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Selenenate Anions ($PhSeO^-$) as Organocatalyst: Synthesis of *trans*-Stilbenes and a PPV Derivative

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Abstract: The selenenate anion ($RSeO^-$) is introduced as an active organocatalyst for the dehydrohalogen coupling of benzyl halides to form *trans*-stilbenes. It is shown that $RSeO^-$ is a more reactive catalyst than the previously reported sulfur analogues (sulfenate anion, RSO^-) and selenolate anions (RSe^-) in the aforementioned reaction. This catalytic system was also applied to the benzylic-chloromethyl-coupling polymerization (BCCP) of a bis-chloromethyl arene to form ppv (poly(p-phenylene vinylene))-type polymers with high yields, M_n (average molecular weight) up to 13,000 and PDI (polydispersity index) of 1.15.

Keywords: Organocatalysis, Selenium, Polymerization, High-throughput screening, *trans*-stilbenes

Introduction.

Over the past few decades, organocatalysis has emerged as one of the pillars of chemical synthesis.[1] Some of the obvious advantages over more traditional catalysts include its environmentally friendliness, avoidance of heavy and precious transition metals, greater availability of catalysts and ease of handling compared to most transition metal complexes. The most significant impact of organocatalysis, however, is in the introduction of new modes of chemical reactivity.

Our team has been interested in the development of chalcogen-based organocatalysts. We recently introduced the first sulfenate anion catalysts for the dehydrohalogen coupling of benzyl chlorides to make stilbenes[2] and the cross-coupling of benzyl chlorides with benzaldehydes under basic conditions to give diaryl acetylenes.[3] The latter reaction represents the first catalytic method for the generation of all three bonds of the alkyne from precursors which do not contain triple bonds. This class of catalysts enabled the introduction of benzylic chloromethyl coupling polymerizations (BCCP), which is useful for the synthesis of poly(stilbenes).[4]

Recently, there has been significant interest and substantial progress in development of organocatalysts based on the heavier chalcogenide, selenium.[5] Most of these works exploit the electrophilic character of selenium intermediates.[6] We have been investigating nucleophilic selenium-based catalysts, and recently disclosed the application of selenolate anions (RSe^-) in the dehydrohalogen coupling of benzyl chlorides.[7]

Our interest in developing the catalytic chemistry of sulfenate anions, RSO^-, inspired us to ponder potential applications of the selenium analogue, $RSeO^-$. The selenenate anion is the conjugate base of selenenic acid (RSeOH),[8] which is a transient intermediate of biological processes[9] and the byproduct of the well-known selenoxide elimination.[10] Despite biological and chemical importance the selenenate anion has rarely been studied.[8b, 11]

There are several properties of organoselenium compounds that led us to hypothesize that they would be better catalysts than the sulfur analogues. First, selenium has a larger atomic radius and higher polarizability, rendering selenenate anions more nucleophilic than sulfenate anions. Second, selenoxide elimination reactions, are estimated to be more than 100,000 times faster than sulfoxide eliminations to generate sulfenate anions.[10b, 12] On the other hand, the decreased electronegativity of selenium compounds will make the benzylic C–H's less acidic than those typically observed in sulfoxides. However, as seen in the pK_a values of $PhSCH_2Ph$ (30.8) vs. $PhSeCH_2Ph$ (31.0) in DMSO, the difference between these congeners is rather small.[13] Accordingly, with these attributes, we expected enhanced catalytic activity of selenenate anions. Herein, we describe the dehydrohalogen coupling reaction of benzylic halides by selenenate anions to give *trans* stilbenes as well as benzylic chloromethyl coupling polymerizations (BCCP), under much milder reaction conditions. These experiments enable comparison of the sulfenate, selenolate, and selenenate anions.

Results and Discussion.

Optimization of Selenenate Anion Catalysts. To probe our hypothesis, the dehydrohalogen coupling of benzyl halides to form *trans*-stilbenes was used to benchmark the catalytic activity of the selenenate anion. The catalytic cycle of this coupling reaction is proposed to possess the same elementary

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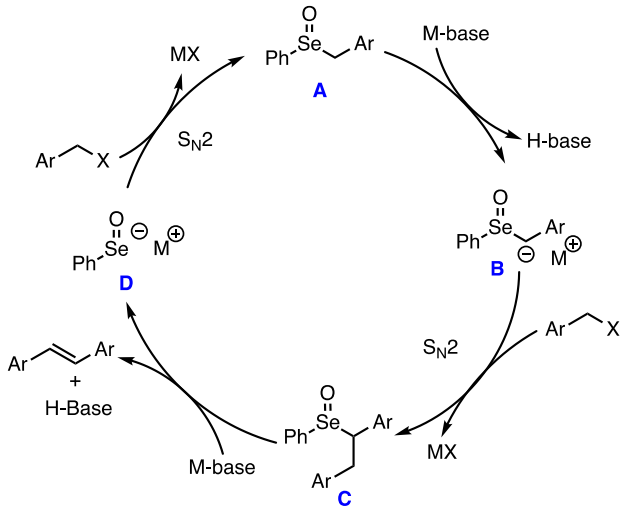
steps as the sulfenate anion catalyzed process (**Scheme 1**). It begins with the deprotonation of a benzylic phenyl selenoxide **A** by base to generate a nucleophilic carbanion **B**, which subsequently couples with a benzyl halide to form a benzylated selenoxide **C**. In the presence of base, the intermediate **C** will quickly undergo elimination to form a symmetric stilbene and selenenate anion **D**, which finally undergoes S_N2 with benzyl halide to close the catalytic cycle.

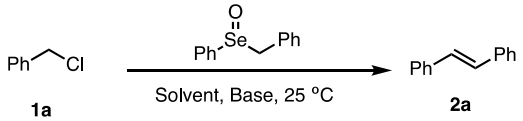


Scheme 1. Proposed mechanism for selenenate-anion-catalyzed coupling of benzyl halides to form *trans*-stilbenes.

To streamline the identification of base, solvent and conditions, High Throughput Experiment (HTE) techniques were employed at 0.01 mmol scale (see the Supporting Information, Table S1, Figure S1). Twelve different solvents [cyclopentyl methyl ether (CPME), THF, 1,4-dioxane, toluene, 1,2-dimethoxyethane (DME), DMSO, DMF, MeCN, dichloroethane, 2-Me-THF, Et_2O and *n*-hexane] and eight different bases [LiO^{t}Bu, NaO^{t}Bu, KO^{t}Bu, LiN(SiMe$_3$)$_2$, NaN(SiMe$_3$)$_2$, KN(SiMe$_3$)$_2$, NaO^{t}Pent, and KOSiMe$_3$] were screened in the presence of 10 mol% benzyl phenyl selenoxide (PhSe(=O)CH$_2$Ph) and one equiv. of benzyl chloride (**1a**). The results showed that NaN(SiMe$_3$)$_2$ and KN(SiMe$_3$)$_2$ worked very well with most of the solvents to give high assay yields (Table S1, assay yields determined by HPLC using 4,4'-di-*tert*-butyl biphenyl as internal standard), whereas the lithium salt LiN(SiMe$_3$)$_2$ was less active. This result may be due to the stronger aggregation of LiN(SiMe$_3$)$_2$ and organolithium species in solution.[14] Alkoxide bases were also less effective in the dehydrohalogen coupling reaction. Given the diversity of solvents examined, and their impact on the solubility and aggregation states of metal alkoxides, speculation about the origin of these observations is unwarranted.

With the results of the microscale screening in hand, several of the most promising conditions were examined on a larger scale (0.1 mmol). As shown in Table 1, using 10 mol% PhSe(=O)CH$_2$Ph in toluene or Et_2O with either KN(SiMe$_3$)$_2$ or NaN(SiMe$_3$)$_2$ gave *trans*-stilbene in 89–96% assay yield (AY, entries 1–3). When the catalyst loading was decreased to 5 mol%, high yields were maintained (85–91% AY, entries 4–5). Further reduction of the catalyst loading to 2.5 mol% resulted in a drop in the yield of *trans*-stilbene (24–84%, AY, entry 6–8), and PhCH$_2$N(SiMe$_3$)$_2$, which formed from the unwanted S_N2 reaction between benzyl chloride and MN(SiMe$_3$)$_2$ (M = K, Na). To reduce this byproduct, the amount of base was decreased to 2.5 and 2.0 equiv, which increased the AY to 92–93% with 2.5 mol% catalyst (entries 9–10). An attempt to increase the concentration of **1a** from 0.1 M to 0.2 M decreased the AY to 86% (entry 11). Monitoring of the reaction by TLC indicated the reaction was complete in 4 h under these conditions (entry 12). When benzyl bromide was used instead of benzyl chloride, *trans*-stilbene was generated in 92% AY (entry 13). Further reduction of the catalyst loading to 1 mol % gave a moderate yield of *trans*-stilbene (69% AY, entry 14). When the reaction was examined in the absence of the selenoxide under otherwise identical conditions to entry 10 (i.e., the background reaction without catalyst), only trace *trans*-stilbene was formed (entry 15). This result demonstrates that the background reaction in the absence of the selenenate anion catalyst is slow. Therefore, the optimized reaction conditions for the selenenate-anion-catalyzed dehydrohalogen coupling of benzyl chlorides (0.1 M in toluene) was determined to be 2.5 mol% of benzyl phenyl selenoxide and 2 equiv of KN(SiMe$_3$)$_2$ at room temperature for 4 h. These conditions can be contrasted with the sulfenate-anion-catalyzed process, which uses KO^{t}Bu in CPME solvent at 80 °C for 12 h, giving stilbene in 95% AY yield. During the optimization for the sulfenate-anion-catalyzed process, KN(SiMe$_3$)$_2$ in CPME was viable, furnishing the product in 80% AY. KO^{t}Bu was used in that study, because it was more effective.

Table 1: Optimization of the formation of *trans*-stilbene (**2a**) from benzyl chloride (**1a**)[a]



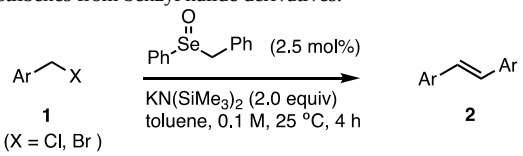
Entry	Solvent	Catalyst [mol%]	Base	**2a**[b][assay yield, %]
1	toluene	10	NaN(SiMe$_3$)$_2$	96
2	toluene	10	KN(SiMe$_3$)$_2$	94
3	Et_2O	10	NaN(SiMe$_3$)$_2$	89
4	toluene	5	NaN(SiMe$_3$)$_2$	91
5	Et_2O	5	NaN(SiMe$_3$)$_2$	85
6	toluene	2.5	KN(SiMe$_3$)$_2$	80
7	Et_2O	2.5	NaN(SiMe$_3$)$_2$	24
8	DME	2.5	NaN(SiMe$_3$)$_2$	61
9[c]	toluene	2.5	KN(SiMe$_3$)$_2$	92
10[d]	toluene	2.5	KN(SiMe$_3$)$_2$	93
11[d,e]	toluene	2.5	KN(SiMe$_3$)$_2$	86
12[f]	toluene	2.5	KN(SiMe$_3$)$_2$	93
13[g]	toluene	2.5	KN(SiMe$_3$)$_2$	92
14[d]	toluene	1	KN(SiMe$_3$)$_2$	69
15	toluene	0	KN(SiMe$_3$)$_2$	trace

[a] Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), base (3.0 equiv), solvent (1 mL), 25 °C, 12 h. [b] Assay yield determined by ^{1}H NMR spectroscopy by integration using CH_2Br_2 as an internal standard. [c] Base (2.5 equiv). [d] Base (2.0 equiv.). [e] **1a** (0.2 mmol). [f] Base (2.0 equiv), reaction time: 4 h. [g] Benzyl bromide was used instead of benzyl chloride

Examination of the substrate scope. With the optimized reaction conditions in hand, the substrate scope was examined (Table 2). For most of the substrates, readily available benzyl chloride derivatives were employed. Benzyl bromides were alternatively used when the chloride analogues were not available. In general, substitutions at the 2- and even 2,6-positions were tolerated. Benzyl chlorides with alkyl groups on the aryl ring (2-Me, 3-Me, 4-Me and 4-^{t}Bu) worked very well with isolated yields ranging from 90–95% (**2b–2e**). Likewise, 1-(chloromethyl)naphthalene (**1k**) provided the product in 82% yield. Halide substituted *trans*-stilbenes (**2f–2k**) were also generated with good yields from the corresponding benzyl halide derivatives bearing 2-I, 3-Cl, 4-Cl, and 2-Cl-6-F. In the above experiments, benzyl bromide derivatives bearing 2-I or 3-Cl were employed while benzyl chlorides hosting 4-Cl and 2-Cl-6-F were used.

Benzyl halides bearing electron withdrawing groups 3-CF_3, 3-OMe, 3,5-$(OMe)_2$ or coupling partners bearing both electron-withdrawing and donating groups, 3,4-$(OMe)_2$, were viable substrates, providing the stilbenes in 71–96% yield. It is noteworthy that methoxy-containing stilbenes are potential anticancer agents.[15] 2-(Chloromethyl)pyridine (**1p**) was selected to construct the corresponding heterocyclic stilbene (**2p**), which was obtained in 48% yield. Heterocyclic stilbene derivatives are reported to exhibit interesting photophysical properties.[16]

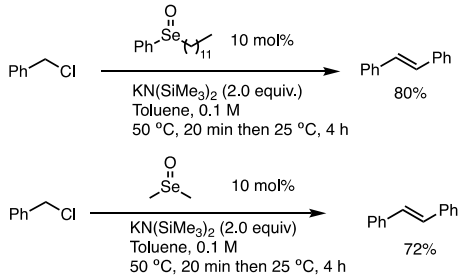
Table 2: Substrate scope of the selenenate-anion-catalyzed formation of *trans*-stilbenes from benzyl halide derivatives.[a]



Entry	Product	Ar	X	Yield
1	**2a**	Ph	Cl	90
2	**2b**	2-Me-C_6H_4	Cl	91
3	**2c**	3-Me-C_6H_4	Cl	94
4	**2d**	4-Me-C_6H_4	Cl	95
5	**2e**	4-^{t}Bu-C_6H_4	Cl	91
6	**2f**	2-I-C_6H_4	Br	98
7	**2g**	3-F-C_6H_4	Br	80
8	**2h**	4-F-C_6H_4	Cl	81
9	**2i**	4-Cl-C_6H_4	Cl	81
10	**2j**	2-Cl-6-F-C_6H_3	Cl	84
11	**2k**	1-naphthyl	Cl	82
12	**2l**	3-CF_3-C_6H_4	Br	79
13	**2m**	3-OMe-C_6H_4	Br	71
14	**2n**	3,4-$(OMe)_2$-C_6H_3	Cl	75
15	**2o**	3,5-$(OMe)_2$-C_6H_3	Br	96
16	**2p**	2-pyridyl	Cl	48

[a] Reactions conditions: benzyl halide (0.4 mmol), catalyst (2.5 mol%), $KN(SiMe_3)_2$ (0.8 mmol), toluene (4.0 mL), [b] All yields refer to isolated yields.

Based on the proposed mechanism shown in Scheme 1, different selenoxides were synthesized and tested to evaluate their viability as precatalysts in the dehydrohalogen coupling of stilbenes. As shown in Scheme 2, *n*-dodecanyl phenyl selenoxide[17] and dimethyl selenoxide[18] worked well under the standard reaction conditions, with the exception of preheating the precatalysts at 50 °C for 20 min. This approach led to conversion of benzyl chloride to *trans*-stilbene with respectable yields (80% and 72%, respectively). It is worth noting that in the case of dimethyl selenoxide, styrene is generated from both methyl groups of the dimethyl selenoxide. Therefore, only 80% of the benzyl chloride enters the catalytic cycle.



Scheme 2. Application of different selenoxide precatalysts to *trans*-stilbene synthesis

We then set out to examine the mechanism of this catalytic reaction (Scheme 1). First, the deprotonation of benzyl phenyl selenoxide (Scheme 1, **A** to **B**) in toluene was confirmed by *in situ* ^{1}H NMR monitoring of the reaction between benzyl phenyl selenoxide and $KN(SiMe_3)_2$ in toluene-d_8 (Figure S2). The two doublets at 3.39 and 3.50 ppm were assigned to the benzylic protons of the neutral selenoxide. The two doublets of **A** disappeared upon addition of $KN(SiMe_3)_2$ and a new singlet at 3.76 ppm integrating to 1H was observed. We attributed this new singlet to the benzylic proton of the deprotonated selenoxide [K][PhSe(=O)C*H*Ph] (**B**). Treatment of intermediate **B** with 1.0 equiv of benzyl chloride resulted in formation of *trans*-stilbene (61%).

To further characterize the deprotonated benzyl phenyl selenoxide, we next attempted to isolate it. Thus, combining $PhSe(=O)CH_2Ph$ and $KN(SiMe_3)_2$ in THF at room temperature was followed by treatment with 18-crown-6. Upon crystallization of the mixture containing [K][PhSe(=O)CHPh] (**B**) in the presence of 18-crown-6, a white solid was obtained. From this solid, two distinct colorless crystals were grown. One of the products was analyzed by ^{1}H, ^{13}C, and ^{77}Se NMR spectroscopy and by X-ray crystallography. It was determined to be [K(18-crown-6)][SePh], which was recently characterized and reported by our group.[7] The second compound was isolated as colorless crystals in the orthorhombic space group $Pna2_1$. The structure was determined to be [K(18-crown-6)][κ^2-O_2SePh] co-crystallized with THF (Figure 1).[19] The structure is similar to the previously reported crystal structure of *N*,*N*′-diphenylguanidinium *m*-chlorobenzeneseleninate.[20] In our seleninate anion both O1 and O2 are coordinated to the encapsulated K^+ with Se1–O1 and Se1–O2 distances of 1.665(3) and 1.667(3) Å.

The ratio of the two compounds from the mixture could not be directly determined, due to their limited solubility. In order to determine the approximate ratio of the two components, we conducted the silylation of the anions with $ClSiMe_3$ in C_6D_6. It is known that the anion $PhSeO_2^-$ reacts with Me_3Si–Cl to form $O(SiMe_3)_2$ and $(PhSeO)_2O$,[21] while $PhSe^-$ undergoes silylation to give $PhSeSiMe_3$.[22] The ratio

of $O(SiMe_3)_2$ to $PhSeSiMe_3$ was determined by ^1H NMR spectroscopy to be 1.6 : 1.0 (Figures S4 and S5). Presumably, [K(18-crown-6)][SePh] and [K(18-crown-6)][κ^2-O_2SePh] formed *via* disproportionation of [K][OSePh] (**D**).[10b] Thus it appears that intermediate **D** is formed from the decomposition of **B**. *trans*-Stilbene (85%, *trans*:*cis* = 4.3:1) was also observed as a reaction product. It is surprising that a mixture of isomers was obtained, given that only *trans*-stilbene is observed in all the other cases in this study (from intermediate **C**, Scheme 1). However, this could be due to the presence of the crown ether and the reaction solvent of THF rather than toluene. Alternatively, the reaction may proceed by a different pathway such as the extrusion of PhHC: from the organoselenium complex to produce a mixture of *cis*- and *trans*-stilbene.[23]

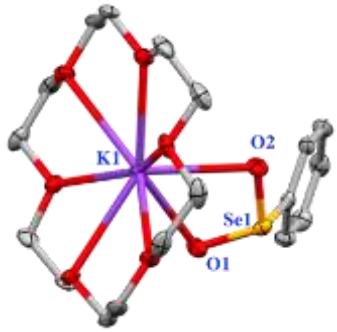
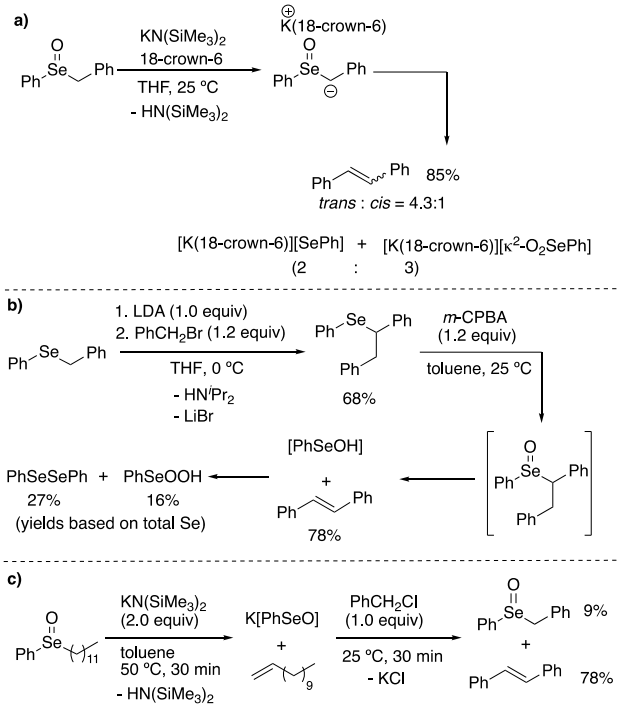


Figure 1. Solid-state structure of [K(18-crown-6)][κ^2-O_2SePh] with thermal ellipsoids at the 50% probability level. Hydrogen atoms and a co-crystallized THF have been omitted for clarity.



Scheme 3. Preliminary mechanistic investigations of the selenenate-anion-catalyzed stilbene formation.

Attempts to identify the benzylated selenoxide intermediate PhSe(=O)CH(Ph)CH_2Ph from the catalytic reactions (Figure 1, **C**) failed, presumably due to its rapid decomposition to form *trans*-stilbene and benzeneselenenic acid.[1e, 10a] Therefore, to probe the reactivity of this intermediate, we conducted *in situ* studies by oxidation of benzylated benzyl phenyl selenide (PhSeCH(Ph)CH_2Ph)[17] using *meta*-chloroperoxybenzoic acid (*m*-CPBA) (Scheme 3b). Accordingly, after oxidation, *trans*-stilbene was isolated in 78% yield, but PhSe(=O)CH(Ph)CH_2Ph) (**C**) was not observed in this process. In this reaction, 27% of the starting selenium [PhSeCH(Ph)CH_2Ph] was isolated in the form of PhSeSePh and 16% as PhSeOOH.[10b] Control experiments showed that no stilbene was formed from PhSeCH(Ph)CH_2Ph in the absence of oxidant under these conditions. The instability of the intermediate **C** toward elimination can be contrasted with the stability of the sulfur analogue, PhS(=O)CH(Ph)CH_2Ph which can be easily isolated without elimination of *trans*-stilbene[2a].

Phenyl selenenate anion (Scheme 1, **D**) was also generated *in situ* from a base-promoted transformation involving *n*-dodecanyl phenyl selenoxide[24] (Scheme 3c). After heating the *n*-dodecane phenyl selenoxide with 2 equiv of $KN(SiMe_3)_2$ in toluene at 50 ºC for 30 min, the reaction was cooled to room temperature and 1.0 equiv of benzyl chloride was added at room temperature. From this mixture was isolated benzyl phenyl selenoxide (9% yield) and *trans*-stilbene (78%) after column chromatography. These results suggest that phenyl selenenate anion is likely an intermediate generated under the catalytic conditions.

Having investigated several of the intermediates in the reaction we wanted to identify the turnover-limiting step in the catalytic cycle proposed in Scheme 1. The catalyst resting state was probed by conducting various reactions using benzyl chloride (1 equiv) at room temperature under otherwise standard conditions (2 equiv $KN(SiMe_3)_2$ and 10 mol% precatalyst) with CH_2Br_2 as an internal standard in C_6D_6 for 10 min. Monitoring this reaction by ^1H NMR spectroscopy after 10 min showed formation of [K][PhSe(=O)CHPh] in 75% AY (Scheme 1, **B**) based on a diagnostic proton resonance at 3.76 ppm for the benzylic C*H* (Figure S6). This result suggested that [K][PhSe(=O)CHPh] (Scheme 1, **B**) is likely the resting state of the catalyst. Furthermore, when the reaction was quenched with an excess of water (30 equiv), 82% of PhSe(=O)CH_2Ph was recovered. A similar experiment performed with the sulfur analogue resulted in 86% recovery of PhS(=O)CH_2Ph.

Compared to sulfenate anions ($ArSO^-$),[2a] the selenenate anion exhibits improved reactivity in the dehydrohalogen coupling of benzyl halides, as judged by the lower reaction temperature (room temperature vs 80 ºC for PhSe(=O)CH_2Ph vs. PhS(=O)CH_2Ph), shorter reaction times (4 vs 16 h) and a lower yield of the undesirable reaction between $KN(SiMe_3)_2$ and the corresponding benzyl chlorides. A comparison, however, was complicated by the different reaction conditions in these two systems. We, therefore, conducted the reactions under identical conditions. Using 2.5 mol% of either PhS(O)CH_2Ph or PhSe(O)CH_2Ph, the reactions were conducted with $KN(SiMe_3)_2$ and benzyl chloride (Scheme 4). After 3 h at room temperature, the reaction catalyzed by $PhSeO^-$ had reached 90% conversion while the sulfur analogue $PhSO^-$ did not catalyze the reaction at this temperature (see Figure S7 for reaction time course). When compared to the selenolate anion ($PhSe^-$),[7] selenenate anion ($ArSeO^-$) is more convenient. While both catalysts function at room temperature, selenolate anion ($PhSe^-$)[7] required

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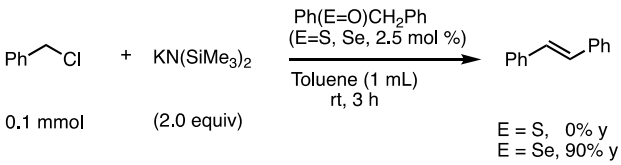
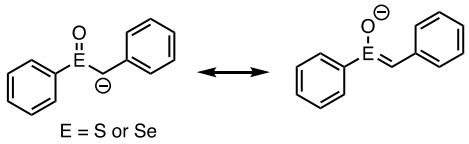
slow syringe pump addition of benzyl chloride to limit the benzylation of the base $KN(SiMe_3)_2$. As a result, the reaction times are also longer.



Scheme 4. Reactivity comparison of selenium- and sulfur-based catalysts.

Finally, we propose that the turnover limiting step of this reaction is the nucleophilic attack of deprotonated benzyl phenyl selenoxide on benzyl chloride (Scheme 1, **B** to **C**). The same step is turnover limiting in the sulfenate anion catalyzed process.[2a] One can rationalize the difference in reactivity stemming from the difference in electronegativity and from resonance stabilization. For instance, sulfur is slightly more electronegative than selenium (2.5 vs. 2.4 on the Pauling scale). Furthermore, the deprotonated sulfoxide will have better orbital overlap between the sulfur and anionic carbon (Scheme 5). This is due to the shorter S–C bond length compared to the Se–C distance, in addition to the closer orbital extent and contribution between sulfur and carbon. Consequently, this combination of factors renders the deprotonated selenoxide more nucleophilic toward benzyl halides than the sulfoxide analogue.

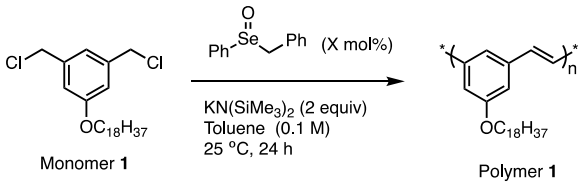


Scheme 5. Resonance structures of deprotonated benzyl phenyl sulfoxide and benzyl phenyl selenoxide.

Application to benzylic chloromethyl coupling polymerizations. As noted in the introduction, we recently developed the benzylic chloromethyl coupling polymerization reaction (BCCP) to produce polymers based on the *trans*-stilbene skeleton. Such polymerizations can generate conjugated poly(phenylene vinylene) (PPV) polymers. PPVs are widely used as OLEDs and conducting materials.[25] Likewise, BCCP can also be used to generate non-conjugated polymers. Given the increased reactivity of the selenenate anion over the sulfenate anion in the dehydrohalogen coupling of benzyl halides, we wanted to explore the selenenate anion's ability to promote dehydrohalogen coupling reactions to make polymers.

Previous work[26] from our laboratories demonstrated that sulfenate anions ($ArSO^-$) can catalyze polymerization of bis-benzylic chlorides yielding PPVs with high yields and low polydispersity indexes (PDI), but required heating at 80 ºC. We expected selenenate anions could provide PPV derivatives under milder conditions. Therefore, 1,3-bis(chloromethyl)-5-(octadecyloxy)benzene (monomer **1**),[26] our standard benchmarking substrate, was employed with different catalyst loadings in the polymer synthesis using the optimized conditions for *trans*-stilbene synthesis (Table 2). Following this recipe, treatment of phenyl benzyl selenoxide with $KN(SiMe_3)_2$ and monomer **1** at room temperature in toluene resulted in the formation of a cloudy solution. The resulting solution was treated with three drops of water and the volatile materials were removed under reduced pressure. Next, $CHCl_3$ was added to the resulting solid to dissolve the products. Then cold methanol was added into the filtrate to precipitate the solid polymer. Finally, filtration of the solid, dissolution in tetrahydrofuran (THF) and analysis by gel permeation chromatography (GPC) against polystyrene standards were performed. The synthesized polymers were characterized in terms of yield, average molecular weight (M_n), PDI and degree of polymerization (DP). The results showed that using catalyst loadings of 2.5, 5.0, and 10 mol %, the BCCP gave excellent yields of polymer with PDI as low as 1.15 and M_n over 13,000 (Table 3, entries 1–3). The highest M_n was with 10 mol% catalyst loading. The high loading may be necessary because of catalyst instability with respect to disproportionation of the selenenate anion, as exemplified in Scheme 3a. Based on the proposed mechanism of the dehydrohalogen coupling reaction, the polymerization should be a polycondensation and would not be expected to exhibit a narrow polydispersity. A similar low PDI was also observed in the sulfenate anion catalyzed polymerization with this same substrate, but at 80 °C. We are currently investigating the origin of these unexpected results.

Table 3. Selenenate anion-catalyzed polymerization and polymer characterization



Entry	X	Yield %	M_n (Da)	PDI	DP
1	10	100	13224	1.15	34
2	5	95	8549	1.33	18
3	2.5	100	7060	1.53	15

In conclusion, selenenate anions have been generated and employed as organocatalysts for the first time. The selenenate anion readily promotes the dehydrohalogen coupling of a variety of benzyl chlorides and bromides at room temperature to form *trans*-stilbenes with good to excellent yields. Compared with sulfenate anions, the selenenate anion promotes the dehydrohalogen coupling of benzyl chlorides under milder conditions with shorter reaction times. Both the sulfenate anion and the selenenate anion share a common turnover limiting step in the dehydrohalogencoupling, which is the reaction of the deprotonated phenyl benzyl K[PhE(=O)CHPh] (E = S, Se) with benzyl halide. The selenenate anion's enhanced reactivity is hypothesized to be due to the greater nucleophilicity of the anion K[PhE(=O)CHPh] toward benzyl halides. We have also demonstrated that the selenenate anion catalyzes polymerization of bis-chloromethyl-arene to form PPV-type polymers with high yields and very low PDI. We continue to investigate the reactivity of selenenate anions to further develop their chemistry.

Experimental Section

General Procedure for Catalyzed Reactions with Benzylphenyl Selenoxide: To an oven-dried microwave vial

equipped with a stir bar was added benzyl phenyl selenoxide (2.6 mg, 0.01 mmol, 0.025 equiv, from a stock solution in 4.0 ml toluene) and $KN(SiMe_3)_2$ (160 mg, 0.8 mmol, 2.0 equiv) under a nitrogen atmosphere followed by dry toluene (4.0 mL) with the yellow and clear solution generated. The microwave vial was sealed with a vial cap with a rubber insert and the sealed vial was removed from the dry box. Benzyl chloride (46 μL, 0.40 mmol, 1.0 equiv) was then added by a syringe under nitrogen. Note that if the benzyl halide was a solid, it was added to the reaction vial inside the dry box before the vial sealed. The reaction mixture was stirred for 4 hours at room temperature. After the reaction was complete, a yellow, orange or red solution was formed, and the sealed vial was opened to air, quenched with three drops of deionized water and the reaction mixture was passed through a short pad of silica gel. The silica gel was then rinsed with ethyl acetate (10 mL). The solvent was removed under reduced pressure. The resulting residue was purified by flash chromatography.

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Article

Selenenate Anions ($PhSeO^-$) as Organocatalyst: Synthesis of *trans*-Stilbenes and a PPV Derivative

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