

Facile Fragmentations of Alkenyl(aryl)iodonium Triflates

Robert J. Hinkle* and David B. Thomas

Department of Chemistry, The College of William & Mary,
P.O. Box 8795, Williamsburg, Virginia 23187-8795

Received June 23, 1997

The last 10–15 years have witnessed a great explosion in the synthesis and uses of hypervalent iodine compounds.^{1,2} Because of the labile aryliodonio moiety, alkenyl(aryl)iodonium salts display significant reactivity as electrophiles in copper-mediated nucleophilic substitutions,³ palladium-catalyzed coupling reactions,⁴ and nucleophilic substitution by enolates.⁵ Ochiai, Okuyama, and co-workers recently quantified the nucleofugality of the phenyliodonio moiety as 10⁶ more reactive than the triflate group. They also reported some elimination product from solvolysis of *trans*-1-decen-1-yl(phenyl)iodonium tetrafluoroborate.⁶

In our use of β -disubstituted alkenyl(aryl)iodonium salts in which the aryl moiety is either phenyl or contains the 4-trifluoromethyl moiety, we observed and report herein remarkably facile fragmentation pathways which may occur *via* the intermediacy of a simple primary vinyl cation and a phenonium ion.^{7–9} To the best of our knowledge, one of the rearrangements we observe represents the first example of leaving group departure (*in absence* of any exogenous nucleophile) from a primary vinyl compound which is neither a cyclopropylidene derivative, nor contains a β -stabilizing group such as phenyl. Although the disubstituted substrates examined fragment and rearrange easily, they are not prone to direct E2 elimination because they lack hydrogen atoms β to the iodonium moiety.

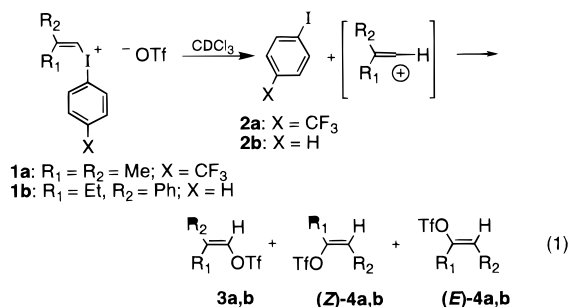
2-Methyl-1-propenyl(4-(trifluoromethyl)phenyl)iodonium triflate (**1a**) was synthesized¹⁰ using 4-(trifluoromethyl)phenyl(cyano)iodonium triflate.¹¹ Salt **1b** was previously reported.¹⁰ The new salt **1a** was characterized by ¹H NMR spectroscopy as well as IR and combustion analysis.¹² Although **1a** does slowly decompose at room

temperature, it can easily be handled at normal temperatures and stored >10 months at –15 °C.

Salt **1a** readily reacts in CDCl₃ and MeOH at elevated temperatures (60–65 °C). A new ¹H NMR spectrum after decomposition in chloroform revealed that 4-(trifluoromethyl)iodobenzene was generated. New proton resonances also appeared at δ 6.40 (br s), 5.60 (q), and 5.34 (q). Four components were identified by GC MS as *p*-(trifluoromethyl)iodobenzene **2a**, and three enol triflates with M⁺ = 204 (*m/z*).

We then synthesized the possible vinyl triflates (**3a**, (*Z*)-**4a** and (*E*)-**4a**) which could result from an initial vinyl cation intermediate generated from **1a**.^{13,14} The *Z/E* ratio of this mixture of stereoisomers (**4**) prepared by addition of TfOH to 2-butyne was 4.5/1 (¹H NMR). Each of these was analyzed by GC and GCMS, and the retention times and masses all corresponded to the decomposition products; the overall reaction is shown in eq 1.

Salt **1b** also decomposes readily in CDCl₃, but provides (*E*)-**4b** as the only detected enol triflate. Contrary to Okuyama and Ochiai's results in which a styryl analog containing a β -hydrogen reacted more slowly than a decen-1-yl analog, our disubstituted styrenyl derivative, **1b**, decomposes far more rapidly than dimethyl analog **1a** in CDCl₃ or alcoholic solvents.¹⁵ Typically, **1b** was completely decomposed at room temperature in CDCl₃ for 12 h before chromatography (*vide infra*). Okuyama and Ochiai's styryl analog required 76 h at 50 °C in AcOH to provide 2.2% of a rearranged enolacetate.¹⁵



* To whom correspondence should be addressed: Tel: 757–221–1501; FAX 757–221–2715; E-mail: rjhink@chem1.chem.wm.edu.

(1) Recent reviews include: Varvoglis, A. *Tetrahedron* **1997**, *53*, 1179–1255. Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **1996**, *96*, 1123–1178.

(2) For advances in organic synthesis, see: Varvoglis, A. *Hypervalent Iodine in Organic Synthesis*; Academic: New York, 1997.

(3) Ochiai, M.; Sumi, K.; Takaoka, Y.; Kunishima, M.; Nagao, Y.; Shiro, M.; Fujita, E. *Tetrahedron* **1988**, 4095–4112.

(4) 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. Moriarty, R. M.; Epa, W. R.; Awasthi, A. K. *J. Am. Chem. Soc.* **1991**, *113*, 6315–6316.

(5) Ochiai, M.; Shu, T.; Nagaoka, T.; Kitagawa, Y. *J. Org. Chem.* **1997**, *62*, 2130–2138.

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

(7) Vinyl cations containing α -alkyl groups are a well-studied class of intermediates. See, *inter alia*: (a) Summerville, R. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 1110–1120. (b) Summerville, R. H.; Senkler, C. A.; Schleyer, P. v. R.; Dueber, T. E.; Stang, P. J. *J. Am. Chem. Soc.* **1974**, *96*, 1100–1109. (c) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. *Vinyl Cations*; Academic: New York, 1979 and references therein.

(8) For more recent references on vinyl cations, including a primary cation derived from hydration of acetylene, see: Bott, K. *Chem. Ber.* **1994**, *127*, 933–939. Lucchini, V.; Modena, G. *J. Am. Chem. Soc.* **1990**, *112*, 6291–6296.

(9) For NMR 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.

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

(11) Zhdankin, V. V.; Stang, P. J. *Tetrahedron Lett.* **1993**, *34*, 6853–6856.

It was possible that adventitious acid caused the decomposition.¹⁶ The acid-sensitivity of the decomposition pathway described herein was tested in two ways: (a) 1.0 equiv of triflic acid was added to a CDCl₃ solution of **1a**; and (b) the CDCl₃ used was filtered through basic alumina. Compound **1a** was found to be stable in the presence of the excess acid and decomposed as described in the alumina-filtered solvent.

The mechanism for decomposition of **1a** (Scheme 1) may involve heterolysis of the vinyl C–I bond to afford the primary vinyl cation **A** and 4-CF₃C₆H₄I, **2a**. This cation is particularly significant as it does not contain a stabilizing group such as a cyclopropylidene or β -phenyl. Attack of the triflate before methyl migration leads to

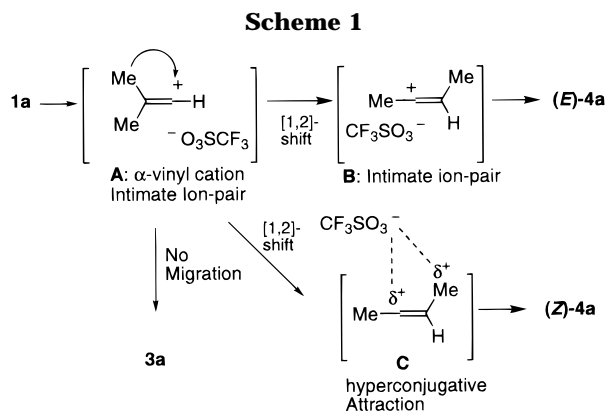
(12) Data for iodonium salt **1a**, including a ¹H NMR spectrum, is contained in the Supporting Information.

(13) Triflate **3a** was synthesized by the hindered base method: Stang, P. J.; Treptow, W. *Synthesis* **1980**, 283–284.

(14) See ref 7a for the preparation of (*E*)-**4a** and (*Z*)-**4a**. Isomers were identified according to chemical shift of the vinylic protons. Also see: Stang, P. J.; Datta, A. K. *J. Am. Chem. Soc.* **1989**, *111*, 1358–1363.

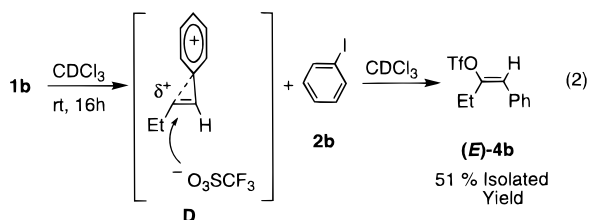
(15) S_N2 and phenonium ion reactions of vinyl iodonium salts were recently reported: Okuyama, T.; Ochiai, M. *J. Am. Chem. Soc.* **1997**, *119*, 4785–4786.

(16) Equilibration of some vinyl triflates to a thermodynamic mixture can be accomplished in the presence of excess triflic acid. See: ref 7b.

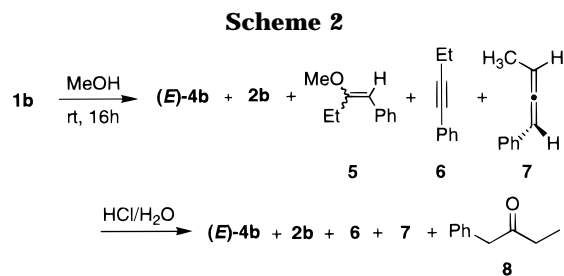


the “unrearranged” 2-methyl-1-propenyl triflate **3a**. This product could also arise by direct in-plane S_N2 displacement of the arylidonio moiety.^{15,17–19} The other two of the four isolated decomposition products require a rearrangement. The primary carbocation intermediate **A** may be involved, or a rearrangement *via* methyl migration followed by nucleophilic attack of the triflate anion on a secondary cation could afford the 2-buten-2-yl triflates (*Z*)-**4a** and (*E*)-**4a**. The final ratio of *Z/E* of the 2-buten-2-yl triflates (*Z*)-**4a**/*E*-**4a** was 1.3:1.0. This ratio is clearly different from the 4.5/1 ratio obtained during the independent synthesis. The overall ratio of **3a**:(*Z*)-**4a**:(*E*)-**4a** was 1.0:3.2:2.4 (¹H NMR).²⁰ The change in ratio depending on whether (*Z*)-**4a** and (*E*)-**4a** were synthesized by addition of TfOH to 2-butyne or from decomposition of **1a** indicates that in the decomposition, the larger relative proportion of (*E*)-**4a** arises because of an intimate ion-pair mechanism in which the methyl trans to the iodoarene moiety migrates more readily due to favorable stereoelectronics and lower steric hindrance.²¹ The low polarity solvent, chloroform, probably favors the formation of the intimate ion pair rather than solvent separated ions.

Compound **1b** decomposes in a similar manner, but involves an unsymmetrical phenonium ion (**D**) which results in frontside attack of the triflate (eq 2). Enol



triflate (*E*)-**4b** was *isolated* in 51% yield after column chromatography, and **1b** decomposes readily and completely in chloroform at room temperature over the course of 12–16 h.²² This trans-isomer was the only enol triflate isolated, and the structure was verified by independent synthesis from 1-phenyl-2-butanone using the hindered



base method (¹H NMR and GC MS).¹³ Decomposition of **1b** was also accomplished in MeOH to afford a mixture of **2b**, **5** and rearranged products 1-phenyl-1-butyne (**6**), 1-phenyl-1,2-butadiene (allene **7**),²³ 1-phenyl-2-butanone (**8**) and (*E*)-**4b** (Scheme 2). Subsequent acid hydrolysis then provided a mixture of products in which **5** was converted to **8**. Compounds **6**, **8**, and (*E*)-**4b** were verified by ¹H NMR and GC MS with authentic samples. Further, the components present in the largest quantities, **2b**, **7**, and **8** were *isolated* by column chromatography in 53, 25, and 35% yields, respectively. The only detected and isolated carbonyl compound was 1-phenyl-2-butanone (**8**), indicating that even in this highly-ionizing and relatively nucleophilic solvent, phenyl migration occurred. This is remarkable given that decomposition of styrenyl(phenyl)iodonium tetrafluoroborate required 7 days at 70 °C.¹⁵ Obviously, the addition of a second β -substituent drastically increases the propensity to form the phenonium ion even in chloroform. This is likely the result of the additional alkyl group stabilizing charge build-up at the site of migration and leading to an increased rate for this step.

In addition to vinyl cation pathways, other mechanisms are possible. Initial homolytic cleavage followed by single electron transfer (SET) has previously been observed, but only as a minor (1%) pathway.⁶ Alkylidene–carbene and migration–elimination–addition modes are also possible. However, no products supporting these alternative mechanisms were identified.

In conclusion, we have documented fragmentations of β -disubstituted alkenyl(aryl)iodonium triflate salts which may occur *via* a primary vinyl cation and a phenonium cation. Direct trapping of the cations by the triflate anion as well as rearrangements by 1,2-shifts were observed. The arylidonio moiety is obviously an exceedingly good nucleofuge and leads to remarkable reactivity in these systems. Such facile fragmentations of iodonium salts could prove very useful in initiating cationic rearrangements in more complex molecules under mild conditions. Further investigations into structural, solvent, and electronic effects on the decomposition pathways and detailed mechanistic studies are underway and will be the subject of future reports.

Acknowledgment. We gratefully acknowledge the College of William & Mary for institutional support of this work.

Supporting Information Available: Experimental procedures, copies of ¹H NMR spectra of **1a**, (*E*)-**4b**, and **7**; ¹³C{¹H} NMR spectra of (*E*)-**4b** and **7** as well as a GC trace of the MeOH decomposition of **1b** (9 pages).

JO971132M

(17) Reaction of an unsymmetrical alkenyl(aryl)iodonium salt will determine if the reaction leading to the minor enol triflate **3a** proceeds *via* a S_N1 or S_N2 mechanism. Several experiments to determine the mode of reaction are underway and will be reported in due course.

(18) A theoretical study of vinylic S_N2 vs Ad_N-E reactions was recently published: Lucchini, V.; Modena, G.; Pasquato, L. *J. Am. Chem. Soc.* **1995**, *117*, 2297–2300.

(19) For a brief report of nucleophilic substitutions of (*E*)- β -alkylvinylidonium tetrafluoroborates with halides, see: Ochiai, M.; Ochiai, K.; Masaki, Y. *J. Am. Chem. Soc.* **1991**, *113*, 7059–7061.

(20) **3a** and (*Z*)-**4a** were not completely separable under a variety of conditions by capillary GC. Therefore, the integrations of the vinylic protons in the ¹H NMR spectrum were used.

(21) For detailed discussions of the factors influencing stereochemistry in the formation of (*Z*)- and (*E*)-**4a**, see refs 7a and 7c.

(22) The structure of (*E*)-**4b** was assigned by comparison of the ¹H NMR spectra with those of (*E*)- and (*Z*)-1-methyl-2-phenylvinyl triflates.²⁴ The presence of (*E*)-**4b** strongly implies a bridging phenonium ion is involved in the rearrangement and stabilization of the primary vinyl cation.

(23) Allene **7** is a known compound with distinctive spectral characteristics. For preparation *via* enol phosphates, see: Brummond, K. M.; Dingess, E. A.; Kent, J. L. *J. Org. Chem.* **1996**, *61*, 6096–6097.

(24) Jäckel, K.-P.; Hanack, M. *Chem. Ber.* **1977**, *110*, 199–207.