
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Abstract: Through zinc-mediated coupling reaction of allylic bromides with alkane- or arenesulfonyl chlorides, β,γ -unsaturated sulfones were obtained with moderate to good yields.
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During the last twenty years, organic sulfur compounds have become increasingly important in organic synthesis. As a useful intermediate, sulfone has been received more attention¹. Allylic sulfones in particular can be used as α -sulfonylallylic carbanions and allylic cations generated by elimination of sulfinate ions², and have important values in organic chemistry. A well known procedure for the preparation of sulfones is the oxidation of sulfides and sulfoxides. The oxidants such as OsO₄-NMO, NaIO₄-RuCl₃ · H₂O and various peroxides are employed to effect this transformation³. Other methods may include the nucleophilic substitution of sulfinate salts, Friedel-Crafts type reaction of sulfonyl chlorides, the rearrangement of sulfinate esters and free radical addition of sulfonyl halides to alkenes and acetylenes^{1,4}. But they often suffer from side reactions, toxic organic solvents and low yields. The preparation of sulfones using palladium catalysis has been studied, and a few of other examples using organometallic reagents have also been reported⁵. However, the very severe conditions are required, and the substrates are limited, so they are difficult to get extensive applications. Developing a simple and efficient method for the synthesis of allylic sulfone become more and more important.

Metals are versatile reagents in organic synthesis. Because of its low cost and availability, zinc has been employed in Barbier-type allylation of carbonyl compounds and imines⁶. Allylzinc reagents formed from allylic halide and zinc have also been used in the synthesis of many cyclic compounds⁷. But to our knowledge, there has been no report on the application of zinc in the preparation of sulfone. We wish to report here a simple and convenient procedure for the synthesis of β,γ -unsaturated sulfones through allylation of alkane- or arenesulfonyl chlorides with allyl bromides in the presence of commercial zinc dust.



In a typical procedure, allyl bromides (1 mmol) was added to a stirring suspension of commercial zinc dust (1 mmol) in ether (3 ml) and stirring was continued for 0.5–1 h at room temperature. Sulfonyl chloride (1 mmol) was then added dropwise to it and the reaction mixture was stirred for a certain period of time as required for completion (monitored by TLC). The reaction mixture was then quenched with saturated NH₄Cl aqueous solution. The product was extracted with diethyl ether and purified by preparative TLC on silica gel. The results are presented in Table. β,γ -Unsaturated sulfones were given with mod-

erate to good yields. The reaction conditions were mild enough and no isomerisation was induced. From (E)-type allyl bromide reagents, the products with the same configuration were obtained (Entries **5-10**)⁸. The trimethylsilyl group present elsewhere in molecules also remained unaffected. The reaction was found to be general being applicable to aliphatic and aromatic sulfonyl chloride.

Table Preparation of β,γ -Unsaturated Sulfones

Entry	R	R'	Time (h)	Yield (%)
1	H	C ₂ H ₅	2.5	65
2	H	C ₆ H ₅	3	76
3	H	p-CH ₃ C ₆ H ₄	3	81
4	H	β -naphthyl	4.5	75
5	SiMe ₃	C ₂ H ₅	4.5	54
6	SiMe ₃	C ₆ H ₅	6	61
7	SiMe ₃	p-CH ₃ C ₆ H ₄	5	58
8	SiMe ₃	β -naphthyl	6	65
9	C ₆ H ₅	C ₂ H ₅	10	42
10	C ₆ H ₅	C ₆ H ₅	12	52

In conclusion, the present work provides a new method for the synthesis of β,γ -unsaturated sulfones through a metal-mediated reaction. The notable advantage of this methodology are mild condition, short reaction time, use of commercial zinc dust without any activation, no prototropic isomerisation during reaction, higher yields and no polluting reagents to be used. It is a new application of organometallic reagents in the synthesis of organic sulfur compounds.

References and Notes

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8. In ¹H NMR spectra of the products, the J_{HH} of the two protons linked on the carbons of C=C double bonds are 18-19Hz (Entries **5-8**), 15-16Hz (Entries **9-10**) respectively.

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