

## Observation of Direct Sulfenium and Selenenium Group Transfer from Thiiranium and Seleniranium Ions to Alkenes

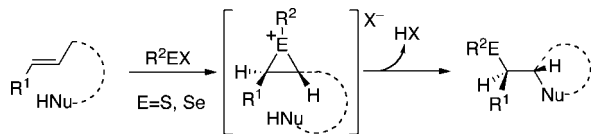
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Electrophilic sulfur- and selenium-promoted additions of nucleophiles to unactivated olefins represent important methods for the rapid and stereoselective introduction of functional and structural subunits in organic molecules (Scheme 1).<sup>1</sup> It is therefore astonishing that in this, the golden age of asymmetric catalysis, no examples of catalytic enantioselective additions of the chalcogenic reagents have been reported.<sup>2</sup> In the context of our ongoing program on Lewis base activation of Lewis acids, we have described preliminary mechanistic and preparative studies toward the ultimate goal of developing catalytic enantioselective chalcogeno-functionalization of unactivated alkenes.<sup>3</sup> Although we have successfully demonstrated highly efficient Lewis base catalysis of selenolactonization,<sup>3a</sup> we have failed to produce enantiomerically enriched products using scores of chiral Lewis bases. To elucidate the underlying causes of this failure and rationally formulate a solution, we needed to firmly establish the mechanistic foundations of these processes.

### Scheme 1



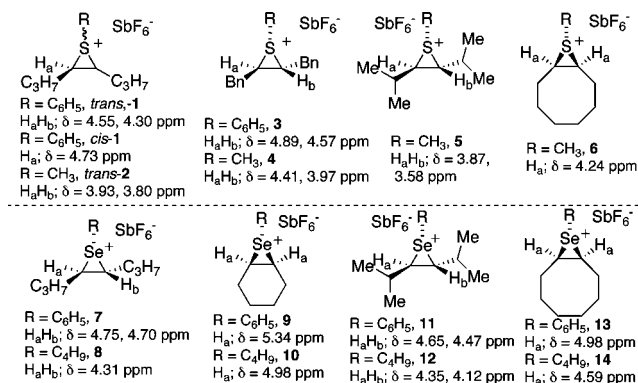
The central tenet of this class of reactions is the formation and subsequent capture of the putative, hyper-reactive thiiranium or seleniranium ions.<sup>4</sup> In fact, several of these ions have been independently synthesized<sup>5</sup> and structurally analyzed.<sup>6</sup> Nevertheless, many of the studies on thiiranium<sup>7</sup> and seleniranium<sup>8</sup> ion reactivity have been performed indirectly with precursors under the assumption that the putative -iranium ions are indeed responsible for the products observed. Whereas the postulate of the intermediacy of the -iranium ions from these studies is secure, the absolute configurational stability of these species has never been directly established.<sup>9</sup> This factor is mechanistically significant, since, even if these ions are formed enantioselectively by chiral Lewis base catalysis, they must be intercepted faster than racemization occurs. Unfortunately, all of the methods to generate -iranium ions *in situ* from stable precursors invariably contain nucleophilic species (such as primary alcohols and water) that produce sulfenyl and selenenyl transfer reagents by attack at the sulfenium or selenenium ion center.<sup>7g,i,j,10,11</sup> As the first part of our study on the configurational stability of these ions, we sought to establish whether a sulfenium or selenenium ion could transfer directly from one olefin to another. This “olefin-to-olefin” transfer process is particularly significant because it has profound implications on the absolute stereochemical course of these reactions.

In their studies with chiral selenylating reagents, Wirth and co-workers have postulated that facile olefin-to-olefin transfer of selenenium cations can occur even at low temperatures.<sup>8h,i</sup> Although no analogous experiments have been reported for thiiranium ions, computational studies by Radom and co-workers on the direct transfer of sulfenium ions between olefins suggest a relatively low

kinetic barrier (~11 kcal/mol).<sup>12</sup> Additionally, Borodkin computationally evaluated the enthalpic barrier for direct, intramolecular thiiranium–olefin and seleniranium–olefin transfer. Significantly, the calculated activation barriers to transfer decrease dramatically from alkylthiiranium to arylthiiranium to arylseleniranium ions.<sup>13</sup> We report herein the first observation of direct olefin-to-olefin transfer of chalcogenium ions and provide experimental support for the order of rates predicted by Borodkin.

These investigations began by evaluating the rate of transfer for both *S*-phenyl- and *S*-methyl-substituted sulfenium groups. The thiiranium ions of interest (Chart 1) were prepared under rigorously anhydrous conditions by treatment of their corresponding chloro sulfide precursors with silver(I) hexafluoroantimonate.<sup>14</sup> Once we were confident in the ability to prepare thiiranium ions 1–6, the direct transfer of sulfenium cations between the thiiranium ions and various olefins was studied by <sup>1</sup>H NMR spectroscopy.

### Chart 1



In the initial transfer experiment, a solution of freshly prepared *trans*-2,3-dipropyl-1-phenylthiiranium hexafluoroantimonate (**1**) in CD<sub>2</sub>Cl<sub>2</sub> was treated with *trans*-1,4-diphenyl-2-butene at 0 °C, and the mixture was monitored by <sup>1</sup>H NMR spectroscopy (Table 1, entry 1). Surprisingly, no reaction was observed over several hours. This unexpected result was reconciled when an authentic sample of *trans*-2,3-dibenzyl-1-phenylthiiranium hexafluoroantimonate (**3**) was treated with *trans*-4-octene to afford a mixture of *trans*-**1** and 1,4-diphenyl-2-butene (entry 2). Apparently, the ground-state energy of *trans*-**1** is significantly lower than that of **3**. More importantly, isomerically pure *trans*-**1** was observed at all time points during this experiment. This observation excludes the possibility of *cis*–*trans* isomerization through discrete carbocations.

To vouchsafe the assumption that no isomerization was taking place, the next crossover experiment combined *trans*-**1** with *cis*-4-octene at 0 °C. <sup>1</sup>H NMR analysis over 5.5 h revealed a slow transfer of the phenylsulfenium cation (entry 3). At equilibrium, a 2:1 ratio of thiiranium ions, favoring *trans*-**1**, was noted. Importantly, the reverse transfer process was also seen when, in a separate experiment, the

stereoisomeric *cis*-2,3-dipropyl-1-phenylthiiranium hexafluoroantimonate (*cis*-1) was treated with *trans*-4-octene (entry 4) to produce approximately the same equilibrium ratio. The equilibrium position for thiiranium ions **1** is not heavily biased, thus confirming that the production of pure *trans*-1 in entry 2 represents a kinetically controlled, stereospecific transfer. To the best of our knowledge, these experiments represent the first experimental evidence for the direct sulfenium group transfer between a thiiranium ion and an olefin. It is worth noting that transfer of the phenylsulfenium ion was still relatively slow at room temperature for these systems. The time course of the experiment in entry 4 is depicted in Figure 1, which illustrates how slow these reactions are at 0 °C. Indeed, the sulfenium transfer is completely suppressed at –20 °C.

**Table 1.** Thiiranium Ion Transfer between Olefins

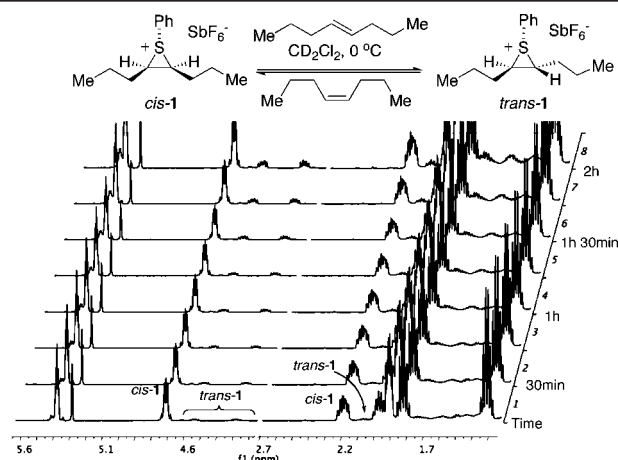
entry	thiiranium ion	R	R <sup>1</sup>	R <sup>2</sup>	thiiranium ion	K <sub>eq</sub> <sup>a</sup>
1	<i>trans</i> -1	C <sub>6</sub> H <sub>5</sub>	( <i>E</i> )- <i>n</i> -C <sub>3</sub> H <sub>7</sub>	( <i>E</i> )-PhCH <sub>2</sub>	<b>3</b>	0
2	<b>3</b>	C <sub>6</sub> H <sub>5</sub>	( <i>E</i> )-PhCH <sub>2</sub>	( <i>E</i> )-C <sub>3</sub> H <sub>7</sub>	<i>trans</i> -1	>100
3	<i>trans</i> -1	C <sub>6</sub> H <sub>5</sub>	( <i>E</i> )- <i>n</i> -C <sub>3</sub> H <sub>7</sub>	( <i>Z</i> )-C <sub>3</sub> H <sub>7</sub>	<i>cis</i> -1	2
4	<i>cis</i> -1	C <sub>6</sub> H <sub>5</sub>	( <i>Z</i> )- <i>n</i> -C <sub>3</sub> H <sub>7</sub>	( <i>E</i> )-C <sub>3</sub> H <sub>7</sub>	<i>trans</i> -1	1 <sup>b</sup>
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5	<i>trans</i> -2	CH <sub>3</sub>	( <i>E</i> )- <i>n</i> -C <sub>3</sub> H <sub>7</sub>	( <i>E</i> )-PhCH <sub>2</sub>	<b>4</b>	NR
6	<i>trans</i> -2	CH <sub>3</sub>	( <i>E</i> )- <i>n</i> -C <sub>3</sub> H <sub>7</sub>	( <i>E</i> )-(CH <sub>3</sub> ) <sub>2</sub> CH	<b>5</b>	NR
7	<i>trans</i> -2	CH <sub>3</sub>	( <i>E</i> )- <i>n</i> -C <sub>3</sub> H <sub>7</sub>	( <i>Z</i> )-(CH <sub>2</sub> ) <sub>6</sub>	<b>6</b>	NR

<sup>a</sup> Calculated by integration of diagnostic signals relative to an internal standard. <sup>b</sup> Because of competing olefin polymerization the same equilibrium point noted in entry 3 could not be reached.

These encouraging results stimulated the investigation of methylsulfenium transfer between *trans*-2,3-dipropyl-1-methyl-thiiranium hexafluoroantimonate (*trans*-2) and three different olefins (Table 1, entries 5–7). In *none* of these experiments was transfer of the methylsulfenium group observed, even when the reaction mixtures were warmed to room temperature. Again, to ensure that these results were not an artifact of inadvertently employing thermodynamically biased systems, the transfer experiments were conducted in the opposite direction, where independently prepared, authentic thiiranium ions **4**, **5**, and **6** were allowed to react separately with *trans*-4-octene. Again, no transfer of the methylsulfenium group was observed over any length of time, indicating that a methylsulfenium cation is incapable of direct transfer from a thiiranium ion to an olefin at room temperature.

The transfer of selenium from ion was investigated next. Because of the remarkable rate differences seen between the aryl- and alkylthiiranium species, both phenyl- and *n*-butylseleniranium ions were synthesized and spectroscopically characterized (Chart 1). As was found for the thiiranium ions, the best method for cleanly and reproducibly generating these species was through the reaction of the respective chloroselenide precursor with silver(I) hexafluoroantimonate. When freed from silver salts by filtration, both aryl- and alkylseleniranium ions are stable in solution and spectroscopically observable for over 24 h at room temperature. To the best of our knowledge, these are the first *alkylseleniranium* ions that have been synthesized and characterized.

In the initial crossover experiment, *trans*-1-phenyl-2,3-dipropylseleniranium hexafluoroantimonate (**7**) was treated with 1 equiv of



**Figure 1.** Crossover experiment from *cis*-1 to *trans*-4-octene.

cyclohexene. Surprisingly, no crossover was observed at any temperature. This unexpected result was easily reconciled as an unfavorable equilibrium because an authentic sample of the cyclohexyl 1-phenylseleniranium ion **9** reacted instantaneously and completely at –70 °C with *trans*-4-octene to generate **7** (Table 2, entry 1). Further evidence for a rapid transfer process was seen when **7** was combined with 1 equiv of 2,5-dimethyl-3-hexene at –70 °C. The two seleniranium ions, **7** and *trans*-2,3-diisopropyl-1-phenylseleniranium hexafluoroantimonate **11**, were immediately observed in equal amounts. The relative amounts of seleniranium ions and their respective olefins did not change over time. The reverse experiment of **11** with *trans*-4-octene produced nearly the same mixture of products, thus confirming that the transfer was under thermodynamic control (Table 2, entry 2). Finally, **7** was combined with 1 equiv of cyclooctene at –70 °C (Table 2, entry 3). As before, an equilibrium mixture of seleniranium ions was instantaneously formed in a ratio that favored the cyclooctyl 1-phenylseleniranium ion, **13**. The reverse reaction of preformed **13** with *trans*-4-octene produced the same product distribution (Table 2, entry 3).<sup>15</sup>

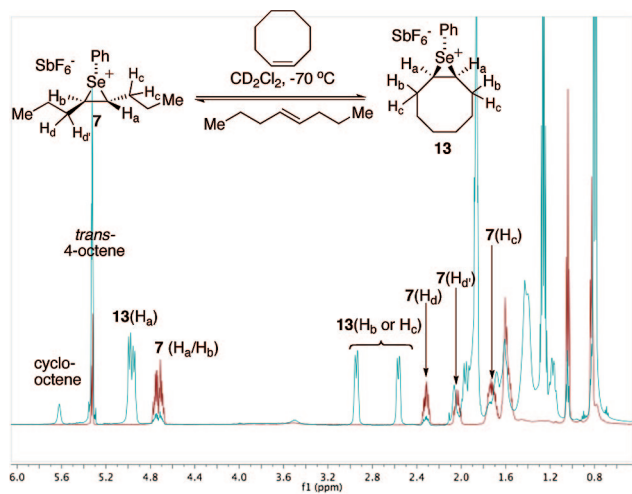
**Table 2.** Seleniranium Ion Transfer between Olefins

entry	R	R <sup>2</sup>	seleniranium ion	K <sub>eq</sub> <sup>a</sup>	K <sub>-1, eq</sub> <sup>a</sup>
1	C <sub>6</sub> H <sub>5</sub> ( <b>7</b> )	( <i>Z</i> )-(CH <sub>2</sub> ) <sub>4</sub>	<b>9</b>	0	>100
2	C <sub>6</sub> H <sub>5</sub> ( <b>7</b> )	( <i>E</i> )-(CH <sub>3</sub> ) <sub>2</sub> CH	<b>11</b>	1.3	0.95
3	C <sub>6</sub> H <sub>5</sub> ( <b>7</b> )	( <i>Z</i> )-(CH <sub>2</sub> ) <sub>6</sub>	<b>13</b>	3.6	0.26
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4	<i>n</i> -C <sub>4</sub> H <sub>9</sub> ( <b>8</b> )	( <i>Z</i> )-(CH <sub>2</sub> ) <sub>4</sub>	<b>10</b>	0	>100
5	<i>n</i> -C <sub>4</sub> H <sub>9</sub> ( <b>8</b> )	( <i>E</i> )-(CH <sub>3</sub> ) <sub>2</sub> CH	<b>12</b>	2.6	0.50
6	<i>n</i> -C <sub>4</sub> H <sub>9</sub> ( <b>8</b> )	( <i>Z</i> )-(CH <sub>2</sub> ) <sub>6</sub>	<b>14</b>	2.6 <sup>b</sup>	

<sup>a</sup> Calculated by integration of diagnostic signals relative to an internal standard. <sup>b</sup> The instability of the seleniranium ion precursor precluded performing the reverse transfer experiment.

The crossover experiments with the *n*-butylseleniranium ions were then performed to determine whether perturbation of the selenenyl group could affect the rate of the transfer process. Thus, *trans*-1-butyl-2,3-dipropylseleniranium hexafluoroantimonate (**8**) was treated with cyclohexene, and again, no crossover was observed. As before, when *trans*-4-octene was added to cyclohexyl

1-butylseleniranium ion **10**, instantaneous and complete crossover occurred at  $-70\text{ }^{\circ}\text{C}$  (Table 2, entry 4). Furthermore, this hyper-reactivity was observed in all subsequent crossovers with the *n*-butylseleniranium ions (**10**, **12**, **14**). In every case the crossover reached equilibrium positions similar to those found with the corresponding phenylseleniranium ions (Table 2, entries 4–6).



**Figure 2.** Crossover experiment from **7** to cyclooctene. Red spectrum: before addition of cyclooctene (only **7**). Blue spectrum: after addition of 1 equiv of cyclooctene (both **7** and **13** present).

These crossover experiments represent the first observation of direct transfer of sulfenium or selenenium cations from one olefin to another. As predicted by Borodkin's computational studies,<sup>13</sup> the rate of transfer depends markedly on both the chalcogenic atom and its substituent. Interestingly, whereas complete suppression of the thiiranium ion crossover process was achieved through simple exchange of the *S*-phenyl substituent for an *S*-methyl substituent, the same control could not be established for the seleniranium ions. This rapid olefin-to-olefin transfer represents one of the most likely pathways for racemization of enantiomerically enriched seleniranium ions and the most reasonable mechanistic rationale for the diastereoselectivity seen in selenylations with chiral, nonracemic selenylating reagents.<sup>8h,i</sup>

Although neither an associative nor a dissociative mechanism of transfer can be clearly distinguished from the seleniranium crossover experiments, computational studies from Houk and Wirth<sup>16</sup> have predicted an exceedingly high barrier for the dissociation of a selenenium cation from an olefin. Experimental and computational efforts to investigate this mode of transfer are currently underway, as are continuing efforts to effect catalytic, enantioselective chalcogeno-functionalization of unactivated alkenes.

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**Supporting Information Available:** Experimental procedures and compound characterization data along with spectra of all crossover experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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