

Vinyl Carbocations: Solution Studies of Alkenyl(aryl)iodonium Triflate Fragmentations

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Generation of vinyl cations is facile by fragmentation of alkenyl(aryl)iodonium trifluoromethanesulfonates. Kinetics and electronic effects were probed by ¹H NMR spectroscopy in CDCl₃. Products of fragmentation include six enol triflate isomers in addition to iodoarenes. The enol triflates arise from direct reaction of a triflate anion with the starting iodonium salts as well as triflate reaction with rearranged secondary cations derived from those salts. G2 calculations of the theoretical isodesmic hydride-transfer reaction between secondary vinyl cation **7** and primary vinyl cation **6** reveal that cation **6** is 17.8 kcal/mol higher in energy. Activation parameters for fragmentation of (*Z*)-2-ethyl-1-hexenyl(3,5-bis-trifluoromethylphenyl)iodonium triflate, **17e**, were calculated using the Arrhenius equation: $E_a = 26.8$ kcal/mol, $\Delta H^\ddagger = 26.2$ kcal/mol, and $\Delta S^\ddagger = 11.9$ cal/mol·K. Added triflate increases the rate of fragmentation slightly, and it is likely that for most β,β -dialkyl-substituted vinylic iodonium triflates enol triflate fragmentation products are derived from three competing mechanisms: (a) vinylic S_N2 substitution; (b) ligand coupling (LC); and (c) concerted arylidonio departure and 1,2-alkyl shift leading to secondary rather than primary vinyl cations.

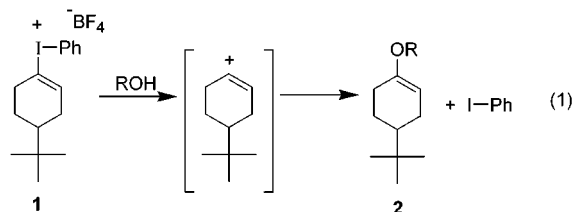
Introduction

It was our expectation that addition of electron-withdrawing substituents to the aryl portion of β,β -disubstituted alkenyl(aryl)iodonium salts would lead to even greater nucleofugality of the iodoarene moiety and produce β,β -disubstituted primary vinyl cations. Herein, we report our results herein indicating that heterolytic cleavage indeed occurs readily, but largely involves a concerted, nonsynchronous shift of the *trans*- β -alkyl group to lead to secondary cations rather than primary cations. Further, unrearranged enol triflate isomers are likely formed by both vinylic S_N2 and ligand coupling (LC) pathways rather than through primary vinyl cations.

Background. Cationic intermediates are involved in a large number of transformations including cyclization, substitution, elimination, and combustion.^{1,2} Alkyl cations³ have long been considered accessible via solvolytic mechanisms as well as acid-catalyzed hydrations of alkenes. Conversely, vinylic cations were only accepted as viable intermediates much later. This was partly because alkenyl halides did not react with silver salts

(to precipitate AgX by halide abstraction) in the classical test for carbenium ions and partly because the energy of the vinyl cation was considered too high to be attainable in solution. However, vinyl cations were first proposed by Jacobs and Searles in 1944 to account for the formation of an enol ether from the acid-catalyzed hydration of alkoxyacetylenes.⁴ It was 20 years later when Grob and co-workers first demonstrated that vinyl cations or carbenium ions can be generated in solution when they discovered that *trans*- β -bromo- and β -chlorocinnamic acids fragment to form acetophenone in 80% ethanol.⁵

Recently, there has been renewed interest in carbenium ion⁶ chemistry, and vinyl cations in particular, due to the development of vinylic hypervalent iodine compounds as well as NMR spectroscopic techniques.⁷ The arylidonio moiety of these compounds has been documented to be extremely labile and solvolysis of cyclohexenyl(phenyl)iodonium tetrafluoroborate **1** (eq 1) occurs



¹⁰6 faster than the corresponding cyclohexenyl triflate.⁸ The nucleofugality of the phenyliodonio moiety is so great

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(1) For an introduction to a variety of carbocations, see: *Stable Carbocation Chemistry*; Prakash, G. K. S., Schleyer, P. v. R., Eds.; John Wiley and Sons: New York, 1997.

(2) *Dicoordinated Carbocations*; Rappoport, Z., Stang, P. J., Eds.; John Wiley and Sons: New York, 1997.

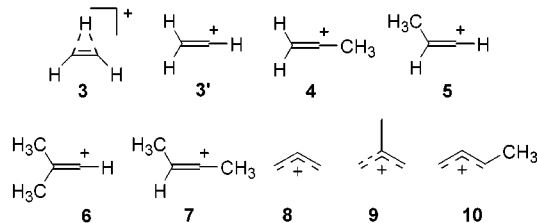
(3) See the following article for recent theoretical calculations: Olah, G. A.; Prakash, G. K.; Rasul, G. *J. Org. Chem.* **2001**, *66*, 2907–2910.

(4) Jacobs, T. L.; Searles, S. *J. Am. Chem. Soc.* **1944**, *66*, 686–689.
(5) Grob, C. A. in ref 2, Chapter 1. This contains a brief outline of the first studies of vinyl cations.

that, to the best of our knowledge, no simple, acyclic, α -alkyl alkenyl(aryl)iodonium salt has been isolated—presumably because fragmentation to the secondary vinyl cation occurs so readily. The extreme nucleofugality of the iodophenyl moiety has allowed the indirect observation of the facile solvolytic generation of a number of vinyl cations in solution.⁹ As further manifestation of the extremely high lability of the arylidonio moiety, alkenyl-(phenyl)iodonium as well as alkynyl and aryl salts have been used as electrophiles in a growing number of reactions^{10–13}

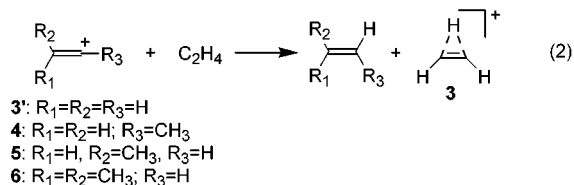
There is widespread belief that allyl cations¹⁴ are viable and, in fact, reasonably long-lived intermediates in a number of reactions, and the 2-butenyl cation **7** (vide infra) has been studied in solution since the late 1960s.¹⁵ Further, there seems to be little doubt that cyclohexenyl cation⁸ is accessible via phenyliodonium salt **1** (e.g., eq 1) and that a variety of substituted vinyl cations have long been generated in solution.¹⁶ Our hope was to generate β,β -disubstituted primary vinyl cations by fragmentations of activated β,β -disubstituted alkenyl-(aryl)iodonium salts.

Energetics. Several cations (**3–10**) should be considered in the context of the current study. Both theory and experiment show that the parent vinyl cation exists as the nonclassical structure **3** rather than the classical structure **3'**. Apeloig and co-workers' calculations based



on the isodesmic reactions shown in eq 2 indicate that at the MP3/6-31G**/HF/6-31G* level, **3** is more stable than **3'** by 0.6 kcal/mol.¹⁷ However, substituents lower the energy of the classical form relative to the nonclassical form so that substituted vinyl cations are often linear rather than bridged.^{9c,17,18} Apeloig and co-workers'

calculations also show that addition of a single α -methyl to produce the 2-propenyl cation **4** leads to a cation



stabilization energy of 27.2 kcal/mol. In contrast, addition of a single β -methyl (e.g., 1-propenyl cation, **5**) only leads to 8.6 kcal/mol of stabilization. The addition of a second β -methyl substituent to afford the β,β -dimethyl-substituted primary vinyl cation **6** provides a remarkable 24 kcal/mol methyl stabilization energy over the monosubstituted β -methyl analogue **5**. Groups larger than Me (e.g., Et, Pr, Bu) in β,β -disubstituted vinyl cations analogous to **6** should stabilize the ion even further, albeit by small amounts. Given the energetics of the isodesmic reaction above, one might expect that with an appropriate leaving group, β,β -disubstituted primary vinyl cations could be accessible.

To place the stability of substituted vinylic cations (vinyl cations) in further context, one should compare the relative energies of the isomeric 2-propenyl cation **4** and unsubstituted allyl cation **8**. According to a calculation performed by Wiberg and co-workers¹⁹ (QCISD(T)(fc)/6-311++G**/MP2(fu)/6-31G*), **4** is only 8.8 kcal/mol higher in energy than **8**. This is in excellent agreement with the experimental gas-phase value of 9 kcal/mol²⁰ and shows that substitution can stabilize vinylic cations extensively and may make them viable in solution. This, along with the isodesmic reactions calculated by Apeloig and co-workers,¹⁷ implies that β,β -disubstituted primary vinyl cations may be of low enough energy to be generated in solution by an S_N1 process.

Results

We are not aware of reports of calculations of cations **3–10** all at the G2 level of theory and were particularly interested in how various substitution patterns affected the energies of the vinyl cations vs the more familiar allyl

(6) For early work on the cubyl cation which was obtained utilizing hypervalent iodine reagents, see: (a) Moriarty, R. M.; Tuladhar, S. M.; Penmasta, R.; Awasthi, S. K. *J. Am. Chem. Soc.* **1990**, *112*, 3228–3230. (b) Eaton, P. E.; Yang, C.-X.; Xiong, Y. *J. Am. Chem. Soc.* **1990**, *112*, 3225–3226. (c) Eaton, P. E.; Cunkle, G. T. *Tetrahedron Lett.* **1986**, 6055–6058.

(7) For NMR spectroscopic studies of stabilized vinyl cations, see: Siehl, H.-U. *Pure Appl. Chem.* **1995**, *67*, 769–775. Siehl, H.-U.; Kaufmann, F.-P.; Hori, K. *J. Am. Chem. Soc.* **1992**, *114*, 9343–9349.

(8) Okuyama, T.; Takino, T.; Sueda, T.; Ochiai, M. *J. Am. Chem. Soc.* **1995**, *117*, 3360–3367.

(9) For recent documentation on vinyl cations in solution, see our preliminary reports as well as a recent report by Okuyama and co-workers: (a) Hinkle, R. J.; McNeil, A. J.; Thomas, Q. A.; Thomas, D. B. *J. Am. Chem. Soc.* **1999**, *122*, 7437–7438. (b) Hinkle, R. J.; Thomas, D. B. *J. Org. Chem.* **1997**, *62*, 7534–7535. (c) Okuyama, T.; Yamataka, H.; Ochiai, M. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2761–2769.

(10) A number of reviews of the chemistry of hypervalent iodine compounds have appeared in recent years: (a) Moriarty, R. M.; Prakash, O. In *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Academic: New York, 1998; pp 1–87. (b) Varvoglis, A. *Tetrahedron* **1997**, *53*, 1179–1255. (c) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **1996**, *96*, 1123–1178. (d) Varvoglis, A. *Hypervalent Iodine in Organic Synthesis*; Academic: New York, 1997.

(11) For formal displacement protocols with cuprates, see: Ochiai, M.; Sumi, K.; Takaoka, Y.; Kunishima, M.; Nagao, Y.; Shiro, M.; Fujita, E. *Tetrahedron* **1988**, 4095–4112.

(12) For nucleophilic substitution reactions with cyclic alkenyl-(phenyl)iodonium salts, see: Ochiai, M.; Shu, T.; Nagaoka, T.; Kitagawa, Y. *J. Org. Chem.* **1997**, *62*, 2130–2138.

(13) For palladium-catalyzed reactions, see: (a) Kang, S.-K.; Lee, H.-W.; Jang, S.-B.; Ho, P.-S. *J. Org. Chem.* **1996**, *61*, 4720–4724. (b) Kang, S.-K.; Ho, P.-S.; Yoon, S.-K.; Lee, J. -C.; Lee, K.-J. *Synthesis* **1998**, 823–825. Ryan, J. H.; Stang, P. J. *J. Org. Chem.* **1996**, *61*, 6162–6165. Hinkle, R. J.; Poulter, G. M.; Stang, P. J. *J. Am. Chem. Soc.* **1993**, *115*, 11626–11627. Moriarty, R. M.; Epa, W. R. *Tetrahedron Lett.* **1992**, 4095–4098. (c) Radhakrishnan, U.; Stang, P. J. *Org. Lett.* **2001**, *3*, 859–860. (d) Moriarty, R. M.; Epa, W. R.; Awasthi, A. K. *J. Am. Chem. Soc.* **1991**, *113*, 6315–6316.

(14) Allyl cations are taught in a plethora of introductory level organic chemistry textbooks as well as advanced monographs. Examples of texts include: Brown, W. H.; Foote, C. S. *Organic Chemistry*, 2nd ed.; Saunders College Publishing: New York, 1998; pp 289–291. Jones, M. *Organic Chemistry*, 2nd ed.; W. W. Norton: New York, 2000; pp 496–497.

(15) Stang, P. J.; Summerville, S. *J. Am. Chem. Soc.* **1969**, *91*, 4600–4601.

(16) For a monograph on vinyl carbenium ion chemistry from its beginnings until ca. 1978, see: Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. *Vinyl Cations*; Academic: New York, 1979.

(17) See ref 2, p 33, Table 13. Chapter 2 of this monograph is dedicated to theoretical calculations.

(18) Van Alem, K.; Lodder, G.; Zuilhof, H. *J. Phys. Chem. A* **2000**, *104*, 2780–2787.

(19) Foresman, J. B.; Wong, M. W.; Wiberg, K. B.; Frisch, M. J. *J. Am. Chem. Soc.* **1993**, *115*, 2220–2230.

(20) Aue, D. H.; Davidson, W. R.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 6700–6703.

Table 1. Cation Heats of Formation from G2 Calculations^{a,b}

cation	$\Delta_{298}H_f$	$\Delta\Delta_{298}H$ (vs 8)	$\Delta\Delta_{298}H$ (vs 9)	$\Delta\Delta_{298}H$ (vs 10)
3	267.1			
3'	271.4			
4	236.8	-8.4		
6	240.3	-20.5	-24.3	-35.5
7	224.1	-2.8	-6.5	-17.7
8	228.5		-3.8	-15.0
9	216.0	3.8		-11.2
10	206.4	15.0	11.2	

^aData are presented in kcal/mol and calculated using the Gaussian 98W suite of basis sets. Negative numbers indicate that the cation in the indicated column is more stable than the cation in listed in column 1. ^b $\Delta_{298}H_f$ (vs **8**), $\Delta_{298}H_f$ (vs **9**), and $\Delta_{298}H_f$ (vs **10**) were calculated theoretical isodesmic hydride-transfer reactions involving calculated G2 values for the cations shown as well as G2 values for propene, isobutene, and *trans*-2-butene. See the Supporting Information for equations and details.

cations. We therefore performed calculations at the G2 level of theory using Gaussian 98W²¹ and determined the heats of formation for vinyl cations **3**–**7**²² and allyl cations **8**–**10** (Table 1). At this level of theory, we found that the parent, bridged vinyl cation **3** is 4.3 kcal/mol more stable than the classical cation **3'**.

Some direct comparisons of the G2 values in Table 1 can be made. The three-carbon vinyl cation **4** is 8.4 kcal/mol less stable than the isomeric allyl cation **8**. This is in excellent agreement with the experimentally determined value (vide supra).¹⁹ For the analogous four-carbon ions, 2-methyl-1-propenyl cation **6** is 24.3 kcal/mol higher in energy than the isomeric 2-methylallyl cation **9**, whereas the secondary vinyl cation **7** is 17.7 kcal/mol higher in energy than 1-methylallyl cation (**10**). Although these results indicate that the presence of an alkyl substituent directly on the cationic carbon significantly lowers the energy of the vinyl cations, they remain considerably less stable than the corresponding allyl cations.

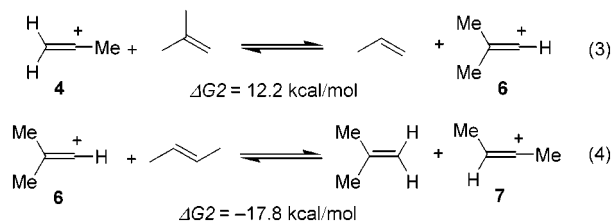
We also wanted an indication of the relative stabilities of vinyl cations with differing structures. These data are based on theoretical isodesmic hydride-transfer reactions and are contained in the data in columns 3–5 of Table 1.²³ We accounted for the structural differences between cations by including structurally similar, neutral alkenes in the equations (see eqs 3 and 4 as well as the Supporting Information for more equations and details).

(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, R. E.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Pople, J. A. *Gaussian 98W*, revision 5.1; Gaussian, Inc.: Pittsburgh, PA, 1998.

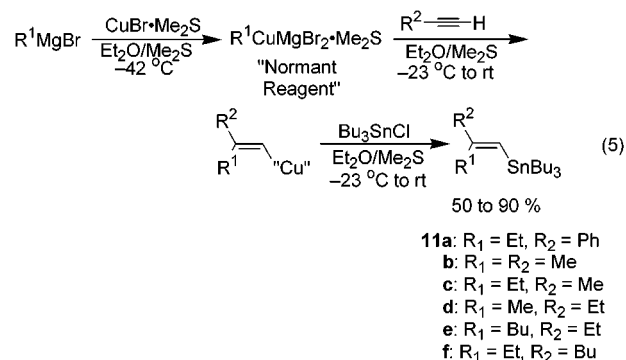
(22) We attempted to minimize and determine ΔH_f of cation **5**, but found that this species is not a stationary point at the MP2/6-311G* level of theory; a 1,2-hydride shift to form cation **4** occurred automatically. This is a good indication of the very low energy barrier to hydride migration in vinyl carbenium ions and is in agreement with the previous calculations in which the 1-propenyl cation, **5**, was found to be 4.0 kcal/mol higher in energy than the transition state for hydride transfer (MP4(SDQ)/6-31G**//HF/6-31G* + ZPVE): McAllister, M.; Tidwell, T. T.; Peterson, M. R.; Csizmadia, I. G. *J. Org. Chem.* **1991**, *56*, 575–580.

(23) Isodesmic equations and a table of G2 results are shown in the Supporting Information.

On the basis of eq 3, secondary α -methylvinyl cation **4** was calculated to be 12.2 kcal/mol more stable than β,β -dimethylvinyl cation **6**. Secondary vinyl cation **7** was calculated to be 17.8 kcal/mol more stable than the primary vinyl cation **6** (eq 4). Further, comparisons of cations (**6** vs **8**, **9** and **10**, **7** vs **8**, **9** and **10**, as well as **8** vs **9** and **10**) clearly show that substitution greatly increases the stability of the cations in both the vinylic and allylic series. Equation 4 also indicates the greater degree of stabilization provided by an α -substituent vs one that is β - to the cationic center.



Salts. We synthesized several alkenyl(aryl)iodonium salts for evaluation in this study. The salts were synthesized by a known method using readily available, stereodefined alkenylstannanes²⁴ (eq 3) and iodonium-transfer reagents developed by Stang and co-workers (eq 4).²⁵ The addition of Normant reagents across terminal alkynes is known to be stereoselective,²⁴ and reaction of the transfer reagents and alkenylstannanes is stereospecific.^{26,27}



We synthesized the analogues with 4-trifluoromethyl (**16b**–**f**) and 3,5-bis-trifluoromethyl (**17b**–**f**) substituents in the aryl portion of the molecules in hopes of increasing the nucleofugality of the iodoarene moiety enough to promote heterolytic cleavage to primary vinyl cations. The salts were characterized by NMR spectroscopy and IR and combustion analysis. For most salts, obtaining a ¹³C NMR spectrum with good S/N was difficult because

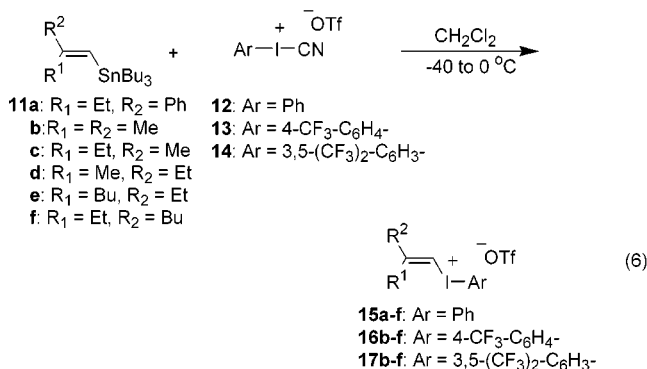
(24) Alkenyl stannanes were synthesized by stereoselective addition of Normant reagents to terminal acetylenes followed by reaction with tri-*n*-butylchlorostannane: (a) Posner, G. H. *An Introduction to Synthesis Using Organocopper Reagents*; John Wiley and Sons: New York, 1980; pp 1–52. (b) Marfat, A.; McGuirk, P. R.; Helquist, P. *J. Org. Chem.* **1979**, *44*, 3888–3901. (c) Marfat, A.; McGuirk, P. R.; Helquist, P. *J. Am. Chem. Soc.* **1977**, *99*, 253–255. (d) Marfat, A.; McGuirk, P. R.; Helquist, P. *Tetrahedron Lett.* **1978**, 2465–2468. (e) Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841–870 and references therein. (f) Commerçon, A.; Normant, J. F.; Villieras, J. *Tetrahedron* **1980**, *36*, 1215–1221. (g) Iyer, R. S.; Helquist, P. *Organic Syntheses*; Wiley: New York, 1990; Collect. Vol. VII, pp 236–241.

(25) Zhdankin, V. V.; Scheuller, M. C.; Stang, P. J. *Tetrahedron Lett.* **1993**, *34*, 6853–6856.

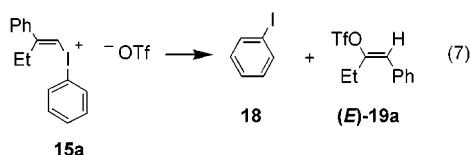
(26) Single-crystal X-ray analysis was also performed on salt **16c** to verify stereochemistry. Hinkle, R. J.; McDonald, R. Unpublished results.

(27) Hinkle, R. J.; Stang, P. J. *Synthesis* **1994**, 393–396.

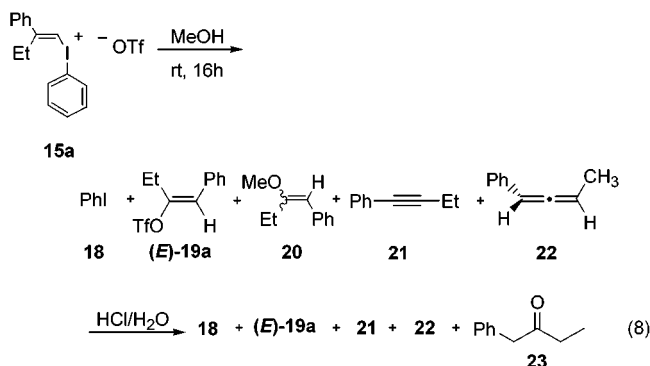
they fragmented readily during acquisition of the spectra. Therefore, when listed, the ^{13}C NMR data do not generally include the CF_3 carbons.



Investigation of a β -phenyl-substituted analogue, **15a**, revealed that fragmentation occurred readily in CDCl_3 or MeOH at ambient temperature over the course of several hours. In chloroform, salt **15a** provided only one enol triflate fragmentation product, (*E*)-**19a** (eq 7).²⁸ As



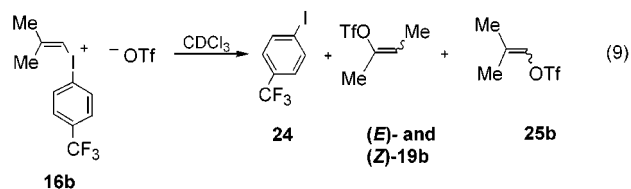
shown in eq 8, performing the fragmentation in MeOH provided a mixture of iodobenzene (**18**), (*E*)-**19a**, a mixture of enol ether stereoisomers (**20**), 1-phenyl-1-butyne (**21**), and 1-phenyl-1,2-butadiene (**22**). To facilitate



characterization, the enol ethers (**20**) were then hydrolyzed under acidic conditions to provide a mixture of (*E*)-**19a**, allene **22**²⁹ and 1-phenyl-2-butanone (**23**). Each of these compounds was verified by GC-MS analysis and ^1H NMR spectroscopy. Further, GC-MS comparisons of (*E*)-**19a**, **21**, and **23** were made with authentic samples. It is particularly noteworthy that phenyl migration always occurred and that the only ketone detected was 1-phenyl-2-butanone, **23**. The high reactivity observed with **15a** was somewhat surprising because Okuyama and co-workers found that a monosubstituted styrenyl iodonium salt required elevated temperatures and ex-

tended times to react in acetic acid.³⁰ Our results reflect the greater stability of an alkyl-substituted phenonium ion versus the parent phenonium ion.

Initial characterization of salt **16b** by obtainment of a ^{13}C NMR spectrum led to fragmentation of the sample in the probe at ambient temperature. After a 2–3 h acquisition, another ^1H NMR spectral analysis revealed new vinylic resonances: a singlet at δ 6.40 and quartets at δ 5.60 and 5.34. The singlet as well as these quartets (300 MHz) were suggestive of enol triflates. Analysis by GC-MS spectroscopy revealed the presence of 4- CF_3 - C_6H_4 I **24** and three components with $m/z = 204$, corresponding to isomers of butenyl trifluoromethane sulfonate (i.e., compounds **19b** and both (*E*)- and (*Z*)-**19b**) shown in eq 9. The identities of the three enol triflates were confirmed by comparison with authentic samples. Triflates (*E*)- and (*Z*)-**19b** were synthesized by electrophilic addition of TfOH to 2-butyne,³¹ whereas triflate **25b** was synthesized by the standard hindered base method³² from 2-methylpropanal.



Although the above fragmentations suggested that both phenonium and primary vinyl cations are intermediates, we sought further substantiation of their involvement. We investigated alkenyl(aryl)iodonium analogues with various β -alkyl substituents and groups with greater electron withdrawing character on the aromatic portion for additional information such as the kinetics of the reactions, electronic effects on the kinetics, and the stereochemistry of the resulting enol triflate products.

We initially attempted to determine the kinetics of the fragmentations using UV-vis spectrophotometry. However, the starting salts and iodoarene byproducts displayed overlapping absorption maxima, and this technique could not be used. We therefore followed the reactions by ^1H NMR spectroscopy at various temperatures. The resonances of the ortho protons in the iodoarene byproduct as well as the starting iodonium salts were analyzed, and the resulting concentrations were plotted ($\ln[A]/[A]_0$ vs time). The fragmentations in CDCl_3 were found to be first-order in alkenyl(aryl)iodonium triflate and this lent credence to our belief that the reactions were occurring by a heterolytic cleavage mechanism. First-order rate constants are shown in Table 2. Included in these data is a slight increase in rate when exogenous triflate is added (row 3).

Fragmentations in MeOH and EtOH were attempted, but in accord with Okuyama and co-workers, α -elimination appeared to be the major pathway in these reactions. Rearrangements of salts **15e-f**, **16c-e**, and **17c-e** at varying temperatures were then investigated by ^1H NMR spectroscopy in dry CDCl_3 . To produce the most accurate results, the temperature of the solvent was equilibrated

(28) The structure of (*E*)-**19a** was assigned by ^1H NMR spectroscopy. The enol triflate geometry was assigned based on comparison to the spectra of both (*E*)- and (*Z*)-1-methyl-2-phenylvinyl triflates described in: Jäckel, K.-P.; Hanack, M. *Chem. Ber.* **1977**, *110*, 199–207.

(29) Allene **22** is a known compound with distinctive spectral characteristics. For a synthesis via enol phosphates, see: Brummond, K. M.; Dingess, E. A.; Kent, J. L. *J. Org. Chem.* **1996**, *61*, 6096–6097.

(30) Okuyama, T.; Ochiai, M. *J. Am. Chem. Soc.* **1997**, *119*, 4785–4786.

(31) Summerville, R. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 1110–1120.

(32) Stang, P. J.; Treptow, W. *Synthesis* **1980**, 283–284.

Table 2. Kinetic Data^a From Fragmentations of Alkenyl(aryl)iodonium Triflate Salts

salt	R ₁	R ₂	Ar	T(°C)	k × 10 ⁴ (s ⁻¹)
17d	Me	Et	3,5-(CF ₃) ₂ C ₆ H ₃	40	2.12
17c	Et	Me	3,5-(CF ₃) ₂ C ₆ H ₃	50	1.50
17c^b	Et	Me	3,5-(CF ₃) ₂ C ₆ H ₃	50	1.90
15e	Bu	Et	Ph	35	0.24
16e	Bu	Et	4-(CF ₃)C ₆ H ₄	35	2.01
17e	Bu	Et	3,5-(CF ₃) ₂ C ₆ H ₃	20	0.67
17e	Bu	Et	3,5-(CF ₃) ₂ C ₆ H ₃	25	1.75
17e	Bu	Et	3,5-(CF ₃) ₂ C ₆ H ₃	30	3.24
17e	Bu	Et	3,5-(CF ₃) ₂ C ₆ H ₃	35	6.62

^a Average rate constants were determined by fragmentation of salts in CDCl₃ and monitored by ¹H NMR spectroscopy for disappearance of starting materials (ortho proton resonances).

^b With 1.0 equiv of added Bu₄NOTf.

in the NMR probe prior to addition and dissolution of the particular salt.

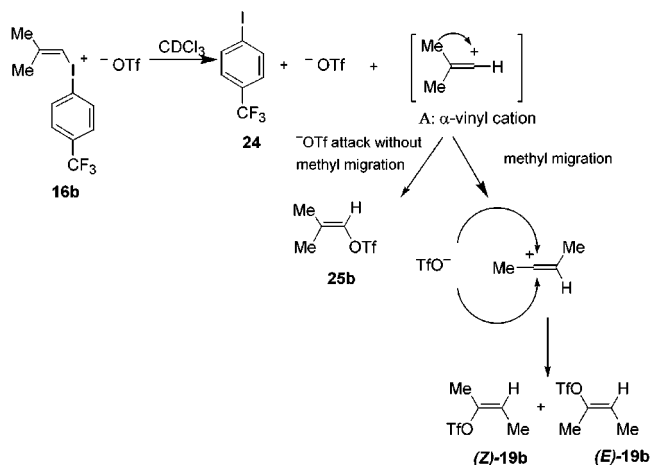
We monitored the reaction of one of the most reactive salts (**17e**) at 20, 25, 30, and 35 °C in order to obtain activation parameters. This salt conveniently fragments near room temperature over the course of a few hours. Activation parameters for fragmentation of salt **17e** were calculated using the Arrhenius equation: $E_a = 26.8$ kcal/mol, $\Delta H^\ddagger = 26.2$ kcal/mol, and $\Delta S^\ddagger = 11.9$ cal/mol·K.

The average rate constants of disappearance of starting materials of the phenyl-, 4-trifluoromethylphenyl-, and 3,5-bis(trifluoromethyl)phenyl-substituted salts (**15e**, **16e**, and **17e**, respectively) were compared. A Hammett plot of kinetic data at 35 °C (σ vs $\log(k/k_0)$) was constructed using $\sigma = 0.00$ (parent phenyl), $\sigma = 0.54$ (*p*-CF₃), and $\sigma = 0.86$ ($2 \times m$ -CF₃).^{33,34} The effect of the electron-withdrawing groups on the fragmentation rate revealed a ρ value of 1.7.

Fragmentations of a variety of salts were analyzed by GC–MS for the relative ratios of the six isomeric enol triflates (Table 3). The last two columns contain the relative amounts of retention and inversion products for nonrearranged enol triflates; these could be produced via triflate trapping of a primary vinyl cation. The most significant general trend is that the products arise predominantly from migration of the *trans*-alkyl group rather than the *cis*-alkyl moiety. The unrearranged products were generated in the lowest quantities. Finally, we evaluated the product ratios for fragmentation of salt **17e** in CDCl₃ at three other temperatures (20, 30, and 35 °C). GC–MS analysis shows that the stereoisomers of the unrearranged products were generated in approximately a 1:1 ratio (ret/inv). This is what one would expect for an S_N1 process.

Discussion

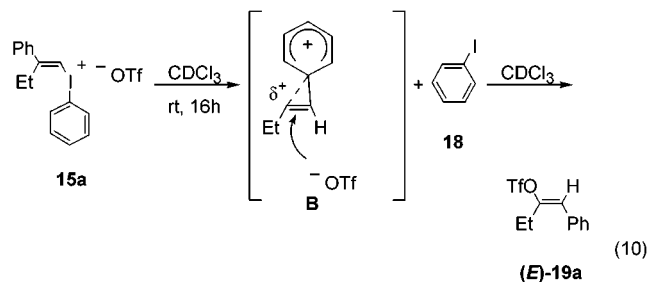
Mechanistic Hypothesis. To account for both **25b** as well as (*E*)-**19b** and (*Z*)-**19b** (eq 9, *vide supra*), we proposed the primary vinyl cation intermediate **A** shown in Scheme 1. Initial heterolytic cleavage of the carbon–iodine bond would afford aryl iodide **24** and primary vinyl cation **A**. The triflate counterion could then trap the resulting vinyl cation directly to generate the “unrearranged” enol triflate **25b**. The unrearranged product **25b** could also arise by direct S_N2 displacement of the

Scheme 1. Observed Products from Rearrangement of Iodonium Salt **16b in CDCl₃**

iodoarene.³⁵ Given that there is little solvent dependence on the rate of heterolysis in the solvolysis of 4-*tert*-butylcyclohexenyl(phenyl)iodonium tetrafluoroborate,⁸ if this primary cation is involved, the cation and triflate are undoubtedly an ion pair.

A mechanism to account for both (*E*)- and (*Z*)-**19b** requires a rearrangement. Migration of the methyl either *cis* or *trans* to the original arylidonium moiety via an S_N1 process followed by triflate anion trapping could explain the formation of both (*E*)- and (*Z*)-**19b**. Although the primary carbocation **A** could be involved, a *trans*-methyl shift with concerted departure of the arylidonium moiety followed by a hydride migration is also possible.³⁶ Alkyl migrations are well-known to occur in carbenium ion chemistry, and this is especially true for unsaturated cations.²

For **15a**, the lone enol triflate isolated ((*E*)-**19a**) indicates that phenyl migration occurred even in a highly polar, relatively nucleophilic solvent such as MeOH. The additional alkyl group β - to the iodonium moiety in **15a** could contribute in two ways to this phenomenon: (a) provide an increase in electron density at the site of migration leading to an increase in the rate for this step, and (b) greater steric crowding at the β -position could compress the bond angle between the phenyl group and the reacting carbon center to promote migration. On the basis of the fact that (*E*)-**19a** was the only enol triflate isolated, the fragmentation of this salt undoubtedly occurs via an unsymmetrical phenonium ion (**B**, eq 10) followed by triflate trapping in CDCl₃ (or solvent in MeOH). Okuyama and co-workers also proposed that a



(33) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper & Row: New York, 1987; p 144.

(34) For multiple substituents contained on an aromatic ring, σ values are additive. Hammett, L. P. *Physical Organic Chemistry*, 2nd ed.; McGraw-Hill: New York 1970; p 367.

(35) A theoretical study of vinylic S_N2 vs Ad_N-E mechanisms indicates that S_N2 reactions are indeed possible depending on the symmetry of the orbitals involved. Lucchini, V.; Modena, G.; Pasquato, L. *J. Am. Chem. Soc.* **1995**, *117*, 2297–2300.

Table 3. Relative Percentages of Products for Fragmentations of Various Salts in CDCl₃^a

salt	R ₁	R ₂	Ar	T (°C)	R ₁ migration	R ₂ migration	retention ^b	inversion ^c
16c	Et	Me	4-(CF ₃)C ₆ H ₄	25	21	36	7	35
17c	Et	Me	3,5-(CF ₃) ₂ C ₆ H ₄	50	35	51	4	9
17c^d	Et	Me	3,5-(CF ₃) ₂ C ₆ H ₄	50	29	52	4	14
17d	Me	Et	3,5-(CF ₃) ₂ C ₆ H ₄	40	43	53	2	2
15e	Bu	Et	Ph	25	13	76	3	8
16e	Bu	Et	4-(CF ₃)C ₆ H ₄	25	18	70	4	7
17e	Bu	Et	3,5-(CF ₃) ₂ C ₆ H ₄	20	20	70	5	5
17e	Bu	Et	3,5-(CF ₃) ₂ C ₆ H ₄	25	16	72	6	5
17e	Bu	Et	3,5-(CF ₃) ₂ C ₆ H ₄	30	16	72	6	6
17e	Bu	Et	3,5-(CF ₃) ₂ C ₆ H ₄	35	21	68	5	5
15f	Et	Bu	Ph	25	14	68	6	13
17f	Et	Bu	4-(CF ₃)C ₆ H ₄	25	29	59	5	7

^a Numbers may not exactly add to 100 because of rounding. ^b Retention refers to the stereoisomeric enol triflate in which the OTf moiety is in the same relative position as the iodoaryl moiety in the starting salt. ^c Inversion refers to the stereoisomeric enol triflate in which the OTf moiety is in the opposite relative position as the iodoaryl moiety in the starting salt. ^d 1.0 equiv of added Bu₄NOTf.

phenonium ion was an intermediate in the reaction between (*E*)-styryl(phenyl)iodonium tetrafluoroborate salt and 2,2,2-trifluoroethanol.^{30,37} However, their β -mono-substituted styryl analogue was much less reactive, and the reaction required 76 h at 50 °C in AcOH. In accord with Apeloig and co-worker's¹⁷ calculations, this phenomenon clearly shows how much cation stability is gained by addition of a second substituent β to the nucleofuge. Further, it indicates that the phenyl migration is intimately involved in iodobenzene departure.

In MeOH, the mixture of enol ethers (**20**) could arise from alkylidenecarbene formation, rearrangement, and addition of methanol.^{9c} However, a mixture of enol triflates would undoubtedly result from such a mechanistic pathway, and we only observed (*E*)-**19a**.

Despite the above results indicating cationic involvement, the lack of stereochemistry in the starting vinyl iodonium salt **16b** did not allow a thorough analysis; it merely suggested that primary vinyl cations could be involved in the fragmentations.

Thermodynamics. The most significant of the thermodynamic values obtained for the transition state are the positive entropy of activation. The ΔS^\ddagger value (11.7 cal/mol) is larger and opposite in sign to that obtained from enol triflate solvolyses and indicates an increase in disorder at the transition state as the arylidonio moiety departs to create the vinyl cation. On the other hand, the ΔS^\ddagger is consistent with the value obtained by Okuyama and co-workers with the cyclic secondary vinyl cation developed from 4-*tert*-butylcyclohexenyl(phenyl)iodonium tetrafluoroborate **1**.⁸ We believe that the heterolytic cleavage of the vinylic C–I bond and *trans*-alkyl migration are concerted events, but not synchronous (i.e., departure of the arylidonio nucleofuge slightly precedes alkyl migration). The ΔH^\ddagger value is very similar to that obtained from solvolyses of enol triflates,³⁸ and the E_a value is what is expected of reactions occurring near ambient temperature.

(36) A recent report indicates that a cyclohexylidene(phenyl)iodonium salt rearranges exclusively with concerted shift of the alkyl portion of the ring *trans* to the departing iodophenyl moiety. However, the electron-withdrawing nature of our arylidonio salts result in a >1 order of magnitude increase in leaving group ability. With the phenylidonio moiety described by Fujita and co-workers, 60 °C was required for reaction; this could have provided the energy necessary for facile migration of the *trans*-alkyl group during fragmentation. Fujita, M.; Sakanishi, Y.; Okuyama, T. *J. Am. Chem. Soc.* **2000**, *122*, 8787–8788.

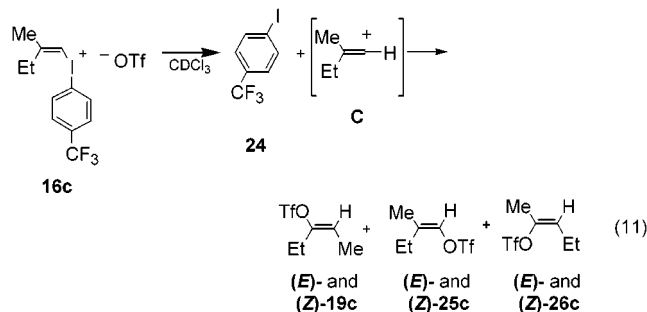
(37) Okuyama, T.; Ishida, Y.; Ochiai, M. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 163–170.

(38) Summerville, R. H.; Senkler, C. A.; Schleyer, P. v. R. Dueber, T. E.; Stang, P. J. *J. Am. Chem. Soc.* **1974**, *96*, 1100–1109.

The Hammett ρ value (1.7) reveals another interesting trend with respect to the electron-withdrawing character of the arylidonio moiety. This positive number is consistent with an increase in the nucleofugality of the arylidonio portion of the salts. In the case of the iodonium salts, the electron-withdrawing groups present in the aromatic ring create an increase in the net positive charge on the iodine atom prior to the transition state. This weakens the vinylic C–I bond to facilitate heterolytic cleavage to the vinyl cation and aryl iodide. However, this Hammett effect would also be present even if arylidonio departure and R₂ migration are concerted and lead directly to a secondary vinyl cation rather than a primary one.

Another mechanism that must be at least considered involves homolytic cleavage of the vinylic C–I bond to create a iodoarene cation radical followed by single electron transfer (SET). However, the observed Hammett value is inconsistent with this mechanism as there is no change in charge at the transition state for homolytic cleavage and the developing iodoarene radical cation would be destabilized by electron-withdrawing groups. Further, no products derived from radical processes (i.e., simple alkenes) were detected by GC–MS even in the presence of the hydrogen donor 1,4-cyclohexadiene.

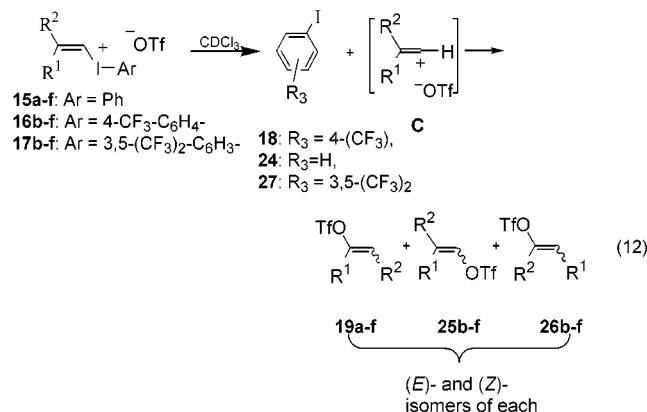
Product Distribution. Fragmentation (eq 11) of (*Z*)-2-methyl(4-trifluoromethyl-phenyl)iodonium triflate (**16c**) was accomplished in CDCl₃. Solvolyses are typically



carried out in polar solvents such as MeOH, H₂O, etc. However, fragmentations of 4-*tert*-butylcyclohexenyl(phenyl)iodonium tetrafluoroborate were affected very little by solvent polarity,⁸ and iodonium salts containing a α -H tend to react via other mechanisms with solvents such as MeOH.^{9c} Kinetics for many of the individual reactions were obtained (Table 2, *vide supra*), and product ratios were determined by GC–MS. Products

were then verified by co-injection with authentic samples.³⁹ Table 3 reveals some interesting trends with regard to the reaction manifolds operative in the reactions. For **16c**, the methyl group that is trans to the iodoarene migrates to a greater extent than the *cis*-ethyl moiety to give isomers of **19** and **26**, respectively. The unrearranged enol triflates (**25c**) are the least abundant products. Although this is true regardless of the temperature at which the fragmentations occurred, decreasing temperature leads to an increase in the relative amounts of unrearranged isomers for salt **16c** and **17c**.

To learn more about the structure of the carbenium ion intermediate, we evaluated the fragmentation of other unsymmetrically substituted iodonium salts **15e**, **16e** as well as **17c**, **17d**, and **17e** (eq 12). On the basis of



ab initio calculations,^{2,17,40} only the parent, unsubstituted cation is a nonclassical, bridged species in its lowest energy conformation. Addition of substituents correspondingly lowers the energy of the classical, linear vinyl carbenium ion. In the classical form, migration of either the *cis* or *trans* substituents to the primary cationic center would afford a more stable, linear secondary cation. It should be noted, however, that once the secondary cation is formed, rapid 1,2-hydride transfers are possible (especially at higher temperatures) leading to other enol triflate products. Okuyama and co-workers recently noted that the transition states for hydride migration are very low in energy (MP2/6-31G(d)).^{9c,41}

We examined several different iodonium salts with varying β -alkyl groups (Table 3, vide supra). New data that sheds light on the mode(s) of fragmentation include the amounts of inversion and retention product enol triflates. For the classical, cation, **C** (eq 12) in which the cationic carbon is sp²-hybridized, migration of either the *cis*- or *trans*-alkyl (R¹ or R²) group should occur in equal amounts. In all cases studied, the alkyl group that is trans to the arylidonio nucleofuge migrated to a greater extent than the group that was *cis*. The most likely explanation for this phenomenon is anchimeric assistance by the *trans*- β -alkyl moiety accompanies departure of the nucleofuge. This group is stereoelectronically positioned to participate in C–I bond cleavage in the rate-determining-step of the fragmentation. The high reactivity of **15a**

implies that participation of this moiety is important to the rate of reaction.

Products that are listed as those arising from *cis*-alkyl migration (R₁ migration) could also be generated by *trans*- β -alkyl shift (R² migration) followed by 1,2-hydride migration. This product would be indistinguishable from that derived from exclusive migration of the *cis*-alkyl (R¹) moiety. The transition state for 1,2-hydride shift in the 2-butenyl cation was calculated to be merely 0.32 kcal/mol above the energy of the linear cation, and the stabilities of the two possible secondary vinyl cations should be nearly identical.^{9c,41} Further, the increasing the size of the *trans*-alkyl moiety significantly increases the rate of fragmentation. Entries 1 and 2 in Table 2 show that **17c** is significantly more labile toward fragmentation than **17d**. Specifically, for the *E*-isomer **17c**, the average first-order rate constant was found to be $2.12 \times 10^{-4} \text{ s}^{-1}$ at 40 °C, whereas a similar rate constant for the *Z*-isomer **17d** is achieved 10 °C higher in temperature. This indicates that participation by the *trans*- β -substituent is important in the fragmentation process and that in the vinylic system the ethyl moiety has a higher migratory aptitude than methyl. Qualitatively, other salts containing a *trans*-methyl substituent were more stable with respect toward fragmentation than those with larger *trans*-alkyl groups such as Et or Bu. This made full spectroscopic characterization easier for *trans*- β -methyl salts.

Unrearranged Enol Triflate Products. A significant portion of the product mixture (Table 3, vide supra) is derived from attack of the triflate anion *without* alkyl migration. There are five possible routes to the *unrearranged* enol triflates **25b–f**: (a) alkylidene-carbene formation followed by reaction with TfOH;⁴² (b) an addition–elimination (Ad_N-E) pathway; (c) S_N2 reaction with the triflate ion as the nucleophile;⁴³ (d) λ^3 iodane formation followed by a reductive elimination (i.e., ligand coupling);⁴⁴ and (e) S_N1 fragmentation.

Alkylidene-carbene formation is facile with alkenyl-(phenyl)iodonium salts that contain an α -hydrogen. Typically, weak bases such as triethylamine can be used to directly generate the free carbenes.⁴⁵ In the present cases, it is exceedingly unlikely that the very weakly basic triflate anion promotes α -deprotonation. It is possible that adventitious water does cause some alkylidene-carbene formation. To minimize this possibility, we distilled the chloroform, stored it over molecular sieves, and conducted the reactions in oven-dried glassware. Further, in the moderately polar, nonnucleophilic solvent, CDCl₃, we do not observe products derived from alky-

(42) Onium salts have been generated by alkylidene-carbene pathways: Ochiai, M.; Sueda, T.; Noda, R.; Shiro, M. *J. Org. Chem.* **1999**, *64*, 8563–8567. Nagaoka, T.; Sueda, T.; Ochiai, M. *Tetrahedron Lett.* **1995**, *36*, 261–264.

(43) Formal S_N2 reactions are documented for simple alkylvinyl-(phenyl)iodonium salts: (a) Okuyama, T.; Takino, T.; Sago, K.; Ochiai, M. *J. Am. Chem. Soc.* **1998**, *120*, 2275–2282. (b) Ochiai, M.; Yamamoto, S.; Sato, K. *J. Chem. Soc. Chem. Commun.* **1999**, 1363–1364. (c) Okuyama, T.; Takino, T.; Sato, K.; Oshima, K.; Imamura, S.; Yamataka, H.; Asano, T.; Ochiai, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 243–257. (d) Ochiai, M.; Ochiai, K.; Masaki, Y. *J. Am. Chem. Soc.* **1991**, *113*, 7059–7066.

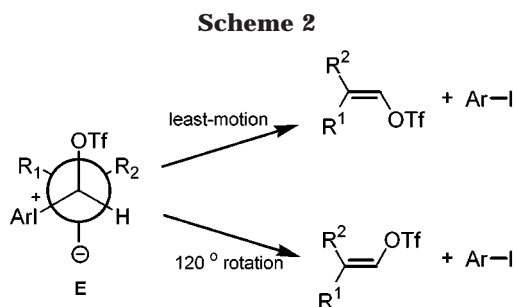
(44) Ligand coupling and vinylic S_N2 were studied computationally. Favored modes of reactivity varied according to both substitution of the salt and medium effects: Okuyama, T.; Yamataka, H. *Can. J. Chem.* **1999**, *77*, 577–583.

(45) Ochiai, M.; Takaoka, Y.; Nagao, Y. *J. Am. Chem. Soc.* **1988**, *110*, 6565–6566. Sueda, T.; Nagaoka, T.; Goto, S.; Ochiai, M. *J. Am. Chem. Soc.* **1996**, *118*, 10141–10149.

(39) Stereochemistry of the unrearranged enol triflates was assigned based on the literature chemical shifts in the ¹H NMR spectrum. For chemical shift assignments, see: Stang, P. J.; Mangum, M. G.; Fox, D. P.; Haak, P. *J. Am. Chem. Soc.* **1974**, *96*, 4262–4269.

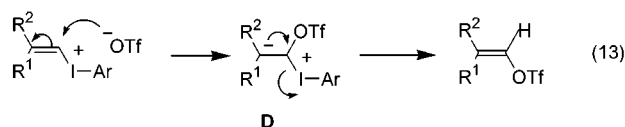
(40) Lindh, R.; Rice, J. E.; Lee, T. J. *J. Chem. Phys.* **1991**, *94*, 8008–8014.

(41) Okuyama, T.; Sato, K.; Ochiai, M. *Chem. Lett.* **1998**, 1177–1178.



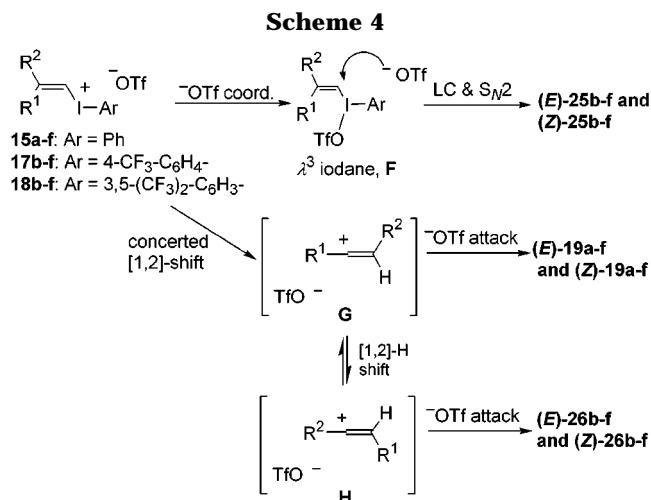
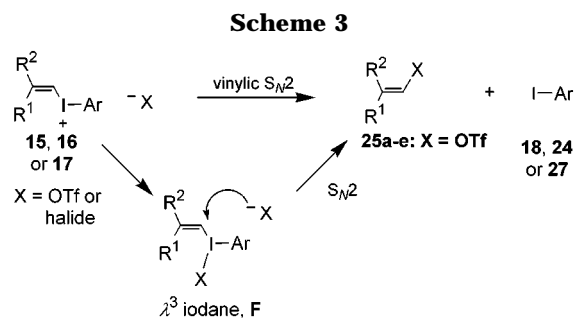
lidenecarbene formation even when larger salts such as **17e** are examined or when cyclohexene was added during fragmentation. In the presence of bases such as triethylamine, added cyclohexene provided adducts expected from alkylidene-carbene reaction with the alkene (GC-MS). Further, both **17e** and **17f** should provide significant quantities of 1-ethyl-2-methylcyclopentene if carbenes were involved.

A $\text{Ad}_N\text{-E}$ mechanism has been documented for alkenyl(phenyl)iodonium tetrafluoroborates that contain an anion-stabilizing group.^{46,47} Addition of benzenesulfinate occurred at the vinylic carbon α - to the arylidonio group to produce a stabilized intermediate. To our knowledge, this is the only example of an $\text{Ad}_N\text{-E}$ process occurring with alkenyl(aryl)iodonium salts and is specific for those that contain atoms or groups which can either stabilize a negative charge in the intermediate or act as leaving groups. Addition of triflate in this fashion (eq 13) would lead to the exceedingly unstable intermediate, **D**, in which a negative charge would reside on a carbon bearing two alkyl groups.⁴⁸ If this mechanism were solely opera-



tive, we would expect to see the major product be the "retention" product shown because of the same least-motion argument that Ochiai and co-workers cite in their studies with benzenesulfinate (Scheme 2).^{47,48}

Halide displacement of iodoarenes from vinylic iodonium salts is known to occur with inversion of configuration. A complex mechanism operates in which a λ^3 iodane intermediate is formed followed by displacement of the arylidonio moiety to provide the formal $\text{S}_\text{N}2$ product of reaction (Scheme 3). Only inversion products were observed when weakly basic halides such as chloride were examined in the reaction. It should be pointed out, however, that the study was performed on less-hindered, monosubstituted (*E*)-alkenyl(phenyl)iodonium salts and the λ^3 iodane intermediate (**F**) also led to formal β -elimination (when $\text{R}^1 = \text{H}$) reactions to afford alkynes. Such an E2 process cannot occur in our systems, but may have simply been more rapid than ligand coupling for the β -monosubstituted salts.



Although much evidence (i.e., linearity of $\ln[A]/[A]_0$, Hammett ρ value and presence of six enol triflate isomers for fragmentation of **15c-f**, **16c-f**, and **17c-f**) indicates that $\text{S}_\text{N}1$ is possible in these systems, several other factors imply that other processes are occurring. These other mechanistic pathways are indicated as follows: (a) the increase in relative proportions of nonrearranged isomers (i.e., **25c-f**) at lower temperatures, (b) the increase in amount of inverted product in fragmentation of **17d** with exogenous triflate, and (c) the greater reactivity of **17d** vs **17c**. If heterolysis is occurring, it is accompanied by a shift of R^2 . Further, our calculations of the theoretical isodesmic hydride-transfer reaction (Table 1 and eqs 3 and 4) indicated that β,β -dimethyl vinyl cation **6** is 17.8 kcal/mol less stable than the secondary α,β -dimethyl cation **7**. Given the high temperatures required to study the solvolyses of 2-buten-1-yl triflate,³⁸ it is doubtful that the much less stable cation **6** is attainable in solution.

The preponderance of evidence indicates that fragmentation of alkenyl(aryl)iodonium salts occurs by several *simultaneous* processes (Scheme 4): (a) direct reaction with triflate anion via *both* $\text{S}_\text{N}2$ and ligand coupling (LC) mechanisms to afford nonrearranged enol triflates (*E*)- and (*Z*)-**25b-f** and (b) heterolytic cleavage of the vinylic C-I bond with participation of the *trans*-alkyl moiety to produce secondary vinyl cation **G**. Reaction of iodane **F** with triflate anion would afford both stereoisomers of **25b-f**. Due to a very low barrier to hydride migration, [1,2]-H shift undoubtedly occurs to provide secondary cation **H**, which is nearly degenerate to **G**. Trapping of this cation by triflate anion would provide both (*E*)- and (*Z*)-**26b-f**. Initial synchronous R^2 -shift and departure of the nucleofuge would afford two stereoisomeric pairs of enol triflates which we previously interpreted as those resulting from R^2 migration and R^1 migration from a primary vinyl cation (i.e., **C** in eq 12; vide supra).

(46) For salts containing a β -halogen, see: Ochiai, M.; Kitagawa, Y.; Toyonari, M.; Uemura, K.; Oshima, K.; Shiro, M. *J. Org. Chem.* **1997**, *62*, 8001-8008.

(47) For salts containing a β -sulfonyl moiety, see: Ochiai, M.; Oshima, K.; Masaki, Y. *Tetrahedron Lett.* **1991**, *32*, 7711-7714.

(48) Fujita and co-workers recently suggested that perpendicular attack of solvent on cyclohexylidene(phenyl)iodonium tetrafluoroborate was a viable explanation for nonrearranged solvolysis products. We believe that the anionic intermediate is unlikely in this case, but eagerly await subsequent publications. See ref 36.

Conclusions. We have examined the fragmentations of several β,β -disubstituted alkenyl(aryl)iodonium triflate salts. In chloroform, alkyl rearrangements occur that result from vinyl carbenium ions in solution. In all cases, the major enol triflate isomer was that which results from migration of the alkyl moiety that is trans to the aryliodonio nucleofuge. Anchimeric assistance provided by the *trans*-alkyl group is the most probable explanation for this phenomenon. In free, classical primary vinyl carbocations, the cationic carbon is linear and both the *cis* and *trans* moieties should migrate with equal facility. However, the low barrier to 1,2-hydride shifts in the incipient secondary vinylic carbocations does not allow one to definitively conclude that the products assigned as those derived from *cis* migration do not in fact result from *trans*-alkyl migration followed by rapid hydride shifts. When opposite stereoisomers (e.g., **17c** and **17d** as well as **17e** and **17f**) were examined, the amount of *trans* migration product detected was always greater than the amount of *cis*-migration product. This implies that the low barrier calculated for hydride shifts is in fact greater in solution than in the gas phase.

Nonrearranged enol triflates were also detected in the fragmentations. Further, *both* stereoisomers of these triflates were present in varying ratios, but usually with the inverted product predominant. Because of the increased amount of nonmigrated enol triflates at lower temperatures as well as the higher rate of fragmentation of salts containing either Ph (**15a**) or Et (vs Me in **17c** vs **17d**) *trans* to the aryliodonio moiety, we now believe that a primary vinyl cation is not involved. The most plausible explanation is that nonrearranged isomers are derived from both S_N2 and ligand coupling (LC) mechanisms. The presence of *all six* enol triflate isomers, the required migrations needed to account for four of the six products, and the kinetic data support a heterolytic mechanism, but one which involves alkyl migrations. We believe that the increase in rate of fragmentation with added triflate is due to an increase in the relative proportion of molecules undergoing S_N2 and LC reactions.

Experimental Section

General Methods. Reactions were carried out under nitrogen atmosphere unless otherwise indicated. ^1H and ^{13}C NMR spectra were recorded on a General Electric QE-300 spectrometer or a Varian Mercury 400 spectrometer, and chemical shifts are reported in ppm downfield from internal TMS or residual protons in the deuterated chloroform (δ 7.26). NMR kinetics of **17e** were performed on a GE QE300 spectrometer whereas salts **17c** and **17d** were analyzed on a Varian Mercury 400. IR spectra were obtained on a Perkin-Elmer 1600 FTIR as KBr pellets, and as films or neat on NaCl plates purchased from International Crystal Laboratories. Analytical gas chromatography was performed with a Supelco SPB-1 CFS 3005A (30 m \times 25 mm) column and an FID detector. GC-MS traces were recorded on a Hewlett-Packard 5890 series II gas chromatograph with an HP Ultra-1 cross-linked (methyl silicone gum; 12m \times 0.2 mm \times 0.33 mm) column, equipped with a 70 eV HP 5971A mass-selective detector. Gas chromatographic separations were achieved using a GOW-MAC Series 580 gas chromatograph with 12' \times 0.25" OD column (60/80 Chromosorb W, 15% SF-19). X-ray analysis was performed on a Melting points were obtained on a Hoover Thomas Uni-Melt capillary melting point device or a MelTemp apparatus and are uncorrected. Column chromatography was performed using flash grade silica gel purchased from Aldrich (60 Å, 200–400 mesh) or Fisher Scientific (60 Å, 200–430 mesh).

Materials. Dichloromethane was distilled from CaH_2 , and Fisher hexanes and ethyl acetate were used as received. All reagents were used as received unless otherwise noted. 1-Phenyl-2-butanone, di-*tert*-butyl-4-methylpyridine, 1-phenyl-1-butyne, 2-butyne, 4-trifluorophenyl-iodobenzene, iodobenzene, isobutyraldehyde, CDCl_3 , and alumina (basic, 58 Å, 150 mesh) were purchased from Aldrich Chemical Co. Triflic anhydride⁴⁹ was synthesized by a standard procedure from triflic acid, which was purchased from 3M. *n*-Butyrophenone, 4-iodobenzotrifluoride, and 1-iodo-3,5-bis(trifluoromethyl)benzene were purchased from Acros division of Fisher Scientific. Iodobenzene, tributyl tin chloride, and 1,2-dibromoethane were purchased from Aldrich Chemical Co. Hydrogen peroxide (50%) was purchased from Fisher and nitrogen was purchased from Air Products. Several of the salts (**15a–f**),²⁷ **16b**^{9b} and (**16c,e,f**, and **17c,f**)^{9a} have been reported previously.

General Procedure for the Preparation of Alkenyl(aryl)iodonium Triflates 16–18: Synthesis of 2-Methyl-1-propenyl(4-trifluoromethylphenyl)iodonium Triflate (16b). Cyano(4-trifluoromethylphenyl)iodonium triflate, **13** (2.26 g, 5.0 mmol), was weighed into a 250 mL round-bottom flask equipped with a magnetic stir bar. Dichloromethane (80 mL) was added and the suspension cooled to -43°C . 2-Methyl-1-propenyl tri-*n*-butylstannane, **11b** (2.06 g, 5.1 mmol), was added via syringe and the suspension stirred for 30 min. Additional dichloromethane (80 mL) was added and the reaction vessel allowed to warm to 0°C over 25 min. During this time, the suspension became light yellow and homogeneous. Diethyl ether (15 mL) and pentane (80 mL) were added to provide a cloudy solution that was placed in a freezer (-15°C) for 48 h. The resulting analytically pure colorless needles of **16b** (1.56 g, 65%) were isolated by vacuum filtration on a medium porosity fritted funnel: mp $120\text{--}122^\circ\text{C}$ dec; IR (KBr) 3088, 1597, 1439, 1401, 1323, 1245, 1181, 1140, 1107, 1067, 1031, 1002, 836, 826, 758, 638, cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 8.09 (d, $J = 8.4$ Hz, 2H), 7.71 (d, $J = 8.4$ Hz, 2H), 6.76 (s, 1H), 2.23 (s, 3H), 2.21 (s, 3H). Anal. Calcd for $\text{C}_{12}\text{H}_{11}\text{F}_6\text{IO}_3\text{S}$: C, 30.27; H, 2.33. Found: C, 30.32, H, 2.32.

Preparation of (Z)-2-Methyl-1-butenyl(4-trifluoromethylphenyl)iodonium Triflate (16c). (Z)-2-Methyl-1-butenyl(4-trifluoromethylphenyl)iodonium triflate **16c** was prepared via the general procedure from cyano(4-trifluoromethylphenyl)iodonium triflate, **13** (0.24 g, 0.54 mmol), and (Z)-2-methyl-1-propenyl tri-*n*-butylstannane, **11c** (0.21 g, 0.59 mmol), in 57% yield: mp $53\text{--}55^\circ\text{C}$. IR (KBr) 3056, 2974, 1595, 1400, 1323, 1251, 1174, 1159, 1133, 1066, 1031, 1000, 826, 769, 635 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ 8.10 (d, $J = 8.4$ Hz, 2H), 7.68 (d, $J = 8.4$ Hz, 2H), 6.74 (s, 1H), 2.51 (q, $J = 7.5$ Hz, 2H), 2.21 (s, 3H), 1.06 (t, $J = 7.5$ Hz, 3H). ^{13}C (CDCl_3 , 100 MHz) δ 162.6, 134.6, 128.3, 128.2, 115.2, 94.7, 33.1, 22.7, 12.1.

Preparation of (E)-2-Methyl-1-butenyl(4-trifluoromethylphenyl)iodonium Triflate (16d). (E)-2-Methyl-1-butenyl(4-trifluoromethylphenyl)iodonium triflate **16d** 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, **11d** (0.387 g, 1.08 mmol), in 70% yield: mp $83\text{--}85^\circ\text{C}$; 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 (CDCl_3 , 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); ^{13}C (CDCl_3 , 100 MHz) δ 163.5, 134.6, 134.0, 128.2, 114.8, 94.7, 32.6, 24.8, 12.2. Anal. Calcd for $\text{C}_{13}\text{H}_{13}\text{F}_6\text{IO}_3\text{S}$: C, 31.85; H, 2.67; S, 6.54. Found: C, 31.64; H, 2.73; S, 6.63.

Preparation of (E)-2-Methyl-1-butenyl(3,5-bis(trifluoromethyl)phenyl)iodonium Triflate (17d). (E)-2-Methyl-1-butenyl(3,5-bis(trifluoromethyl)phenyl)iodonium triflate **17d** was prepared via the general procedure from cyano(4-trifluoromethylphenyl)iodonium triflate, **14** (0.401 g, 0.78 mmol), and (E)-2-methyl-1-propenyl tri-*n*-butylstannane, **11d** (0.34 g, 0.93

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mmol), in 49% yield: mp 67–69 °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, cm^{-1} ; ^1H NMR (CDCl_3 , 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 $\text{C}_{14}\text{H}_{12}\text{F}_9\text{IO}_3\text{S}$: C, 30.12; H, 2.17; S, 5.74. Found: C, 30.39; H, 2.29; S, 5.77.

Preparation of (Z)-2-Ethyl-1-hexenyl(4-trifluoromethylphenyl)iodonium Triflate (16e). (Z)-2-Ethyl-1-hexenyl(4-trifluoromethylphenyl)iodonium triflate was prepared according to the general procedure using cyano(4-trifluoromethylphenyl)iodonium triflate, **13** (0.12 g, 0.27 mmol), and (Z)-2-ethyl-1-hexenyl tri-*n*-butylstannane, **11d** (0.12 g, 0.30 mmol), to afford **16e** as a white crystalline solid in 65% yield: mp 38–40 °C; IR (KBr) 3087, 2963, 2872, 1596, 1466, 1400, 1325, 1277, 1249, 1169, 1128, 1067, 1029, 1000, 823, 771, 680, 662, 638 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.07 (d, $J = 8.4$ Hz, 2H), 7.71 (d, $J = 8.4$ Hz, 2H), 6.71 (s, 1H), 2.43–2.53 (m, $J = 7.5$ Hz, 4H), 1.60–1.67 (m, 2H), 1.26–1.33 (m, 2H), 1.14 (t, $J = 7.5$ Hz, 3H), 0.90 (t, $J = 7.5$ Hz, 3H). Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{F}_6\text{SO}_3\text{I}$: C, 36.10; H, 3.60; S, 6.02. Found: C, 36.39; H, 3.48; S, 5.82.

Preparation of (Z)-2-Ethyl-1-hexenyl(3,5-bis(trifluoromethyl)phenyl)iodonium Triflate (17e). (Z)-2-Ethyl-1-hexenyl(3,5-bis(trifluoromethyl)phenyl)iodonium triflate was prepared according to the general procedure using cyano(3,5-bis(trifluoromethyl)phenyl)iodonium triflate, **14** (0.120 g, 0.23 mmol), and (Z)-2-ethyl-1-hexenyl tri-*n*-butylstannane, **11e** (0.11 g, 0.27 mmol), to afford 0.10 g (72%) of **17e** as a white crystalline solid: mp 83–84 °C; IR (KBr) 3015, 2970, 2862, 2369, 1739, 1718, 1436, 1364, 1343, 1277, 1226, 1144, 1082, 1034, 892, 739, 697, 636 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.07 (s, 2H), 8.05 (s, 1H), 6.81 (s, 1H), 2.53 (q, $J = 7.3$ Hz, 2H), 2.48 (t, $J = 7.1$ Hz, 2H), 1.29–1.38 (m, 4H), 1.14 (t, $J = 7.3$ Hz, 3H), 0.90–0.95, (overlapping m, 2H), 0.88 (t, $J = 7.1$ Hz, 3H). Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{F}_9\text{SO}_3\text{I}$: C, 34.02; H, 3.02; S, 5.32. Found: C, 34.01; H, 3.06; S, 5.52.

Preparation of (E)-2-Ethyl-1-hexenyl(4-trifluoromethylphenyl)iodonium Triflate (16f). (E)-2-Ethyl-1-hexenyl(4-trifluoromethylphenyl)iodonium triflate was prepared via the general procedure from cyano(4-trifluoromethylphenyl)iodonium triflate, **13** (0.20 g, 0.45 mmol), and (E)-2-ethyl-1-hexenyl tri-*n*-butylstannane, **11d** (0.35 g, 0.87 mmol), in 63% yield: mp 54–56 °C; IR (KBr) 3076, 2964, 2871, 1594, 1466, 1400, 1323, 1251, 1179, 1128, 1066, 1046, 1025, 1000, 830, 769, 661, 635 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.07 (d, $J = 8.4$ Hz, 2H), 7.71 (d, $J = 8.4$ Hz, 2H), 6.68 (s, 1H), 2.45–2.52 (m, 4H), 1.40–1.55 (m, 2H), 1.25–1.37 (m, 2H), 1.06 (t, $J = 7.5$ Hz, 3H), 0.91 (t, $J = 7.5$ Hz, 3H).

Isolation of (E)-19a Fragmentation of (E)-1-Phenyl-1-buten-1-yl Trifluoromethanesulfonate ((E)-15a) in Chloroform. Iodonium salt **15a** (0.200 g, 0.413 mmol) was weighed into an oven-dried 25 mL round-bottom flask equipped with a magnetic stir bar and 2.0 mL of chloroform added. The homogeneous solution was stirred at room temperature for 12 h, during which time the solution turned dark brown. Silica gel (ca. 1.5 g) was added and the solvent removed in vacuo on a rotary evaporator. The adsorbed product mixture was chromatographed on 10 g of SiO_2 using hexanes followed by 98/2 hexanes/EtOAc as eluant to provide 0.059 g (51%) of (E)-**19a** as a colorless liquid: R_f (98/2 hexanes/EtOAc) 0.29; IR (neat, NaCl) 3074, 3033, 2981, 2941, 1416, 1242, 1211, 1140, 1110, 1074, 1036, 954, 921, 899, 823, 754, 726, 697 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.20–7.50 (m, 5H Ar), 6.60 (s, 1H, vinyl), 2.61 (q, $J = 7.5$ Hz, 2H), 1.21 (t, $J = 7.5$ Hz, 3H); ^{13}C -{ $^1\text{H}}$ } (CDCl_3 , 125 MHz) δ 152.3, 131.6, 127.7, 127.6, 127.1, 120.8, 117.6 (q, $J = 320$ Hz, CF_3), 23.2, 10.1.

Fragmentation of 15a in MeOH. Iodonium salt **15a** (0.300 g, 0.619 mmol) was added to a 25 mL round-bottom flask equipped with a magnetic stir bar. MeOH (3.0 mL) was added and the solution stirred for 16 h at room temperature. Water (2 mL) and pentane (5 mL) were added with rapid

stirring, and the pentane layer was examined by gas chromatography and GC–MS and compared to authentic samples. HCl (2.0 mL, 1.0 M) was then added to the two-layer system and the system stirred vigorously for 30 min at room temperature. The organic phase was separated and the aqueous phase extracted with pentane (5×3.0 mL). The pentane was dried (MgSO_4) and concentrated under reduced pressure to ca. 3 mL. The organic layer was again analyzed by GC–MS, concentrated further, and chromatographed on silica gel with hexanes and 98/2 hexanes/EtOAc as eluants; iodobenzene (**18**, 0.067 g, 53%), 1-phenyl-1,2-butadiene (**22**, 0.020 g, 25%) and 1-phenyl-2-butanone (**23**, 0.032 g, 35%) were recovered. Neither (E)-**19a** nor 1-phenyl-1-butyne (**21**) was recovered, but their presence was verified by GC–MS analysis of authentic samples.

1-Phenyl-1,2-butadiene (22).²⁹ This elimination product was isolated as described above to provide 0.020 g (25%) of **24** as a light yellow liquid: IR (neat, NaCl) 3044, 3029, 2991, 2921, 1945 (allene), 1595, 1494, 1464, 1370, 1264, 1069, 873; ^1H NMR (CDCl_3 , 300 MHz) δ 7.30–7.20 (m, 5H), 6.12–6.07 (m, 1H), 5.58–5.49 (m, 1H), 1.80–1.77 (dd, $J = 3.0, 7.0$ Hz, 3H); ^{13}C { $^1\text{H}}$ } NMR (CDCl_3 , 125 MHz) δ 206.0 (central carbon), 135.1, 128.5, 128.1, 126.6, 94.0, 89.6, 14.1; GC–MS m/z for $\text{C}_{10}\text{H}_{10}$, 130.

Kinetic Procedures. The alkenyl(aryl)iodonium triflate (ca. 15 mg) was weighed into an oven-dried NMR tube. Chloroform-*d* was filtered through a short plug of basic aluminum oxide to remove any acidic impurities and then placed in a separate NMR tube. The variable temperature probe on the 300 MHz NMR was set to the appropriate temperature (between 20 and 35 °C) and the chloroform-*d* was allowed to equilibrate to the probe temperature. Then the chloroform-*d* (0.5 mL) was added to the sample tube via syringe and the timing begun. Either glyme or 1,2-dibromoethane (2 μL) was then added as an internal standard. The cap was sealed with Parafilm and the sample was placed in the NMR spectrometer. Spectra were obtained in timed intervals through at least one half-life. Integration was used to determine the concentrations of each species at time *t*.

The rate constants (*k*) were determined from the slope of the first-order rate law plot: $\ln [A]_t/[A]_0$ vs time. The initial concentration ($[A]_0$) was determined by averaging the total concentration calculated via integration (i.e., $[\text{mol}_{\text{starting material}} + \text{mol}_{\text{decomposed product}}]/0.5\text{ mL solvent}$). The concentration at time *t* ($[A]_t$) was determined by the relative integration of the fragmented product to that of the internal standard. The time was considered to be halfway through the pulse sequence for each spectrum (e.g., for 256 pulses (13 min 58 s), halfway was considered to be 128 pulses (6 min 59 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.

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Supporting Information Available: Isodesmic reaction equations, plot of **17e** at 20–35 °C; table of G2 data; GC trace of product mixture from **15a**; ^1H and ^{13}C NMR spectra of allene **22** and enol triflate **19a**; a copy of the Hammett plot (**15e**, **16e**, **17e**) and representative kinetic plots of disappearance of iodonium salts **15e**, **16e**, **17c**, and **17e**; copies of representative GC MS traces (**15e**, **15f**, and **16c**) of fragmentation. This material is available free of charge via the Internet at <http://pubs.acs.org>.