

Fragmentations of (*E*)- and (*Z*)- isomers of 2-methylbuten-1-yl(aryl) iodonium triflates: competing mechanisms for enol triflate formation

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This article is dedicated to Dr. Anastasios Varvoglis on the occasion of his 65th birthday
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Abstract

We examined fragmentation reactions of (*E*)- and (*Z*)-2-methylbuten-1-yl(aryl)iodonium triflates (aryl = C₆H₅-, 4-(CF₃)C₆H₄-, 3,5-(CF₃)₂C₆H₄-) to afford aryl iodides and six enol triflates. Four of these vinyl triflates involve alkyl migrations followed by triflate trapping of secondary vinyl cations whereas two do not involve migrations. Fragmentation rates in dry, neutral CDCl₃ were determined as were the distributions of enol triflate products. The ratios of rate constants for the (*E*)-/(*Z*)- isomers ranged between 5.0 and 8.5 and, in all salts, the rearranged enol triflate derived from migration of the alkyl moiety *trans*- to the aryl-iodonio- nucleofuge was observed in the greatest quantities. These data indicate that the fragmentation rates are significantly determined by the migratory aptitude of the *trans*-β-alkyl substituent and departure of the aryl-iodonio- nucleofuge occurs by anchimeric assistance. The ratios of inverted “unrearranged” enol triflate products were greater for the (*Z*)-isomers of the iodonium salt precursors indicating that steric effects play a role and implies that these inverted, unrearranged products are derived from in-plane (σ*) S_N2 reaction. The presence of the remaining, retained, unrearranged enol triflate can be explained by a ligand coupling mechanism (π* S_N2) and the fragmentation mechanism(s) do not require the intermediacy of a primary vinyl cation.

Keywords: Vinyl cation, iodonium salt, ligand coupling, hypervalent iodine, vinyl iodonium, substitution

Introduction

Over the last several years, we¹ as well as others² have discussed primary cation involvement in fragmentation processes of vinylic hypervalent iodine salts. The phenyliodonio - moiety is an

outstanding nucleofuge³ and both $\tilde{\beta}$ monosubstituted and β,β -disubstituted alkenyl(aryl)iodonium salts participate in both substitution and fragmentation reactions. Whereas Okuyama and co-workers have generally focused on chiral^{2b-c} and β,β -disubstituted alkenyl(phenyl)iodonium tetrafluoroborate salts,^{2a} we have investigated dialkyl substituted arylidonium salts in which the aryl moieties commonly include one and/or two strongly electron-withdrawing trifluoromethyl groups.¹ The current study examines the differences in reactivity between stereoisomeric pairs of salts containing three different aryl moieties (**Figure 1**).

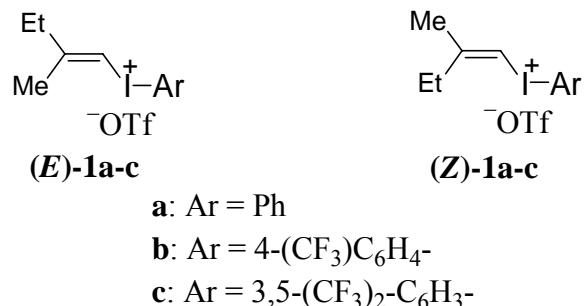
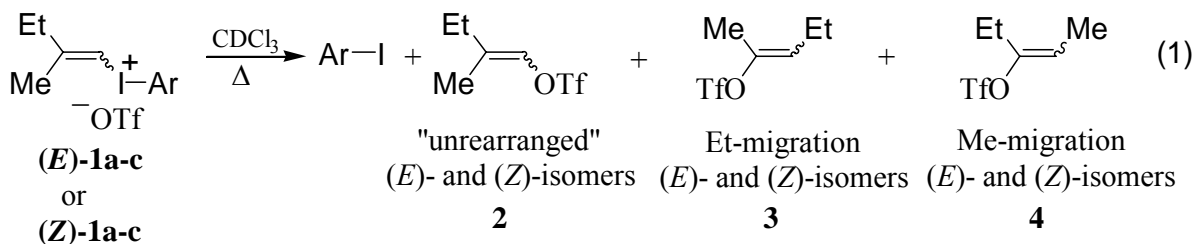


Figure 1. Salts used for fragmentation studies in CDCl₃.

Results and Discussion

We synthesized six salts by established methods^{4,5} and examined the fragmentations of (*E*)- and (*Z*)-2-methyl-1-butenyl(aryl)iodonium triflate salts, where aryl was phenyl, 4-trifluoromethylphenyl, or bis-3,5-trifluoromethyl-phenyl ((*E*)- and (*Z*)-**1a-c**, **Fig. 1**). The fragmentation products of alkenyl(aryl)iodonium triflate salts include the aryl iodide and six enol triflate isomers;⁶ all of these have been identified by comparison to authentic samples using GC MS (as shown for the (*E*)-isomer in eq 1). The same seven products were also obtained upon fragmentation of the (*Z*)-isomer, albeit in different ratios (vide infra, **Table 2**).



We utilized ¹H NMR spectroscopy with 1,2-dibromoethane as an internal standard to study the rate of fragmentation by observing the decrease in the *ortho*-proton resonances in the starting material and the increase in the *ortho*-proton resonances in the iodoarene fragmentation product

(Ar-I) in the spectra. We then constructed first-order kinetic plots ($\ln [A]/\ln[A]_0$ vs. time), and obtained rate constants for the fragmentations (**Table 1**).

Analysis of the reaction products was then performed by GC MS analysis of the samples resulting from the NMR-tube kinetics experiments. The samples were filtered through a short plug of silica gel using pentane as eluent and the solutions analyzed were compared to the authentic samples of enol triflate mixtures (**Table 2**).⁶ These data show that in the cases of the (*E*)- isomers, a higher degree of ethyl migration indicates that the β -alkyl moiety *trans*- to the nuleofuge occurs to a greater extent than the group that is *cis*- (methyl). In the (*Z*)-isomers, a preponderance of migration of the group *trans*- to the arylidonio- moiety (i.e., methyl) also occurs.

Table 1. Kinetic data for fragmentations of 2-methyl-1-butenyl(aryl)iodonium triflate salts in CDCl₃

Entry	Isomer	Salt	Ar	Temp (°C)	k x 10 ⁴ (sec ⁻¹)
1		(E)-1a	Ph	50	0.372
2		(E)-1a	Ph	55	0.651
3		(E)-1a	Ph	60	1.38
4	<i>(E)</i>	(E)-1b	4-CF ₃ C ₆ H ₄	30	0.109
5		(E)-1b	4-CF ₃ C ₆ H ₄	40	0.485
6		(E)-1b	4-CF ₃ C ₆ H ₄	50	1.62
7		(E)-1c	3,5-(CF ₃) ₂ C ₆ H ₃	30	0.722
8		(E)-1c	3,5-(CF ₃) ₂ C ₆ H ₃	40	2.12
9		(E)-1c	3,5-(CF ₃) ₂ C ₆ H ₃	45	3.89
10		(Z)-1a	Ph	60	0.279
11		(Z)-1b	4-CF ₃ C ₆ H ₄	50	0.295
12		(Z)-1b	4-CF ₃ C ₆ H ₄	55	0.561
13	<i>(Z)</i>	(Z)-1b	4-CF ₃ C ₆ H ₄	60	1.27
14		(Z)-1c	3,5-(CF ₃) ₂ C ₆ H ₃	40	0.248
15		(Z)-1c	3,5-(CF ₃) ₂ C ₆ H ₃	50	1.50
16		(Z)-1c	3,5-(CF ₃) ₂ C ₆ H ₃	60	4.26

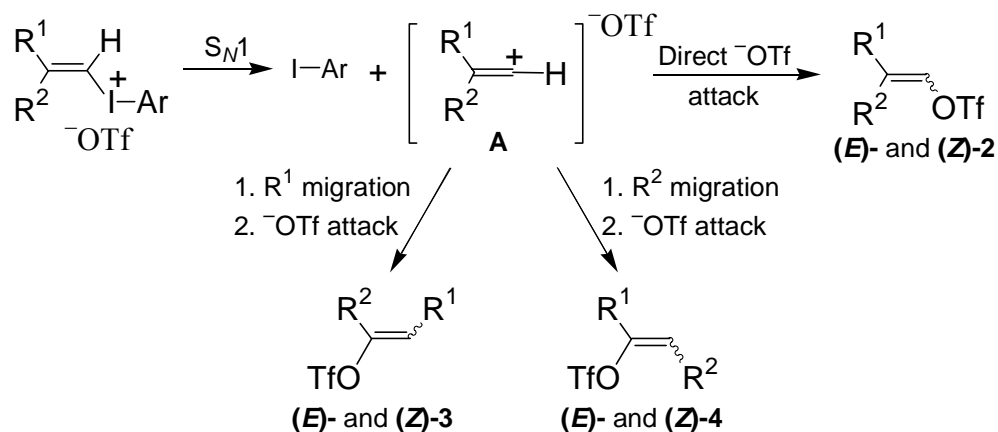
Table 2. Relative percentages of fragmentation products of (*E*)- and (*Z*)-2-methyl-1-butenyl(aryl)iodonium triflate salts in CDCl₃ filtered through basic alumina

Compound	Ar	Temp (°C)	Me migration	Et migration	Retention ^a	Inversion ^b
(<i>E</i>)-1a	Ph	50	40	56	1.8	2.6
(<i>E</i>)-1a	Ph	55	30	62	4.7	3.5
(<i>E</i>)-1a	Ph	60	43	54	0.9	2.1
(<i>E</i>)-1b	4-CF ₃ C ₆ H ₄	30	20	69	3.7	4.4
(<i>E</i>)-1b	4-CF ₃ C ₆ H ₄	40	28	64	3.5	4.3
(<i>E</i>)-1b	4-CF ₃ C ₆ H ₄	50	39	53	5.5	5.3
(<i>E</i>)-1c	3,5-(CF ₃) ₂ C ₆ H ₃	30	21	73	3.6	2.3
(<i>E</i>)-1c	3,5-(CF ₃) ₂ C ₆ H ₃	40	43	53	2.0	1.8
(<i>E</i>)-1c	3,5-(CF ₃) ₂ C ₆ H ₃	45	18	69	4.8	8.3
(<i>Z</i>)-1a	Ph	60	40	23	5.9	32
(<i>Z</i>)-1b	4-CF ₃ C ₆ H ₄	50	50	32	3.1	15
(<i>Z</i>)-1b	4-CF ₃ C ₆ H ₄	55	50	31	3.2	16
(<i>Z</i>)-1b	4-CF ₃ C ₆ H ₄	60	47	24	6.3	23
(<i>Z</i>)-1c	3,5-(CF ₃) ₂ C ₆ H ₃	40	52	29	5.3	14
(<i>Z</i>)-1c	3,5-(CF ₃) ₂ C ₆ H ₃	50	51	35	4.4	9.6
(<i>Z</i>)-1c	3,5-(CF ₃) ₂ C ₆ H ₃	60	54	33	3.3	9.4

^a Retention refers to the resulting enol triflate in which the OTf moiety is in the same relative position as the iodoaryl moiety in the starting material.

^b Inversion refers to the resulting enol triflate in which the OTf moiety is in the opposite relative position as the iodoaryl moiety in the starting material.

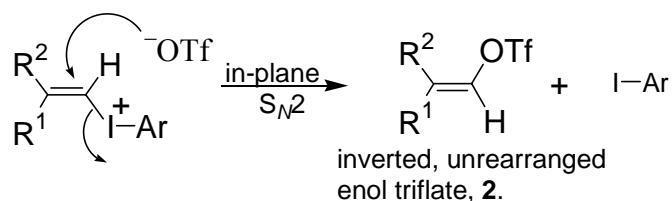
Four mechanisms have been discussed with regard to fragmentation mechanisms leading to the six enol-triflate isomers: (a) S_N1 departure of the aryliodonio moiety to provide a primary vinyl cation, **A**; (b) in-plane S_N2 reaction (c) out-of-plane S_N2 reaction also termed “ligand coupling;” and; (d) concerted alkyl migration and aryliodonio- nucleofuge departure. These mechanisms are shown, respectively in **Schemes 1-4**. Both we^{1b-c} and the Okuyama group⁷ had reported rearrangement products that could have occurred by S_N1 fragmentation of various iodonium salts. If an S_N1 process were operative, it would lead to a primary vinyl cation, **A**, that could be trapped by triflate directly to form (*E*)- and (*Z*)-**2**. Migration of a β-alkyl group before trapping would then provide a more stable secondary vinyl cation (**B** and/or **C** in Scheme 4, *vide infra*) that could then be trapped to provide mixtures of (*E*)- and (*Z*)-**3** as well as (*E*)- and (*Z*)-**4**. For the linear primary cation, both unrearranged isomers (*E*)- and (*Z*)-**2** should be produced in approximately equal ratios. Further, migration of either β-alkyl moiety in **B** should be equally facile in a free cation and isomers of **3** and **4** should also be present in approximately equal ratios.



Scheme 1

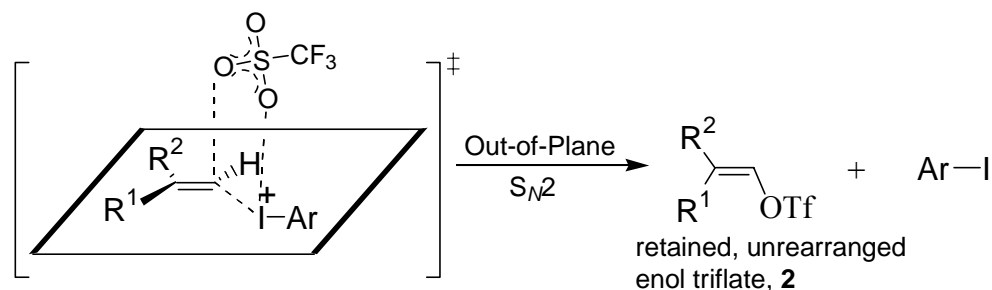
Detection of “unrearranged” isomers (e.g., **(E)-** and **(Z)-2**) in varying ratios as well as products developed by alkyl shifts were believed to provide evidence for primary vinyl cation formation.^{1b-c,7} However, competing, alternative mechanisms (i.e., Schemes 2 and 3, *vide infra*) could also account for the unrearranged products. Strong support for this assertion has been provided by Fujita and co-workers’ descriptions of fragmentations of chiral 4-methylcyclohexylidenyl(aryl)iodonium salts^{1b-c} as well as the data presented herein.

An in-plane $\text{S}_{\text{N}}2$ mechanism has been documented to proceed with weakly basic nucleophiles such as bromide ion.^{8,9} This process leads to complete inversion at the α -carbon and is supported by computational studies using MP2 calculations with polarized double-zeta basis sets.^{7b}



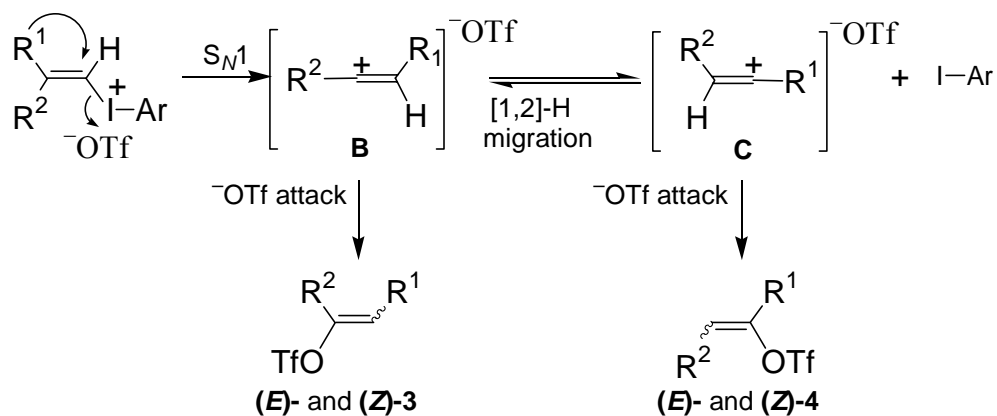
Scheme 2

A third mechanism has been studied computationally, is possible for iodonium salts and is sometimes referred to as ligand coupling (LC).^{7b,8,10} The nucleophile (triflate counter ion in this case) attacks the π^* orbital at the α -carbon perpendicular to the plane defined by the alkene; this leads to displacement of the aryl iodonio- moiety and net retention of configuration in the unrearranged product (e.g., product **2**). As was found for acetate, the triflate counter ion likely is involved in partial coordination with the iodine, forming a λ^3 -iodane complex^{2c,7,8} and reductive elimination occurs to form the retained, unrearranged enol triflate, **2**, as well as the aryl iodide byproduct.



Scheme 3

The fourth mechanism (Scheme 4) related to the $\text{S}_{\text{N}}1$ process involves departure of the aryliodonio- moiety in which there is concerted migration of the *trans*-alkyl group. The concerted migration results in the direct formation of a linear secondary vinyl cation (e.g., **A** or **B** in Scheme 4), that is attacked by the triflate counter ion; this results in two of the four “rearranged” triflate isomers (*(E)*- and *(Z)*-**3** from Et migration in *(E)*-**1a-c**). This mechanism also avoids the high energy primary vinyl cation as an intermediate. The resulting secondary vinyl cation can also undergo a rapid [1,2] hydride shift,¹¹ which would provide another secondary vinyl cation, **C**; this linear cation is also attacked from both sides by triflate, resulting in two additional “rearranged” isomers.



Scheme 4

Comparison of the fragmentation rates of *(E)*- and *(Z)*- isomers in clearly shows that when the ethyl moiety is *trans*- to the aryliodonio- nucleofuge, fragmentation is significantly more facile (**Table 3**). We have found this same effect in earlier studies of alkenyl(aryl)iodonium salts containing larger β -alkyl groups.^{1a}

Table 3. Ratios of reaction rates between the *(E)*- and *(Z)*-isomers

Ar	Temp ($^{\circ}\text{C}$)	$k(E)/k(Z)$
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Ph	60	5.0
4-CF ₃ C ₆ H ₄	50	5.8
3,5-(CF ₃) ₂ C ₆ H ₃	40	8.5

A Hammett plot was constructed for the (*Z*)-isomers using the fragmentation of (*Z*)-2-Methyl-1-butenyl(phenyl)iodonium triflate as the reference equation. The sigma values for the *meta*- and *para*- CF₃- substituents are 0.54 and 0.86,¹² respectively.¹³ A ρ value of 1.4 indicates that the fragmentation is facilitated by electron withdrawing groups. This is clear in that the 4-trifluoromethylphenyl substituted isomer has a lower rate constant than the 3,5-trifluoromethylphenyl analog because the extra electron withdrawing group in the latter increases iodine's effective positive charge thus increasing the nucleofugality of the arylidonio- moiety.

The activation parameters (**Table 4**) for the salts in this study also provide evidence for the fourth mechanism involving neighboring group participation in the fragmentations. The ΔH^\ddagger , and ΔG^\ddagger values are both also consistent with fragmentation reactions occurring slightly above ambient temperatures. The E_a values for both isomers reflect the greater nucleofugality of the aryl rings containing one and two trifluoromethyl groups. The activation energies of the (*Z*)-isomers are greater than the activation energies for the (*E*)-isomers. This is consistent with anchimeric assistance of the *trans*- β -alkyl moiety and alkyl migration favors groups that can better stabilize a positive charge, e.g., Et > Me > H.¹⁴ The calculated entropies of activation for the (*E*)-salts **1a-c** decreased with increasing electron-withdrawing character present in the arylidonio- moiety. The (*Z*)-isomer, however, showed an increase in entropy of activation when a second CF₃- group was present in the aromatic ring. At present, we do not know the source of this phenomenon, but ΔS^\ddagger for enol triflates varied according to substitution and solvent¹⁵ and our numbers were determined over a somewhat narrow temperature range.

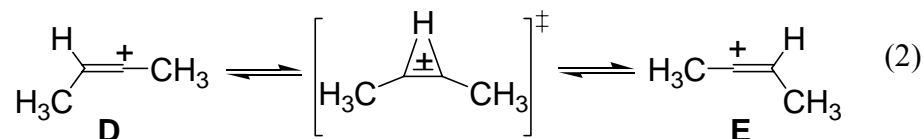
Table 4. Activation parameters for salts used in this study

Compound	Ar	E_a (kcal/mol)	ΔH^\ddagger (kcal/mol)	ΔG^\ddagger (kcal/mol)	ΔS^\ddagger (kcal/mol)
(E)-1a	Ph	28.0	27.4	27.2	5.8
(E)-1b	4-CF ₃ C ₆ H ₄	26.3	26.3	25.3	3.6
(E)-1c	3,5-(CF ₃) ₂ C ₆ H ₃	21.3	20.7	23.5	-9.2
(Z)-1b	4-CF ₃ C ₆ H ₄	31.2	30.6	30.1	1.8
(Z)-1c	3,5-(CF ₃) ₂ C ₆ H ₃	29.6	29.0	25.1	12.9

The relative proportion of rearranged products in the current study is lower than in the previous study.^{1a} We attribute this to two effects: (a) the lower steric requirements for σ^* and π^* S_N2 processes with these smaller alkyl groups at the β -position and (b) the smaller alkyl groups do not contribute as much electron density to the developing secondary cation (i.e., **B** and **C** in **Scheme 4**) and thus slightly decrease their stability. In the previous studies, the alkyl groups

were butyl and ethyl rather than methyl and ethyl and these larger salts fragmented at significantly lower temperatures.^{1a-b}

In terms of the rearranged products (i.e., **3** and **4**), the comparative proportion of (*E*)- β -alkyl vs. (*Z*)- β -alkyl migration does, however, have the potential to be misleading since the transition state for hydride migration between the resulting secondary vinyl cations, **D** and **E** (eq 2) was calculated to lie 0.32 kcal/mole above the secondary cations in the case of 2-butenyl cations (eq 2).¹¹



Conclusions

We have studied the fragmentations of (*E*)- and (*Z*)-2-methylbuten-1-yl-(aryl)iodonium triflate salts in CDCl₃ by using ¹H NMR spectroscopy. The fragmentation products include aryl iodide and six enol triflate isomers. The significantly increased fragmentation rate of the (*E*)-2-methylbuten-1-yl(aryl)iodonium salt isomers vs. the corresponding (*Z*)-isomers as well as the increased quantities of inverted, unrearranged enol triflate products for the less hindered, (*Z*)-isomers, the reaction manifold involving a primary vinyl cation is unlikely. If occurring via simple S_N1 process, there should be no difference in fragmentation rates between the two isomers and the relative ratios of unrearranged isomers would not vary. Three mechanisms including both in-plane (σ^* attack) and out-of-plane (π^* attack) S_N2 as well as concerted *trans*- β -alkyl shift and arylidonio- departure account for the formation of all the enol triflate products. The positive Hammett ρ -value is also consistent with anchimeric assistance, the preponderance of trisubstituted enol triflate isomers derived from *trans*-alkyl migration and literature experiments provide support for the aforementioned mechanisms. Secondary deuterium kinetic isotope effect measurements are now being conducted to evaluate the extent to which alkylidene-carbenes are involved in the formation of unrearranged enol triflate products. Preliminary data indicate that the isotope effect could be primary rather than secondary. This implies a significant contribution from a fifth mechanism involving α -deprotonation and intermediacy of an alkylidene-carbene.

Experimental Section

General Procedures. All reactions were carried out under nitrogen atmosphere. Dichloromethane was distilled from CaH₂. Pentane, ethyl acetate, acetonitrile, hydrogen

peroxide and magnesium sulfate were purchased from Fisher and used as received unless otherwise noted. Deuterated chloroform, trimethylsilyl cyanide, dimethyl sulfide, copper(I) bromide-dimethyl sulfide, tri-*n*-butyl-stannane, methyl magnesium bromide, ethyl magnesium bromide, tetramethylene-diamine, and 2-iodosobenzoic acid were purchased from Aldrich Chemical Company. Trifluoroacetic anhydride, 1-iodo-3,5-bis(trifluoromethyl)benzene and 4-iodobenzotrifluoride were purchased from Acros and used as received. Anhydrous ether was purchased from J.T. Baker, 1-propyne and butyne from GFS Chemicals and nitrogen from Air Products. The salts examined in this study were synthesized by common methods that we have utilized previously.^{1a-c,4,5} Salts (*E*)- and (*Z*)-1a were previously reported,⁴ (*Z*)-1b and (*Z*)-1c were recently described by X-ray,⁵ and (*E*)-1b and (*E*)-1c are described herein.

All NMR spectroscopic data were obtained using a Varian Mercury 400 MHz nuclear magnetic resonance spectrometer and chemical shifts are reported in ppm downfield from TMS and referenced to residual protons from the NMR solvent ($\delta = 7.26$ and 77.0 for ^1H and ^{13}C , respectively in CDCl_3). IR spectra were obtained on a Perkin-Elmer 1600 FTIR using NaCl plates purchased from International Crystal Laboratories. GC-MS traces were recorded on a Hewlett-Packard 5890 Series II Gas Chromatograph with an Ultra-1 crosslinked (methyl silicone gum; $12\text{ m} \times 0.2\text{ mm} \times 0.33\text{ }\mu\text{m}$) column, equipped with a 70 eV HP 5971A mass selective detector. Melting points were obtained on a Hoover Thomas Uni-Melt[®] capillary melting point device or a MelTemp[®] apparatus and are uncorrected.

Experimental procedure for kinetic runs

Chloroform-*d* (0.5 mL) was filtered through basic alumina to remove any acidic impurities and placed in an oven-dried NMR tube. The probe on the spectrometer was heated to the specific temperature and the chloroform was allowed to equilibrate to the probe's temperature for 15 minutes. Then ca. 14-18 mg of salt and 2 μL of dibromoethane, were added to the heated chloroform. The NMR tube was placed back into the probe and the sample was allowed to return to the temperature for about 5 minutes, at which time the collection of data was begun. The duration of data collection lasted from 3.5 to 11 hours, depending on reactivities of the salts. After the experiment ended the mixture was placed into a 20mL scintillation vial that was stored in a refrigerator at 15°C .

The rate constants (*k*) were determined from the slope of the first-order rate law plot: $\ln [A]/[A]_0$ vs. time. The concentration at time *t* ($[A]_t$) was determined by the relative integration of the starting material to that of the internal standard. The time plotted was considered to be halfway through the pulse sequence for each spectrum (e.g., for 96 pulses (5 min 0 s), halfway was considered to be 48 pulses (2 min 30 s)). Any rate constants taken from plots with an R^2 value exceeding 0.9500 and a rate constant within 10% of the other values were used in determining the average rate constant at each temperature.

General procedure for the preparation of alkenyl(aryl)iodonium triflates

Distilled CH_2Cl_2 (5 mL) and cyano(aryl)iodonium triflate (0.27 mmol) were placed in an oven-dried 100 mL round bottom flask equipped with a stir bar and N_2 inlet. The flask was placed in

an acetonitrile/dry-ice cooling bath and the temperature lowered to $-40\text{ }^{\circ}\text{C}$. The alkenyl tri-*n*-butylstannane^{4b} (1.1-1.3 equiv.) was then added *via* syringe. The reaction mixture was warmed until homogeneity was achieved at which time Et₂O (ca. 5 mL) was added and, with rapid stirring, an excess of hexanes was added until the solution became turbid. Cooling overnight to $-15\text{ }^{\circ}\text{C}$ afforded white, crystalline solids in 40-90% yields.

Representative example. Preparation of (*E*)-2-methyl-1-butenyl(4-trifluoromethylphenyl)iodonium triflate ((*E*)-1b). (*E*)-2-Methyl-1-butenyl(4-trifluoromethylphenyl) iodonium triflate ((*E*)-1b) was prepared *via* the general procedure from cyano(4-trifluoromethylphenyl)iodonium triflate, **13** (0.401 g, 0.897 mmol), and (*E*)-2-methyl-1-propenyl tri-*n*-butylstannane^{4b} (0.387g, 1.08 mmol). The product was isolated as a white, crystalline solid in 70% yield: mp 83-85 $^{\circ}\text{C}$. IR (film, NaCl) 3089 m, 2978 m, 1554 m, 1394 m, 1317 s, 1267 s, 1156 s, 1139 s, 1081 s, 1028 s, 1000 s, 828 m, 739 s, 639 s, cm^{-1} . ¹H NMR (CDCl₃, 400 MHz) δ 8.09 (d, $J = 8.8$ Hz, 2H), 7.69 (d, $J = 8.8$ Hz, 2H), 6.78 (s, 1H), 2.50 (q, $J = 7.3$ Hz, 2H), 2.17 (s, 3H), 1.12 (t, $J = 7.3$ Hz, 3H). ¹³C (CDCl₃, 100 MHz) δ 163.5, 134.6, 134.0, 128.2, 114.8, 94.7, 32.6, 24.8, 12.2. Anal calcd for C₁₃H₁₃F₆IO₃S: C, 31.85; H, 2.67; S, 6.54. Found: C, 31.64; H, 2.73; S, 6.63.

Preparation of (*E*)-2-methylbuten-1-yl(3,5-bis(trifluoromethyl)phenyl)iodonium triflate ((*E*)-1c). This salt was prepared by the general procedure using cyano(3,5-bis(trifluoromethyl)iodonium triflate, (0.401 g, 0.779 mmol), and (*E*)-2-methyl-1-propenyl tri-*n*-butylstannane^{4b} (0.336 g, 0.934 mmol). The product was isolated as a white, crystalline solid in 48 % yield (0.211g): mp 67-69 $^{\circ}\text{C}$. IR (film, NaCl) 3067 s, 2978 s, 1622 m, 1461 m, 1378 m, 1344 s, 1278 s, 1167 s, 1139 s, 1028 s, 889 s, 694 s, 633 s. ¹H NMR (CDCl₃, 400 MHz) δ 8.40 (s, 2H), 8.04 (s, 1H), 6.87 (s, 1H), 2.52 (q, $J = 7.3$ Hz, 2H), 2.20 (s, 3H), 1.13 (t, $J = 7.3$ Hz, 3H). Anal calcd for C₁₄H₁₂F₉IO₃S: C, 30.12; H, 2.17; S, 5.74. Found: C, 30.39; H, 2.29; S, 5.77.

Preparation of enol triflates, (*E*)- and (*Z*)-2-methylbuten-1-yl triflate. An oven-dried 500 mL round bottomed flask was equipped with a stir bar and charged with CH₂Cl₂ (370 mL), and 2,6-di-*tert*-butylmethylpyridine (2.258g, 11.0 mmol). Triflic anhydride (1.80 mL, 10.7 mmol) and 2-methylbutyraldehyde (0.855g, 9.93 mmol) were added and the reaction mixture stirred overnight (ca. 12h). The solvent was removed in *vacuo* to afford a thick suspension of 2,6-di-*tert*-butylmethylpyridinium•TfOH and pentane (125 mL) was added to the suspension. The pyridinium salt was collected on a fritted funnel and the filtrate concentrated in *vacuo*. Short-path distillation of the concentrated filtrate afforded two fractions containing the two known,^{6b} desired triflate stereoisomers. Formation of these vinyl triflates was verified by ¹H NMR spectroscopy as well as GC MS ($M^+ = 218$).

Preparation of (*E*)- and (*Z*)-2-penten-3-yl triflates (methyl migration products). An inseparable mixture of these triflates was synthesized from 3-pentanone (0.77mL, 7.6 mmol), 2,6-di-*tert*-butylmethylpyridine (1.72 g, 8.36 mmol) and triflic anhydride (1.36 mL, 8.08 mmol). Isolation by kugelrohr distillation afforded the known isomers¹⁵ which were dissolved and stored in pentane (GC MS, (*Z*)- and (*E*)-isomers with stereochemistry of isomers *not* determined, $M^+ = 218$).

Preparation of (*E*)- and (*Z*)-2-penten-2-yl triflates (ethyl migration products). A mixture of the *ethyl migration products* was synthesized from 2-pentanone (1.20 mL, 10.9 mmol), 2,6-di-*tert*-butylmethylpyridine (2.442 g, 11.9 mmol) and triflic anhydride (1.95 mL, 11.6 mmol). Isolation by kugelrohr distillation afforded the known isomers¹⁵ which were dissolved and stored in pentane. The isomers were not separated (GC MS, (*Z*)- and (*E*)-isomers with stereochemistry of isomers not determined, $M^+ = 218$).

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References and Notes

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