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Silver-Catalyzed Rearrangement of Propargylic Sulfinates to Allenic Sulfones

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Dedicated to an outstanding scientist and friend, Andreas Pfaltz, on the occasion of his 60th birthday.

Supporting information for this article is available on the WWW under http://asc.wiley-vch.de/home/.

Abstract: Treatment of propargylic sulfinate esters with 2 mol% of silver hexafluoroantimonate results in the rapid formation of allenic sulfones in essentially quantitative yield.

Keywords: allenes; sigmatropic rearrangements; silver; sulfones

Allenic sulfones are very important intermediates in organic synthesis.^[1] They have been used as precursors of enol ethers in the context of both carbanion-accelerated Claisen rearrangements and [4+3]-cyclo-addition reactions.^[2,3] They are reactive dienophiles, enophiles and dipolarophiles.^[4] They have been used in the synthesis of both carbocycles^[5] and heterocycles^[6] *via* inter- and intramolecular addition of nucleo-philes. They can participate in organometallic processes like the Heck and Pausen–Khand reactions.^[7] They are capable of engaging in cyclization reactions to form aromatic diradicals and can cleave DNA.^[8]

The typical procedure for the synthesis of allenic sulfones involves the thermal rearrangement of propargylic sulfinates, often prepared by the reaction of sulfinyl chlorides with propargylic alcohols.^[9] This sigmatropic shift is subject to catalysis and both palladium and rhodium have been used to effect the conversion of propargylic sulfinates to allenic sulfones. For example, Hiroi and Kato reported that the treatment of **1** with Pd(OAc)₂ in the presence of various phos-

phine ligands afforded **2** in 65% yield after about 16 h at room temperature (Scheme 1).^[10] The reaction was highly stereoselective. Mukai and co-workers have used $[RhCl(CO)_2]_2$ as a catalyst to form allenic sulfones. The reaction of **3** with 5 mol% of this catalyst in toluene solution afforded an 82% yield of **4** after 30 min at room temperature (Scheme 2).^[11] Other propargylic sulfinates reacted similarly so the process appears to be general.

Rearrangements of other propargylic systems and their catalysis have been known for some time and are still an active area of research.^[12] For example, Cookson and co-workers reported the conversion of propargylic esters to allenic esters using silver ion over 30 years ago.^[13] More recently, allenyl phosphates and tosylates have all been prepared by formal, metal-catalyzed [3,3]-sigmatropic rearrangements of propargyl systems.^[12]

Our interest in allenic sulfones^[3] and the current interest in gold- and silver-catalyzed reactions^[14] led us to investigate the silver-catalyzed rearrangement of **5** to **6**. We quickly found that treatment of **5** with 2 mol% AgSbF₆ gave **6** in essentially quantitative yield





$$\frac{5 \text{ mol } \% \text{ Pd}(\text{OAc})_2, 7.5 \text{ mol } \% \text{ dppe}}{\text{O}^- \text{ H Me}} \xrightarrow{p-\text{TolSO}_2} C=C=C \begin{pmatrix} \text{Me} \\ \text{THF, r.t., 16 - 18 h, 65\%, 88\% ee} \end{pmatrix}$$

Scheme 1.

972

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Scheme 3. Rearrangement of propargylic sulfinate 5.

at room temperature (Scheme 3).^[15] We thus set out to study the scope of this process.

The propargylic sulfinates used in this study were synthesized using the process introduced by Toru.^[16] Braverman has prepared trifluoromethyl sulfinates using a similar method introduced by Sharpless.^[17] The results from our work are summarized in Table 1.

With a selection of sulfinates in hand, we proceeded to attempt silver-catalyzed rearrangements. The typical reaction procedure consisted of adding 2 mol% of $AgSbF_6$ to a 0.1 M solution of the substrate in nitromethane The results are summarized in Table 2. This reaction worked incredibly well. The rearrangement products were formed very rapidly and cleanly at room temperature.

As shown in Table 2, primary, secondary and tertiary sulfinates all demonstrated equal aptitude for rearrangement to the corresponding allenic sulfones. When enantiomerically pure (R)-3-butyn-3-ol was used in the process, two separable, enantiomerically pure, diastereomeric sulfinates were obtained (Table 1, entry 12). Both of these rearranged to the same sulfone with essentially complete stereoselectivity when exposed to silver anion.

We have done a small amount of investigation with respect to catalyst and solvent changes. Silver nitrate is ineffective as a catalyst, but $AgBF_4$ works as well as $AgSbF_6$. Dichloromethane and chloroform are as good a solvent as nitromethane for this process.

Table 1. Preparation of propargyl sulfinates.

R ¹	OH R ³⁺ R ²	p-ToISO ₂ C	$\frac{TEA, PP}{THF, r.t}$	$R^1 \longrightarrow R^1$	OSO- <i>p</i> -Tol
Entry	\mathbf{R}^1	R ²	R ³	Product	Yield [%]
1	Н	Н	Me	1	72 ^[a]
2	Η	Me	Me	5	65
3	Н	Н	Н	7	40
4	Η	Н	Et	9	67 ^[a]
5	Me	Н	Н	11	73
6	Η	Me	Et	13	60 ^[a]
7	Н	Et	Et	15	55
8	Ph	Н	Н	17	50
9	Η	Ph	Н	19	37 ^[a]
10	Et	Н	Me	21	75 ^[a]
11	Н	–(CH	$_{2})_{4}$	23	80
12	Н	Ĥ	Me	1	74 ^[b]

^[a] A 1:1 mixture of diastereomers was formed.

^[b] The alcohol was *R* and two diastereomers were formed in a 1:1 ratio.

Adv. Synth. Catal. 2008, 350, 972-974

Table 2. Rearrangements of propargylic sulfinates to allenyl sulfones.

D ¹	OSO- <i>p</i> -	p-ToISO2	R^2			
R^{2} R^{3}		MeNO ₂ , r.t., 2 min			R^1 R^3	
Entry	Sulfinate ^[a]	\mathbf{R}^1	\mathbf{R}^2	R ³	Allene	Yield [%]
1	1	Н	Н	Me	2	97
2	5	Η	Me	Me	6	97
3	7	Η	Н	Η	8	98
4	9	Η	Н	Et	10	96
5	11	Me	Н	Η	12	99
6	13	Η	Me	Et	14	97
7	15	Η	Et	Et	16	97
8	17	Ph	Н	Η	18	99
9	19	Η	Ph	Η	20	99
10	21	Et	Н	Me	22	98
11	23	Η	-(CH	$H_2)_4$	24	98
12	1	Η	Η	Me	2	99 ^[b]

^[a] All sulfinates are racemic or racemic mixtures of diastereomers unless otheriwse noted.

^[b] Two separate enantiomerically pure diastereomers of **1** derived from enantiomerically pure (R)-1-butyn-3-ol were reacted. The resulting allenes showed 100% and 97% *ee* based on HPLC analysis on a Chiralpak AD column.

Being interested in minimizing the use of catalyst and scaling up the reaction, we examined the syntheses and rearrangement of sulfinates **1** and **11**. These were prepared in 46% and 49% yields, respectively, when their corresponding alcohols were esterified on a 10-gram scale. Exposure of each to 2 mol% of AgSbF₆ afforded the corresponding allenic sulfones **2** and **12** in essentially quantitative yield.

In conclusion, we have presented an very facile and mild process for the conversion of propargylic sulfinates to the corresponding allenic sulfones. This should greatly facilitate the use of allenic sulfones in organic synthesis, particularly in view of the fact that propargylic sulfinates can be prepared from sulfonyl, rather than sulfinyl, chlorides. Further exploration of this process, explorations of allenic sulfone chemistry and attempting to apply the reaction to allenic sulfoximines are currently under exploration. Results will be reported in due course.

Experimental Section

General Procedure for the Synthesis of Sulfinate Esters

To a solution of *p*-tolylsulfonyl chloride (1.0 mmol), an alcohol (1.0 mmol), and triethylamine (10 mmol) in CH_2Cl_2 (3 mL) was added a solution of triphenylphosphine (1.1 mmol) in CH_2Cl_2 (3 mL) dropwise over a period of 30 min. The reaction mixture was quenched with water, extracted with CH_2Cl_2 (10 mL, 3×), washed with brine, and

dried over Na_2SO_4 . Removal of the solvent under vacuum afforded the crude product, which was purified by column chromatography to afford the sulfinate ester.

General Procedure for the Rearrangement of Propargylic Sulfinates to Allenyl Sulfones

To the sulfinate ester (0.5 mmol), 1 mL of CH_3NO_2 and 2 mol% AgSbF₆ were added to the solution with stirring. After 2 min, TLC shows no starting material. The reaction mixture was diluted with Et_2O (5 mL) and filtered through a small plug of celite and silica gel. Removal of solvent afforded the pure allene.

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