[2,3] Sigmatropic Rearrangement of Propargylic Sulfinates by a Pale Ag¹-USY Zeolite and Silver Salts

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Dedicated to the memory of Carl E. Hampton (August 22, 1931 - December 14, 2013)

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Abstract: The sigmatropic rearrangement of propargylic sulfinates to allenic sulfones is catalyzed by the silver cation. The Ag¹-USY zeolite, as well as non-coordinating silver salts, lead to essentially quantitative yields of the corresponding allenic sulfones.

Keywords: allenes; sigmatropic rearrangement; silver; sulfones; zeolites

The [2,3] sigmatropic rearrangement of propargylic sulfinate esters to allenic sulfones was first demonstrated in the mid 1960s, concurrently by Stirling and by Braverman and Mechoulam.^[1] The rearrangement was suggested to occur via a cyclic intramolecular mechanism. Later kinetic studies,^[1a,2] deuterium labeling studies,^[3] and stereochemical studies^[3] definitively categorized this rearrangement as a concerted, cyclic, intramolecular, and irreversible process rather than one occurring by dissociation/recombination. An analogous transformation is also seen in the [2,3] sigmatropic rearrangement of trivalent propargylic or allylic phosphorus compounds.^[4] Typical rearrangements of propargylic sulfinates to allenic sulfones can be accomplished by thermolysis.^[1] The conversion has also been catalyzed by rhodium,^[5] palladium,^[6] and recently, silver.^[7]

In 2008, we reported the silver-catalyzed rearrangement of propargylic sulfinates to allenic sulfones by silver hexafluoroantimonate [Eq. (1)].^[7b] This was a straightforward and mild process giving excellent yields of the corresponding allenic sulfones.



Given our interest in allenic sulfones,^[8] the current interest in silver-catalyzed reactions,^[9] and the growing interest in green chemistry,^[10] we wondered whether there was another way to catalyze the rearrangement. An emerging area of synthetic chemistry utilizing metal-doped zeolite catalysts^[11] led us to determine whether a zeolitic catalyst could be of use in our allenic sulfone preparation.

Many zeolites are easily recoverable and reusable and therefore pose an advantage over some other catalyst systems. Zeolites have a storied history of use in industry,^[12] but more recently work has been performed using metal-doped zeolites to catalyze organic transformations. Copper-doped zeolites are gaining recognition in the area of cycloadditions and homocoupling,^[11a,d,e,13] but there are very few examples of silver zeolite-catalyzed reactions.^[11c,14]

Given the facility of the [2,3] sigmatropic rearrangement in the presence of catalytic silver hexafluoroantimonate,^[7b] the notion of silver-doped zeolite catalysts was an ideal route to pursue. The zeolite used in this study is the Ag¹-USY introduced by Pale, whose framework consists of spherical cage-like pores with average diameter of 7.4 Å wherein the rearrangement may occur.^[13e,14,15]

Initially, we began with an examination of several solvents to determine the most efficient medium for the reaction. We believed that dichloromethane or nitroethane would be the best choice as per previous work^[7b] and this turned out to be correct. 1,2-Dichloroethane also worked well. The reaction required much longer reaction times in other solvents, but resulted in similarly excellent yields, with the exception of diethyl ether and trifluorotoluene, in which the reaction did not go to completion. In most cases, the majority of the zeolite catalyst was recovered by filtration through a nylon membrane. The results are summarized in Table 1.

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Table 1. Solvent effects on the Ag¹-USY-catalyzed rear- Table 3. Successive reuse of Ag¹-USY zeolite. rangement.

p	O Me Me	Ag ¹ -USY solvent ((3.5 mol%) 0.05 M), r.t.	Ts Me Me	
Entry	Solvent	Time [h]	Catalyst Recovered [%] ^[a]	Yield [%]	
1	CH_2Cl_2	4.5	60	97	
2	THF	78	_[b]	73	
3	toluene	32	81	97	
4	Et_2O	_	-	_[c]	
5	ClCH ₂ CH ₂ Cl	7.5	77	100	
6	MeCN	66	_[b]	100	
7	1,4-dioxane	36	97	100	
8	EtNO ₂	8	94	100	
9	PhCF ₃	_	-	_[c]	
10	EtOAc	24	60	100	

[a] The recovered catalyst was scraped from the nylon membrane before weighing, rather than determining the difference of the membrane with and without recovered catalyst. Therefore, observed recovery is lower than actual recovery due to adherence of particles to the membrane.

[b] Catalyst not able to be recovered.

[c] The reaction did not go to completion even after 1 week.

Table 2. Effects of Ag¹-USY zeolite catalyst loading.

<i>p</i> -Toľ	O Me Me S O CH ₂ C	Ag ¹ -USY XI ₂ (0.05 I	M), r.t.	Me Me
Entry ^[a]	Catalyst Loading [mol%]	Time [h]	Catalyst Recovered [%] ^[a]	Yield [%]
1	3.5	5.5	100	100
2	4.5	4.5	94	99
3	7.0	4	100	100
4	10.0	3	100	95

Recovered catalyst determined by difference of nylon membrane mass with and without zeolite recovered.

After determining that dichloromethane was a suitable solvent, we examined the effect of catalyst loading.^[16] When the sulfinate was treated with a loading of 3.5 mol% of silver cation, the rearrangement was concluded in 5.5 h. As the catalyst loading was increased upwards to 15 mol%, no significant improvement on the reaction was observed other than slightly shorter reaction times (Table 2).

Previously, silver zeolite catalysts have been activated prior to use and after recovery by heating at very high temperatures to prevent silver reduction.[11c,14] We found that the zeolites can also be used directly without preactivation between runs. We examined the recyclability of the zeolites and found that they can be used at least three times without any significant

p-Toľ	O Me Me	Ag ¹ -L	JSY (3.5 mol%) Cl ₂ (0.05 M), r.t.	Me Me
Entry ^[a]	Catalyst	Time [h]	Catalyst Recovered [%] ^[a]	Yield [%]
1 2 3	Run 1 Run 2 Run 3	4.5 5 6	76 78 74	99 100 93

^[a] The recovered catalyst was scraped from the nylon membrane before weighing, rather than determining the difference of the membrane with and without recovered catalyst. Therefore, observed recovery is lower than actual recovery due to adherence of particles to the membrane.

Table 4. Ag¹-USY zeolite rearrangements of propargylic sulfinates.

$\begin{array}{ccc} 0 & R^1 & R^2 \\ \vdots & & \checkmark \end{array}$	Ag ¹ -USY (3.5 mol%)	ArO ₂ S R ²
Ar O	CH ₂ Cl ₂ (0.05 M), r.t.	ן R1

Entry	Ar	R^{1}/R^{2}	Time [h]	Catalyst Recovered [%] ^[a]	Yield [%]
1	Ph	Me/Me	4	94	98
2	2-naphthyl	Me/Me	32	42	96
3	Tris ^[b]	Me/Me	30	96	99
4	<i>p</i> -Tol	-(CH ₂) ₅ -	3 d	59	99

^[a] The recovered catalyst was scraped from the nylon membrane before weighing, rather than determining the difference of the membrane with and without recovered catalyst. Therefore, observed recovery is lower than actual recovery due to adherence of particles to the membrane.

^[b] Tris = 2,4,6-triisopropylbenzene.

decrease in yield, but that reaction times increased with each successive reuse (Table 3).

The catalyst was removed by filtration over a nylon membrane and air-dried by aspiration. Weighing the dried catalyst on the membrane indicated nearly quantitative recovery, but when scraped from the nylon membrane, collected in a vial, and weighed, a less than quantitative recovery was observed due to some particles that remain adsorbed in or on the membrane.

We also tested the ability of the Ag¹-USY to catalyze the rearrangement of a few other propargylic sulfinates. The results can be seen in Table 4. The reaction of the simple phenyl system was similar to the aforementioned para-toluene system with respect to both time and yield. The other more hindered sulfinates required longer reaction times for complete

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	∑ Me_Me AgX	Ts	Me
p-Tol	$CH_2CI_2 (0.0)$	5 M), r.t.	Me
Entry	AgX (3.5 mol%)	Time	Yield [%]
1	AgSbF ₆	<5 min	100
2	$AgBF_4^{a)}$	<15 min	100
3	AgOTf	<10 min	100
4	$AgClO_4$	<15 min	99
5	$AgCO_2CF_3$	30 min	100
6	AgNO ₃	3 h	98
7	Ag_3PO_4	12 h	100
8	AgOAc	15 h	100
9	Ag_2CO_3	15 h	100
10	AgF	6 h	100
11	AgBr	24 h	_[b]
12	AgI	24 h	_[c]
13	AgCN	24 h	_[d]
14	Ag_2SO_4	24 h	_[e]
	AgX (2 mol%)		
15	AgSbF ₆	<1 min	99
16	$AgBF_4^{[a]}$	2 min	99
17	AgOTf	3 min	99
18	$AgClO_4$	6 min	100
19	AgCO ₂ CF ₃	50 min	98

^[a] The reagent was deliquesced.^[17]

^[b] 5% conversion to product.

^[c] 5% conversion to product.

^[d] 7% conversion to product.

^[e] 7% conversion to product.

conversion to the allenes, but still resulted in excellent yields.

After a detailed examination of the catalytic activity of the Ag¹-USY on the [2,3] signatropic rearrangement of propargylic sulfinates, we decided to compare the activity of other silver(I) salts as well. The results are seen in Table 5. Strongly non-coordinating silver salts resulted in very rapid reaction times (entries 1-5). Less active catalysts were silver fluoride, nitrate, phosphate, acetate, and carbonate, which required longer times but still gave excellent yields of the allenic sulfone (Table 5, entries 6-10). Salts such as silver bromide, iodide, cyanide, and sulfate were ineffective at catalyzing the rearrangement in dichloromethane (Table 5, entries 11–14). The five most reactive silver salts were reduced in catalyst loading to 2 mol% and subjected to a careful evaluation of the reaction time (Table 5, entries 15–19) The previously reported silver hexafluoroantimonate effected an essentially instantaneous reaction, followed very closely by silver tetrafluoroborate, trifluoromethanesulfonate, and perchlorate, all reactions being complete within 6 min. The trifluoroacetate salt required a slightly longer reaction time of 50 min.

We have now demonstrated that the [2,3]sigmatropic rearrangement of propargylic sulfinates can be effectively performed in the presence of multiple sources of silver cations. The more non-coordinating the anion, the faster the reaction occurs. The process is also able to occur in a zeolitic framework; therefore, the process can become more "green," but at the expense of reaction time. Studies on the chemistry and further applications of allenic sulfones are currently underway and results will be reported in due course.

Experimental Section

General Procedure

The propargylic sulfinate was dissolved in the solvent (0.05 M). The silver catalyst was added and the heterogeneous mixture was stirred at room temperature and monitored by TLC. Upon complete conversion to the product, the catalyst was removed by filtration [using a Sterilite nylon membrane $(0.2 \ \mu\text{m}, 47 \ \text{mm})$ for the zeolite catalyst, or through a short pad of Celite for the silver salts] and rinsed with dichloromethane. The zeolite catalyst was dried by aspiration and then recovered by carefully scraping it from the membrane; traces remained adsorbed to the membrane and prevented complete recovery. The filtrate was concentrated on a rotary evaporator and trace solvent removed under high vacuum to yield the allenic sulfone.

Acknowledgements

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- [16] The Ag¹-USY zeolite catalyst contains 1.02 mmol of silver cation per gram of zeolite. Catalyst loadings are based on molar equivalents of silver cation used. The Ag¹-USY was prepared by the Pale group as detailed in ref.^[14]
- [17] The initial silver tetrafluoroborate sample that was used was deliquesced (Table 5, entries 2 and 16). The rearrangement proceeded very quickly and was complete in 2 min. To ensure that any adsorbed water on the silver salt was not contributing to the rate of reaction, a new bottle of AgBF₄ was purchased and the [2,3] sigmatropic rearrangement was performed with the new dry sample. The reaction was monitored by TLC every minute and was completed within 2 min and yielded the allenic sulfone in 97% yield. To learn the effect of water on the reaction, 0.6 equivalents (10 µL) of water was added to the $AgBF_4$ (2 mol%) in dichloromethane (9 mL, 0.1 M) and stirred. Then the sulfinate ester was added to the flask and the reaction mixture was stirred at room temperature, monitoring by TLC every minute. This reaction required 8 min to achieve complete conversion and resulted in a 96% yield of the allenic sulfone.

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