

## Primary Vinyl Cations in Solution: Kinetics and Products of $\beta,\beta$ -Disubstituted Alkenyl(aryl)iodonium Triflate Fragmentations

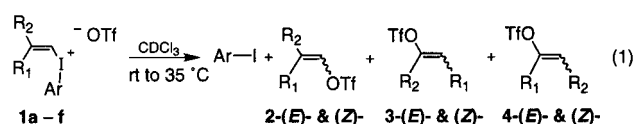
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Received May 17, 1999

Hypervalent iodine intermediates have been utilized as outstanding nucleofuges in the generation of unstable carbenium ions.<sup>2</sup> More specifically, alkenyl(phenyl)iodonium salts<sup>3</sup> have served as vinyl cation<sup>4–6</sup> equivalents in a number of transformations, including: (a) cross-coupling reactions with organic stannanes<sup>7</sup> as well as acrylates,<sup>8</sup> (b) reactions with enolates,<sup>9</sup> and (c) reactions with various nucleophiles under copper-mediated conditions.<sup>10</sup> Further, the phenyliodonio moiety is a much better leaving group than triflate (by a factor of 10<sup>6</sup>) during solvolytic generation of a cyclohexenyl cation.<sup>11</sup> We have synthesized several new, highly activated  $\beta,\beta$ -disubstituted alkenyl(aryl)iodonium triflates and observed their fragmentations.<sup>12</sup> Members of this class of salts were chosen for two reasons: (a) a second  $\beta$ -substituent is calculated to stabilize the primary vinyl cation<sup>13</sup> and (b) direct  $\beta$ -elimination is impossible. Herein, we report new kinetic data and the effects of electron-withdrawing groups on the reaction. These values, in addition to studies on stereoisomeric alkenyl(aryl)iodonium salts, now provide firm evidence of the generation of primary vinyl cations in solution.<sup>14</sup>

Salts **1a–f** were stereospecifically synthesized from alkenylstannanes using standard procedures.<sup>15</sup> Fragmentations of these salts in CDCl<sub>3</sub> lead to enol triflate isomers **2–4** (eq 1). Although



Cmpd	R <sub>1</sub>	R <sub>2</sub>	Ar
<b>1a</b>	Et	Me	4-(CF <sub>3</sub> )C <sub>6</sub> H <sub>4</sub>
<b>1b</b>	Et	Bu	Ph
<b>1c</b>	Et	Bu	4-(CF <sub>3</sub> )C <sub>6</sub> H <sub>4</sub>
<b>1d</b>	Bu	Et	Ph
<b>1e</b>	Bu	Et	4-(CF <sub>3</sub> )C <sub>6</sub> H <sub>4</sub>
<b>1f</b>	Bu	Et	3,5-(CF <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>

chloroform is not a typical medium for solvolyses, solvent polarity has very little effect on the reaction rate of solvolyses of cyclohexenyl(aryl)iodonium salts because there is no net change in charge as well as no significant charge-separation in the transition state.<sup>11</sup>

Enol triflates from decomposition of all of the starting materials were observed by GC-MS analysis of consumed salts. At temperatures between 20 and 35 °C, a total of six enol triflate isomers were detected. Authentic stereoisomeric mixtures of enol triflates were then synthesized and co-injected with those derived from decomposition to verify their identities.<sup>16</sup>

The most important of these vinyl triflate compounds are **2-(E)-** and **2(Z)-**. These enol triflates result from heterolytic C–I bond cleavage followed by direct <sup>-</sup>OTf trapping of cation **I** (Scheme 1). The four other enol triflate isomers result from migration of R<sub>1</sub> and/or R<sub>2</sub> to form a more stable secondary vinyl cation (**II** or **III**) which is then trapped by triflate anion. A concerted alkyl (*trans*) shift of R<sub>2</sub> followed by triflate anion trapping would only lead to enol triflate isomers **4(E)-** and **4(Z)-** and not the corresponding regioisomers, **3(E)-** and **3(Z)-**. Alternatively, a synchronous alkyl shift (*trans*) of R<sub>2</sub> could be followed by a simple hydride migration between secondary cations **III** and **II**. Subsequent trapping by the triflate anion would then lead to products which appear to be derived from migration of *either* R<sub>1</sub> or R<sub>2</sub>.

However, it is the presence of *both* **2(E)-** and **2(Z)-** in nonnucleophilic solvent which offers firm support for the primary vinyl cation. The presence of all six isomers is excellent support for a mechanism involving heterolytic C–I bond cleavage and migration of both the *trans* and *cis*  $\beta$ -alkyl groups as well as trapping of the *unrearranged* cation (Scheme 1). If a simple S<sub>N</sub>2 mechanism were operative, only one nonrearranged isomer of **2** (via S<sub>N</sub>2) would be present (Scheme 2).<sup>17–19</sup>

Another possible mechanism involving initial coordination of the triflate to the positively charged iodine atom to form  $\lambda^3$ -iodane **5** followed by S<sub>N</sub>2 displacement would lead to the same stereoisomer (Scheme 2).<sup>17a</sup> The involvement of a  $\lambda^3$ -iodane in this mode of in-plane S<sub>N</sub>2 reactivity was reported by Okuyama and co-workers for several  $\beta$ -monosubstituted iodonium salts. However, only inverted products were observed rather than a mixture of stereoisomers. Other mechanisms involving ligand coupling or addition/elimination are unlikely with such a poorly nucleophilic and weakly basic anion such as triflate.

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(15) Hinkle, R. J.; Stang, P. J. *Synthesis* **1994**, 393–396. Zhdankin, V. V.; Scheuller, M. C.; Stang, P. J. *Tetrahedron Lett.* **1993**, *34*, 6853–6856.

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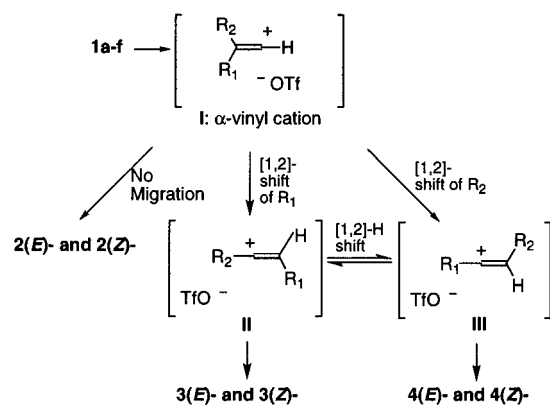
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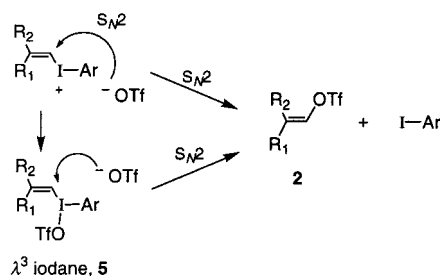
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## Scheme 1



## Scheme 2

**Table 1.** Kinetic Data<sup>a</sup> from Decompositions of Alkenyl(aryl)iodonium Triflate Salts

salt	R <sub>1</sub>	R <sub>2</sub>	Ar	temp (°C)	k × 10 <sup>4</sup> (mol/L·sec)
<b>1d</b>	Bu	Et	Ph	35	0.24
<b>1e</b>	Bu	Et	4-(CF <sub>3</sub> )C <sub>6</sub> H <sub>4</sub>	35	2.01
<b>1f</b>	Bu	Et	3,5-(CF <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	20	0.67
<b>1f</b>	Bu	Et	3,5-(CF <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	25	1.75
<b>1f</b>	Bu	Et	3,5-(CF <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	30	3.24
<b>1f</b>	Bu	Et	3,5-(CF <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	35	6.62

<sup>a</sup> Rate constants were determined by fragmentation of salts in CDCl<sub>3</sub> filtered through basic alumina immediately before use and monitored by <sup>1</sup>H NMR spectroscopy for disappearance of starting materials.

**Table 2.** Relative Percentages of Products in Decomposition Reactions of **1c**, **1d**, **1e**, and **1f** in Basic Alumina-Filtered CDCl<sub>3</sub>

salt	R <sub>1</sub>	R <sub>2</sub>	Ar	R <sub>2</sub> migration	R <sub>1</sub> migration	no migration
<b>1c</b>	Et	Bu	4-(CF <sub>3</sub> )C <sub>6</sub> H <sub>4</sub>	59	29	12
<b>1d</b>	Bu	Et	Ph	74	14	12
<b>1e</b>	Bu	Et	4-(CF <sub>3</sub> )C <sub>6</sub> H <sub>4</sub>	71	16	13
<b>1f</b>	Bu	Et	3,5-(CF <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	69	25	8

Reactions of the activated salt **1f** in the prototypical solvolysis solvent (MeOH) afford acetylenes and allenes as the predominant products. This most likely occurs because of the increase in nucleofugality of the iodoarene moiety and because increased basicity of the solvent promotes  $\alpha$ -elimination to the corresponding alkyldiene-carbene in addition to cationic intermediates. Performing the reaction in trifluoroacetic acid produced a mixture of enol triflates, albeit with the presence of large amounts of unidentified byproducts.

We attempted to utilize spectrophotometric techniques to measure the rates of fragmentation, but the absorbances of the substituted aryl iodide product of cleavage and the iodonium salt were not clearly separable. Instead, kinetic measurements of the reactions were performed by analysis of time-arrayed <sup>1</sup>H NMR spectra at 20, 25, 30, and 35 °C using basic alumina filtered CDCl<sub>3</sub> (Table 1). The resonances of the ortho-protons in the iodonium salts as well as the iodoarene byproduct were analyzed. Plots of the decompositions were found to be first order in iodonium substrate, bolstering our belief that the reactions are occurring

via an S<sub>N</sub>1 mechanism. Further, using the Arrhenius equation, we obtained the following kinetic parameters for salt **1f**: E<sub>a</sub> = 26.8 kcal/mol;  $\Delta H^\ddagger$  = 26.2 kcal/mol;  $\Delta S^\ddagger$  = 11.9 cal/mole·K.

These values are consistent with the heterolytic cleavage of the alkene–iodine bond in the transition state in the vicinity of room temperature. Most notable is the positive entropy of activation indicating an increase in disorder as the arylidonio moiety departs.

For information on the effects of electron-withdrawing groups on the iodoarene moiety, kinetic measurements of **1d**, **1e**, and **1f** were performed at 35 °C. As we expected, increasing the electron-withdrawing nature of the aromatic ring significantly increased the rates for fragmentation and rearrangement of the salts. For comparison, complete consumption of **1d** required ca. 10 h at 35 °C whereas **1f** only took ca. 1.5 h. Further, using Hammett constants for CF<sub>3</sub> groups ( $\sigma$  para = 0.54;  $\sigma$  meta = 0.43), we calculated a  $\rho$  value of +1.7.<sup>20</sup> This electronic effect is consistent with data reported by Okuyama and co-workers and a heterolytic cleavage mechanism (Scheme 1) in which the increased relative charge at the iodine atom in the salts would increase the nucleofugality of the entire iodoarene moiety.<sup>11</sup> It is inconsistent, however, with a homolytic mechanism followed by SET.<sup>11</sup> In the latter case, the iodobenzene cation radical would be destabilized by the presence of electron-withdrawing substituents.

Investigation of a stereoisomeric pair of iodonium salts (**1c** and **1e**) reveals that the alkyl group *trans* to the iodonium moiety generally migrates to a greater extent than the alkyl group which is *cis* (Table 2). This evidence indicates that the cation is either: (a) free, but not linear as expected, or (b) there may be some migration which occurs simultaneously with iodoarene cleavage, or (c) the vinyl cation is a member of a tight-ion pair. This latter possibility is most likely in the relatively nonpolar solvent investigated (chloroform). However, we do not observe any “internal return” products (electrophilic aromatic substitution with the iodoarene) such as those described by Okuyama and co-workers and therefore the ion pair likely involves the triflate anion.<sup>11</sup>

We have demonstrated a definitive example of the generation of a primary vinyl cation in solution. The increased nucleofugality of the arylidonio moiety of  $\beta,\beta$ -disubstituted alkenyl(aryl)iodonium salts was accomplished by incorporation of strongly electron-withdrawing trifluoromethyl groups into the aromatic ring. This in turn, allowed the determination of kinetic parameters for decompositions as well as quantitative evaluation of the effects of electron-withdrawing groups on the reaction ( $\rho = +1.7$ ). We are in the process of further investigating the solvolyses of these compounds in a wider variety of solvents as well as with a greater variety of substituents. The results of these studies will be reported in due course.

**Acknowledgment.** We gratefully acknowledge support of this work by The College of William & Mary, the Research Corporation (Grant CC4659), and the Arnold and Mable Beckman Foundation for a scholarship (AJM).

**Supporting Information Available:** Experimental procedures, copies of GCMS traces of fragmentation products resulting from compounds **1a**, **b**, **e**, and **f**, and kinetic plots of disappearance of iodonium salts (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA9916310

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