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Solvolysis of Cyclohexenyliodonium Salt, a New Precursor for the Vinyl Cation: Remarkable Nucleofugality of the Phenyliodonio Group and Evidence for Internal Return from an Intimate Ion−Molecule Pair

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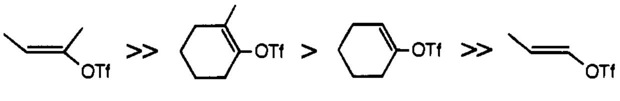
Abstract: Solvolysis of (4-*tert*-butyl-1-cyclohexenyl)aryliodonium tetrafluoroborates was examined in alcohol and aqueous solutions at 25−70 °C. Phenyliodonio group was found to be a remarkably good nucleofuge with a leaving ability about 10^6 times greater than triflate. In addition to the expected solvolysis products, 1-alkoxycyclohexene and/or cyclohexanone and iodobenzene, the internal return products, (4-*tert*-butyl-1-cyclohexenyl)iodobenzenes, were obtained in yields of 13−15% in methanol and aqueous solutions and of 30−40% in trifluoroethanol. The *ortho* derivative is the predominant isomer of these products, and this isomeric distribution is taken as indicating that the return is occurring from the intimate ion−molecule pair. The formation of a free-radical product, 4-*tert*-butylcyclohexene (1%), was detected during the solvolysis in the presence of 1,4-cyclohexadiene or in 2-propanol, while a considerable amount of the cationic rearrangement product, cyclopentyl methyl ketone, was obtained in the solvolysis of (2-methyl-1-cyclohexenyl)phenyliodonium tetrafluoroborate. A proposed mechanism involves mainly heterolysis to give the cyclohexenyl cation−iodobenzene pair with accompanying single electron transfer (or with competing homolysis) to lead to a free radical intermediate.

Vinyl(phenyl)iodonium salts serve as highly activated species of vinyl halides in nucleophilic vinylic substitutions. Reactions of vinyliodonium salts with thiolate, halides, and stable enolate anions proceed smoothly even at room temperature.[1,2] They also undergo very facile β-elimination to yield the corresponding terminal alkynes and/or α-elimination to generate alkylidenecarbenes.[3] The high reactivities of vinyliodonium salts are ascribed to a large nucleofugality of the phenyliodonio group. We wanted to determine a quantitative nucleofugality of this leaving group. However, simple solvolysis of 1-alkenyliodonium salts to give the primary vinyl cations could not be observed, while 1-alkyl-substituted 1-alkenyliodonium salts (leading to secondary vinyl cations) were too unstable to study at normal temperatures.

Simple vinyl derivatives are generally unreactive toward nucleophiles, and vinyl solvolysis can be observed only with a very good nucleofuge like triflate.[4−6] The relative solvolysis rates of vinyl triflates are reported to be in the order:[5]



(no reaction)

These reactivities reflect the stabilities of the intermediate vinyl cations, and the cyclohexenyl derivatives show intermediate reactivity.

Solvolysis of (4-*tert*-butyl-1-cyclohexenyl)phenyliodonium tetrafluoroborate (**1a**) was found to proceed at reasonable rates at normal temperatures, and thus we examined solvolysis of **1a** and some related iodonium salts in alcohol and aqueous solutions. The phenyliodonio group was found to be a remarkable nucleofuge, some 10^6 times more reactive than triflate. Furthermore, the rearranged products, (4-*tert*-butyl-1-cyclohexenyl)iodobenzenes, were obtained with the *ortho* isomer as the major one. This finding is taken as evidence for *internal return from an intimate ion−molecule pair.*

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(1) (a) Nesmeyanov, A. N.; Tolstaya, T. P.; Petrakov, A. V. *Dokl. Akad. Nauk SSSR* **1971**, *197*, 1337. (b) Nesmeyanov, A. N.; Tolstaya, T. P.; Petrakov, A. V.; Leshcheva, I. F. *Dokl. Akad. Nauk SSSR* **1978**, *238*, 1109. (c) Ochiai, M.; Sumi, K.; Nagao, Y.; Fujita, E. *Tetrahedron Lett.* **1985**, *26*, 2351. (d) Ishikura, M.; Terashima, M. *Heterocycles* **1988**, *27*, 2619. (e) Ochiai, M.; Oshima, K.; Masaki, Y. *J. Am. Chem. Soc.* **1991**, *113*, 7059. (f) Ochiai, M.; Oshima, K.; Masaki, Y. *Tetrahedron Lett.* **1991**, *32*, 7711. (g) Zefirov, N. S.; Koz'min, A. S.; Kasumov, T.; Potekhin, K. A.; Sorokin, V. D.; Brel, V. K.; Abramkin, E. V.; Struchkov, Y. T.; Zhdankin, V. V.; Stang, P. J. *J. Org. Chem.* **1992**, *57*, 2433. (h) Stang, P. J.; Schwarz, A.; Blume, T.; Zhdankin, V. V. *Tetrahedron Lett.* **1992**, *33*, 6759. (i) Ochiai, M.; Oshima, K.; Masaki, Y.; Kunishima, M.; Tani, S. *Tetrahedron Lett.* **1993**, *34*, 4829.

(2) For copper- or palladium-catalyzed reactions of vinyl(phenyl)iodonium salts, see: (a) Ochiai, M.; Sumi, K.; Takaoka, Y.; Kunishima, M.; Nagao, Y.; Shiro, M.; Fujita, E. *Tetrahedron* **1988**, *44*, 4095. (b) Ishikura, M.; Terashima, M. *J. Chem. Soc., Chem. Commun.* **1989**, 727. (c) Moriarty, R. M.; Epa, W. R.; Awasthi, A. K. *J. Am. Chem. Soc.* **1991**, *113*, 6315. (d) Moriarty, R. M.; Epa, W. R. *Tetrahedron Lett.* **1992**, *33*, 4095. (e) Hinkle, R. J.; Poulter, G. T.; Stang, P. J. *J. Am. Chem. Soc.* **1993**, *115*, 11626.

(3) (a) Brainina, E. M.; Freidlina, R. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1947**, 623. (b) Nesmeyanov, A. N.; Tolstaya, T. P.; Petrakov, A. V.; Goltsev, A. N. *Dokl. Akad. Nauk SSSR* **1977**, *235*, 591. (c) Ochiai, M.; Takaoka, Y.; Nagao, Y. *J. Am. Chem. Soc.* **1988**, *110*, 6565. (d) Ochiai, M.; Kunishima, M.; Tani, S.; Nagao, Y. *J. Am. Chem. Soc.* **1991**, *113*, 3135. (e) Ochiai, M.; Uemura, K.; Masaki, U. *J. Am. Chem. Soc.* **1993**, *115*, 2528.

(4) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. *Vinyl Cations*; Academic Press: New York, 1979.

(5) Pfeifer, W. D.; Bahn, C. A.; Schleyer, P. v. R.; Bocher, S.; Harding, C. E.; Hummel, K.; Hanack, M.; Stang, P. J. *J. Am. Chem. Soc.* **1971**, *93*, 1513.

(6) Stang, P. J. *Acc. Chem. Res.* **1978**, *12*, 107.

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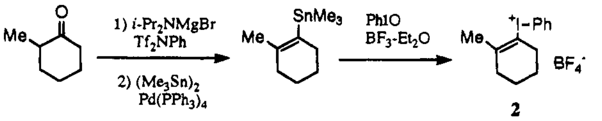
Results

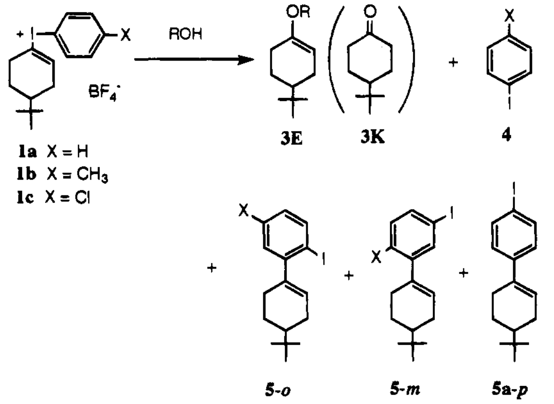
Preparation of Vinyliodonium Salts. The vinyliodonium salt **1a** and the *p*-chloro derivative **1c** were prepared by the BF_3-catalyzed silicon−iodonium exchange reaction of 4-*tert*-butyl-1-(trimethylsilyl)cyclohexene with iodosylbenzene and *p*-chloroiodosylbenzene, respectively, as described previously,[2a] while the *p*-methyl derivative **1b** was obtained from the reaction of the silylcyclohexene with *p*-(diacetoxyiodo)toluene.

For the preparation of (2-methyl-1-cyclohexenyl)phenyliodonium tetrafluoroborate (**2**), the corresponding cyclohexenylstannane was employed as a precursor (eq 1), since the BF_3-catalyzed tin−iodonium exchange reaction of the vinylstannane proceeds more readily than the silicon−iodonium exchange of the vinylsilane.[2a,3c] No α-alkyl-substituted vinyliodonium salts have been synthesized, presumably because of instability of the salts. The stannane was prepared by the palladium(0)-catalyzed coupling of hexamethyldistannane with 2-methyl-1-cyclohexenyl triflate.[7] The tin-iodonium exchange reaction between the stannane and iodosylbenzene took place at 0 °C within 1 min to give the highly labile vinyliodonium salt **2** (eq 1). Since **2** decomposes even at room temperature, purification was carried out at −78 °C by repeated decantations using diethyl ether.



(1)

Product Studies. The iodonium salts **1a** and **1b** were subjected to solvolysis in methanol, 2,2,2-trifluoroethanol (TFE), and aqueous ethanol solutions at 25 and 50 °C. Products were mainly 1-alkoxy-4-*tert*-butylcyclohexene (**3E**), and/or 4-*tert*-butylcyclohexanone (**3K**) as well as the iodobenzene (**4**). Some 4-*tert*-butyl-1,1-dimethoxycyclohexane (**3A**) was also detected from the reaction in an unbuffered methanol. These products are easily hydrolyzed to **3K** during the usual acid workup and determined as **3K**. In addition to these expected solvolysis products, some rearranged products, (4-*tert*-butyl-1-cyclohexenyl)iodobenzenes (**5**), were obtained (eq 2, Table 1). The isolated products were characterized and identified as described in the Experimental Section. Yields of the products and the isomeric ratios of **5** were determined by gas chromatography (GC). No free-radical product, 4-*tert*-butylcyclohexene (**6**), was detected in the solvolysis of **1a** in methanol at 50 °C in spite of a careful search by GC. However, the formation of about 1% of **6** was observed in the presence of 0.91 M 1,4-cyclohexadiene, a hydrogen donor, in methanol. The same radical product **6** (1%) was also found during the solvolysis in 2-propanol at 50 °C.



(2)

Solvolysis of the 2-methyl-1-cyclohexenyliodonium salt **2** was carried out in 60:40 (v/v) ethanol−water at −20 °C and in TFE at 0 °C. The reaction temperatures were gradually raised to room temperature, and the workup with 10% aqueous HCl afforded mixtures of 2-methylcyclohexanone (**7**) and cyclopentyl methyl ketone (**8**) in more than 70% total yield, along with the quantitative formation of iodobenzene. A considerable amount of the rearranged ketone **8** was obtained. The ratios of the rearranged to the unrearranged ketones **8**/**7** were 14/86 in the aqueous ethanol and 46/54 in TFE, respectively.

Kinetic Measurements. Rates for solvolysis of the vinyliodonium salts **1** were measured spectrophotometrically in alcohol and aqueous solutions. The pseudo-first-order rate constants k_{obsd} obtained at 50 °C in various solvents and solvent mixtures are given in Table 2. Temperature dependence of the rate was examined in 60:40 (v/v) ethanol−water at temperatures between 35 and 69 °C, and the results are summarized in Table 3.

Solvolysis rates of 2-methyl-1-cyclohexenyliodonium salt **2**

Table 1. Product Distribution of Solvolysis of **1a** and **1b**[a]

			product yield/ % from **1a**		product yield/ % from **1b**	
solvent	temp/ °C	reaction time[b]	**3**	**5a** (**5a**-*o*:**5a**-*m*:**5a**-*p*)	**3**	**5b** (**5b**-*o*:**5b**-*m*)
60E[c]	50	6 h (12 h)	77	15 (86:6:8)	76	14 (79:21)
60E[c]	25	8 d (20 d)	72	13 (89:5:6)	83	15 (83:17)
MeOH	50	6 h (10 h)	60	14 (82:8:10)	59	16 (74:26)
MeOH	25	9 d (15 d)	79	13 (85:6:9)	71	15 (76:24)
TFE	50	5 h (8 h)	56	37 (88:3:9)	51	31 (79:21)
TFE	25	7 d (14 d)	48	35 (92:2:6)	48	39 (78:22)

[a] Yields of products and the isomeric ratios of **5** were determined by GC. [b] Values in parentheses are reaction times for **1b**. [c] 60:40 (v/v) ethanol−water.

Table 2. Observed Rate Constants ($10^4k_{obsd}/s^{-1}$) for Solvolysis of **1** at 50 °C

solvent[a]	**1a**	**1b**	**1c**
EtOH	1.10		2.65
80E	1.86		4.68
60E	2.32	1.23	5.74
50E	2.55	1.37	6.46
40E	3.45		7.53
20E			8.74
10E			13.9
H_2O			23.1
MeOH	2.87		5.53
i-PrOH			2.02
t-BuOH			3.56
TFE			8.70
50/50 TFE−EtOH			4.21
50/50 TFE−H_2O			7.26

[a] 80E = 80:20 (v/v) EtOH−H_2O, 10E = 10:90 (v/v) EtOH−H_2O, and so on.

Table 3. Observed Rate Constants ($10^4k_{obsd}/s^{-1}$) for Solvolysis of the Vinyliodonium Salts in 60:40 (v/v) Ethanol−Water

	temp/°C					
substrate	25	35	50	69	$\Delta H^{\ddagger}$/ kcal/mol	$\Delta S^{\ddagger}$/ cal/mol deg
1a	(0.0449)[a]	0.229	2.32	26.9	28.7	13.3
1b		0.114	1.23	14.0	28.5	11.8
1c		0.594	5.74	60.3	27.9	12.8
2	11.4					

[a] Calculated from the activation parameters.

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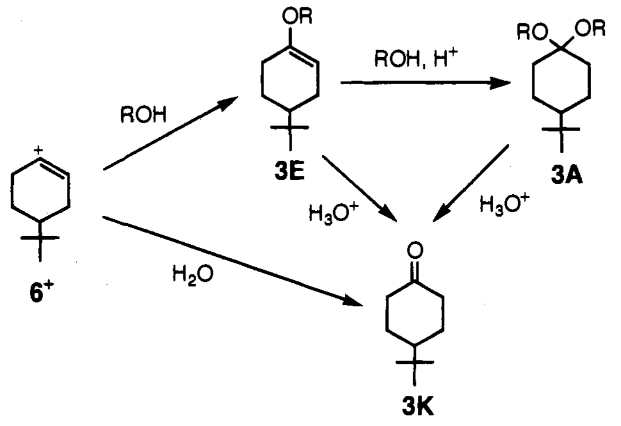
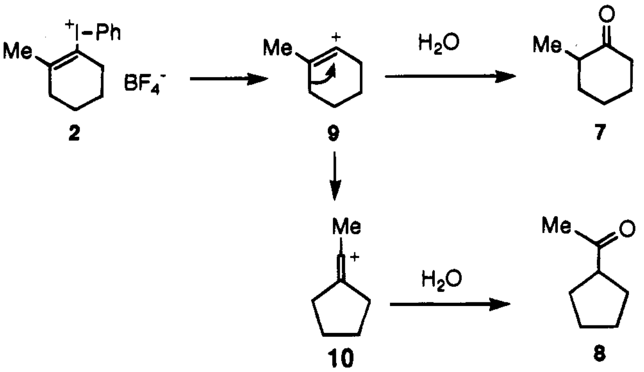
(7) (a) Wulff, W. D.; Peterson, G. A.; Bauta, W. E.; Chan, K.-S.; Faron, K. L.; Gilbertson, S. R.; Kaesler, R. W.; Yang, D. C.; Murray, C. K. *J. Org. Chem.* **1986**, *51*, 277. (b) Scott, W. J.; Crisp, G. T.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4630. (c) Crisp, G. T.; Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7500. (d) Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 3033.

Scheme 1



Scheme 2



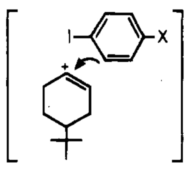
were measured in 60:40 (v/v) ethanol−water at 25 °C. The stock solution of **2** was prepared by dissolving the salt in ethanol at −20 °C and the cold stock solution was introduced to the solvent equilibrated at the constant temperature to start the reaction. The halflife was about 10 min and the rate constant is recorded in Table 3. In comparison of the rate constants under the same conditions (evaluated by the activation parameters), **2** is about 250 times as reactive as **1a**.

Discussion

Solvolysis Products. The major products of the solvolysis of **1** are those expected for the cyclohexenyl cation intermediate $\mathbf{6}^+$, the cyclohexanone derivatives **3** (Scheme 1). When the alcohol was not buffered, some acetal **3A** was formed by the acid-catalyzed reaction of the enol ether **3E** with the alcohol. The catalyzing acid may be generated during the solvolysis (HBF_4).

Intermediacy of the cyclohexenyl cation was confirmed also by the observation of carbocation rearrangement during the solvolysis of (2-methyl-1-cyclohexenyl)phenyliodonium tetrafluoroborate (**2**). It is well established that a bent destabilized vinyl cation, 2-methyl-1-cyclohexenyl cation **9**, if formed, rearranges to a more stable linear secondary vinyl cation **10**, which leads to the rearranged ketone **8** as a final product (Scheme 2).[8] The ketone **8** was actually obtained among the solvolysis products from **2**. Of an about 70% yield of the ketone products, the ratio of the rearranged to the unrearranged ones, **8**/**7** was 14/86 in 60:40 (v/v) ethanol−water at −20 °C. The solvolysis of 2-methyl-1-cyclohexenyl triflate in the same solvent at 125 °C was found to give a similar mixture of the ketones with **8**/**7** = 30/70.[8] Since the tendency of rearrangement of the vinyl cation **9** to **10** was shown to increase with increasing reaction temperature,[8] the lower yield of the rearranged ketone **8** obtained in the solvolysis of **2** at −20 °C may be ascribed to the temperature effect. (The activation energy for the rearrangement is greater than that for the nucleophilic reaction of the solvent.) The prolonged lifetime of the intermediate vinyl cation in less nucleophilic TFE must increase the chance of rearrangement to give a higher yield of **8**. These results are compatible with a mechanism involving the vinyl cation for solvolysis of cyclohexenyliodonium salts.

Internal Return. In addition to the usual solvolysis products **3**, some rearranged products **5** were obtained in the solvolysis of **1a** and **1b** (Table 1). These unexpected products may be formed by the Friedel−Crafts-type reaction between the cyclohexenyl cation $\mathbf{6}^+$ and the iodobenzene **4** formed by ionization of **1**. Noteworthy here is the isomeric distribution of **5**, predominantly *ortho*. In a usual Friedel−Crafts alkylation (with benzyl chloride) of iodobenzene, the *ortho*/*para* ratio was found to be 31/69.[9] Predominant formation of the *ortho* isomer in the present reaction must be a result of recombination within (or internal return from) the intimate cyclohexenyl cation−iodobenzene pair [$\mathbf{6}^+$ **4**], where the orientation of the iodobenzene moiety in the initial state **1** still would be retained. The solvent-separated ion pair, where the orientation of the iodobenzene would be equilibrated, would have given rise to a "normal" *ortho*/*para* ratio of about 3/7.



[$\mathbf{6}^+$ **4**]

A decrease in solvent nucleophilicity as in TFE resulted in a large increase in the yield of the rearranged product **5**, while the effects on the isomeric distribution of **5** are small. Effects of temperature on the product ratio **3**/**5** are also small, but the fraction of the *ortho* isomer **5-*o***, a product from the intimate ion-molecule pair, appears to be greater at a lower temperature. Effects of *p*-methyl substitution (**1b**) on the ratio **3**/**5** are again small, but the *ortho* directing effects of the methyl group increase the *meta* (with respect to iodine) product **5b-*m***. The normal Friedel−Crafts alkylation of *p*-iodotoluene (**4b**) should give predominantly **5b-*m***,[10] and the observed formation of **5b-*o*** as a major product again indicates the importance of the return from the intimate ion-molecule pair like [$\mathbf{6}^+$ **4**].

The ion-pair mechanism of solvolysis of saturated systems has been proposed by Winstein and involves the intimate and solvent-separated ion pairs as discrete intermediates.[12] This proposal is based on the detailed kinetic analysis of solvolysis of chiral substrates. For detection of the return after ionization, polydentate leaving groups have been employed.[12b] Such nucleofuges used previously include thiocyanate, sulfinate, and thiobenzoate as well as ^{18}O-labeled benzoate and sulfonate, but information regarding the nature of the ionic intermediates is limited because of the structural simplicity of these groups: differentiation between intimate and solvent-separated ion pairs

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(8) Hanack, M.; Fuchs, K.-A.; Collins, C. J. *J. Am. Chem. Soc.* **1983**, *105*, 4008.

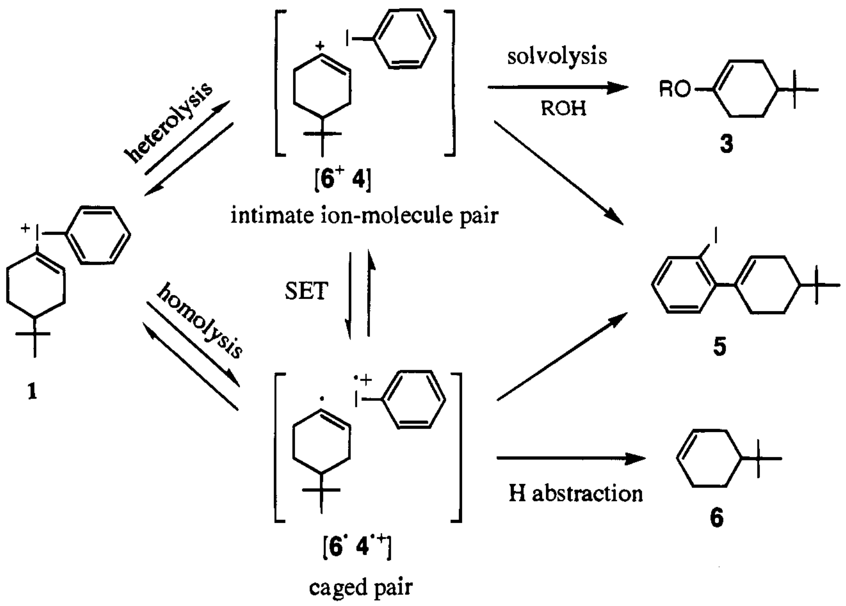
(9) Olah, G. A.; Kuhn, S. J.; Flood, S. H. *J. Am. Chem. Soc.* **1962**, *84*, 1695.

(10) The Friedel−Crafts acylations of **4b** show this tendency.[11]

(11) Gore, P. H.; Thorburn, S.; Weyell, D. J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2940.

(12) (a) Winstein, S.; Clippinger, E.; Fainberg, A. H.; Robinson, G. C. *J. Am. Chem. Soc.* **1954**, *76*, 2597. (b) Raber, D. J.; Harris, J. M.; Schleyser, P. v. R. In *Ions and Ion Pairs in Organic Reactions*; Szwarc, M., Ed.; John Wiley: New York: 1974; Vol. 2, pp 247−373.

Scheme 3

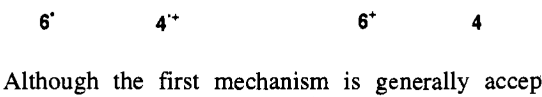


simply is not possible without kinetic analysis. The present leaving group, iodobenzene, is neutral but has four different reaction sites (iodine and *ortho*, *meta*, and *para* positions), and the *ortho*/*para* isomeric ratio of the recombination products may be a good criterion for the return from the intimate or solvent-separated ion−molecule pair. The product distribution tells us about the states of the intermediate ionic pairs.

The partner of the ionic pair in the present reaction is a neutral molecule, and the interaction between the two components of the pair must be smaller than that experienced by a pair consisting of a carbocation and a nucleofugal anion in the usual solvolysis. Nonetheless, clear observation of the return from the intimate ion-molecule pair could be made. This may be ascribed to the instability of the vinylic cation involved that could be generated owing to an extremely high nucleofugality of the leaving group. Similar observations of the ion−molecule (phenyl cation−nitrogen) pair were previously reported for the dediazoniation of some diazonium salts.[13] These observations were also possible probably because of the instability of the cation and the extreme nucleofugality of the leaving neutral molecule. Any unstable intermediates of lifetime shorter than one vibration (10^{-13} s) cannot be discrete solvent-equilibrated intermediates,[14] but they could exist only in a transient paired form, e.g., as an intimate ionic pair. The cyclohexenyl cation can only exist as an intimate pair but not as a discrete solvent equilibrated species in hydroxylic solvents.

Electron Transfer. The internal return products **5** could also be explained by a free-radical mechanism, shown in Scheme 3, in which homolytic cleavage of the vinylic carbon−iodine (III) bond generates a caged pair consisting of the vinyl radical and iodobenzene cation radical [$\mathbf{6}^{\bullet}\,\mathbf{4}^{\bullet+}$]. The caged pair could undergo recombination to give the rearranged products **5**. A possible competitive reaction of the free radical is a hydrogen abstraction (from the solvent or other molecules present) to give 4-*tert*-butylcyclohexene **6**. The initial attempts were unsuccessful in detecting **6** in the solvolysis of **1a** in methanol at 50 °C, in spite of a careful search by comparison with the authentic sample. However, a small amount (1%) of **6** was detected in the presence of a hydrogen donor, 1,4-cyclohexadiene at 0.91 M. Furthermore, about 1% of **6** was also found among the products from the solvolysis of **1a** in 2-propanol, which is a much better H donor than methanol. The formation of the radical product **6** shows that the present reaction involves the vinyl radical intermediate $\mathbf{6}^{\bullet}$ in addition to the vinyl cation $\mathbf{6}^{+}$.

Both the heterolytic and homolytic cleavages of the carbon−iodine(III) bond of **1** are occurring under the reaction conditions. How do these two processes occur? There are three possibilities: (1) the initial homolysis followed by single electron transfer (SET) from the cyclohexenyl radical $\mathbf{6}^{\bullet}$ to the iodobenzene cation radical $\mathbf{4}^{\bullet+}$ within the caged pair, [$\mathbf{6}^{\bullet}\,\mathbf{4}^{\bullet+}$] → [$\mathbf{6}^{+}\,\mathbf{4}$], (2) the initial heterolysis followed by SET from **4** to $\mathbf{6}^{+}$ within the intimate ion−molecule pair, [$\mathbf{6}^{+}\,\mathbf{4}$] → [$\mathbf{6}^{\bullet}\,\mathbf{4}^{\bullet+}$], and (3) the parallel (competitive) homolysis−heterolysis reactions (without SET). The magnitudes of the ionization potentials (IP) (or electron affinities) of the intermediate species determine the pathway that actually occurs. Although the IP of the cyclohexenyl radical is not known, it may be close to that of iodobenzene (8.685 eV)[15] which is somewhat smaller than that of the vinyl radical $CH_2{=}CH^{\bullet}$ (8.9 eV).[15] If the two IP's are close to each other, SET equilibrium reaction 3 occurs readily from either side to the other and the iodonium ion **1** can undergo homolysis or heterolysis to lead to either side of equilibrium 3. This situation seems to be the case in the present system, and the differentiation of the above three possibilities may become less important.

 (3)

Although the first mechanism is generally accepted for photosolvolysis of alkyl halides,[16,17] the experimental implications seem to support that the initial bond cleavage of **1** is mainly heterolysis to give [$\mathbf{6}^{+}\,\mathbf{4}$]. The accompanying cyclohexenyl radical $\mathbf{6}^{\bullet}$ may be formed by SET of the heterolysis products or by a minor competitive (direct) homolysis. If cyclohexenyl-

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(13) (a) Szele, I.; Zollinger, H. *J. Am. Chem. Soc.* **1978**, *100*, 2811. (b) Hashida, Y.; Landells, R. G. M.; Lewis, G. E.; Szele, I.; Zollinger, H. *J. Am. Chem. Soc.* **1978**, *100*, 2816. (c) Ravenscroft, M. D.; Takagi, K.; Weiss, B.; Zollinger, H. *Gazz. Chim. Ital.* **1987**, *117*, 353.

(14) Jencks, W. P. *Acc. Chem. Res.* **1976**, *9*, 425; **1980**, *13*, 161. Jencks, W. P. *Chem. Soc. Rev.* **1981**, *10*, 345.

(15) Chemical Society of Japan, Ed. *Kagaku Binran (Handbook of Chemistry)*, 4th ed.; Maruzen: Tokyo, 1993.

(16) (a) Kropp, P. J. *Acc. Chem. Res.* **1984**, *17*, 131. (b) Lodder, G. In *The Chemistry of Halides, Pseudo-halides and Azides*; Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, 1983; Chapter 29.

iodonium ion **1** could readily undergo the initial homolysis, the 1-cyclopentenyliodonium salt would also have undergone homolysis. Stability of this iodonium salt under the solvolysis conditions can be interpreted by the extreme instability of a highly bent 1-cyclopentenyl cation, but the cyclopentenyl radical (with the sp^2-hybridization at the radical center) should not be so unstable. The radical product, cyclopentene, could not be detected even in the presence of 1,4-cyclohexadiene, but the iodonium salt was recovered unchanged after 2 weeks reaction in methanol at 50 °C. Furthermore, the substituent polar effects observed on the solvolysis rate of **1** (see below) are also consistent with a mechanism involving direct heterolysis.

A mechanism involving the initial homolysis with accompanying SET has been established for the photosolvolysis of alkyl halides, especially for that of iodide.[16,17] Irradiation of 1-iodocyclohexene in methanol at 254 nm gave a mixture of 1,1-dimethoxycyclohexane, an ionic product, and cyclohexene, a radical product.[17e] Photolysis of 1-iodocyclopentene in methanol gave a high yield of a radical product, cyclopentene, but not ionic products.[17e] That is, photoinduced homolysis occurs with both the cyclohexenyl and cyclopentenyl systems. Only the fomer undergoes SET to give cyclohexenyl cation but the latter does not. The yield of cyclohexene was quite high, 26% at 40 °C, in the photolysis of 1-iodocyclohexene in methanol.[17e] By contrast, we could detect such a radical product only marginally in the presence of an effective H donor in the solvolysis of the cyclohexenyliodonium salt **1**. This difference must come from the relatively low electron affinity of iodine (3.0591 eV)[15] as compared with the iodobenzene cation radical; the lifetime of the radical in the iodocyclohexene system must be longer.

No previous example of (thermal) solvolysis that takes place *via* homolysis followed by SET has been reported. We wonder why the photosolvolysis starts with homolysis followed by SET but the present solvolysis starts with the initial heterolysis accompanied by SET (or by direct homolysis). In the photosolvolysis, the electronic energy obtained through photoexcitation transfers to the vibrational levels of the substrate to lead to rapid bond cleavage; the homolysis of a neutral substrate may be favored here over the heterolysis which requires solvent reorganization, but SET occurs to give ionic intermediates when the solvent reorganization is allowed. By contrast, a charged species requires little solvent reorganization either by homolysis or heterolysis since both processes involve no charge separation, and so the heterolysis occurs more readily in the present system. Nucleophilic reactions of iodonium salts involving SET are known, but SET occurs from anionic nucleophiles to the substrate in these reactions.[18] A similar SET has been found in a class of nucleophilic displacement reactions that is designated as S$_{RN}$1.[19] However, the situations are quite different from the present reaction where the possible SET occurs between the fragments of the substrate. The solvolysis of the iodonium salts is mechanistically unique in this sense.

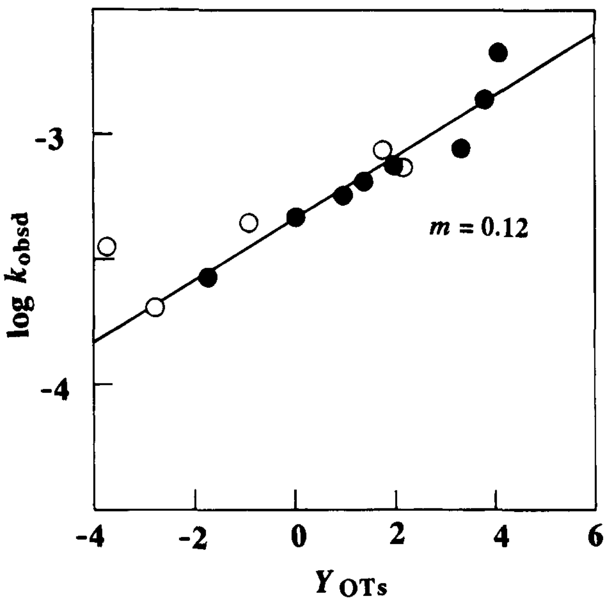

Figure 1. Solvent effects on the solvolysis rates of **1c** at 50 °C. For the values of k_{obsd}, see Table 2. Closed circles show data obtained in ethanol–water solvents.

The rearranged products **5** could be formed by the free-radical recombination within the caged radical pair [**6**$^{\bullet}$ **4**$^{\bullet+}$], but the ionic recombination within the intimate ionic pair [**6**$^{+}$ **4**] seems to be more probable. There is a hint which mechanism of the recombination is operative. The yield of **5** considerably increased when the solvent was changed from methanol (or aqueous ethanol) to TFE. This tendency strongly supports the ionic recombination rather than the radical mechanism. If the latter were the case, the change in solvent polarity or nucleophilicity would not have affected the yield of **5** much. We propose at the present moment that the internal return from the intimate ion–molecule pair [**6**$^{+}$ **4**] gives the rearranged products **5** with the predominant *ortho* isomer, reflecting the original substrate configuration retained in the intermediate ion–molecule pair.

In conclusion, the solvolysis of cyclohexenyliodonium salt **1** proceeds by the initial heterolysis to form the intimate 1-cyclohexenyl cation–iodobenzene pair [**6**$^{+}$ **4**] which is trapped by the nucleophilic solvent with the accompanying internal return to give the rearranged products **5**. Another competitive but minor reaction to give 1-cyclohexenyl radical takes place by single electron transfer within the intimate ion–molecule pair or by minor direct homolysis.

Kinetic Results. Kinetic characteristics are consistent with a reaction of a positively charged substrate. Dependence of the rate on solvent polarity is quite small, as seen in the logarithmic plot of k_{obsd} for **1c** against the solvent ionizing power Y_{OTs}[20] (Figure 1). The slope is small but positive ($m = 0.12$). Similar observations were reported for solvolysis of the 1-adamantyldimethylsulfonium ion ($m = 0.05$).[21] Solvation of the positively charged substrate may not be much changed on going to the reaction transition state where no formal charge separation occurs. With little effect of solvent polarity, solvent nucleophilicity may show up in the S$_N$1 heterolytic transition state as in the solvolysis of some tertiary systems like the *tert*-butylsulfonium ion.[22] The cyclohexenyl planar system may hardly undergo nucleophilic solvation at the S$_N$1 transition state, as is the case in the adamantyl system. The positive activation

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(17) (a) McNeely, S. A.; Kropp, P. J. *J. Am. Chem. Soc.* **1976**, *98*, 4319. (b) Suzuki, T.; Sonoda, T.; Kobayashi, S.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1976**, 180. (c) Suzuki, T.; Kitamura, T.; Sonoda, T.; Kobayashi, S.; Taniguchi, H. *J. Org. Chem.* **1981**, *46*, 5324. (d) Kitamura, T.; Kobayashi, S.; Taniguchi, H. *J. Org. Chem.* **1982**, *47*, 2323. (e) Kropp, P. J.; McNeely, S. A.; Davis, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 6907. (f) Taniguchi, H. *J. Synth. Org. Chem. Jpn.* **1994**, *52*, 121.

(18) (a) Lubinkowski, J. J.; Knapczyk, J. W.; Calderon, J. L.; Petit, L. R.; McEwen, W. E. *J. Org. Chem.* **1975**, *40*, 3010. (b) Lubinkowski, J. J.; Gomez, M.; Calderon, J. L.; McEwen, W. E. *J. Org. Chem.* **1978**, *43*, 2432. (c) Scherrer, R. A.; Beatty, H. R. *J. Org. Chem.* **1980**, *45*, 2127.

(19) (a) Rossi, R. A.; de Rossi, R. H. *Aromatic Substitution by the S$_{RN}$1 Mechanism, ACS Monograph 178;* American Chemical Society: Washington, DC, 1983. (b) Norris, R. K. In ref 16b, Chapter 16.

(20) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667.

(21) Kevill, D. N.; Anderson, S. W. *J. Am. Chem. Soc.* **1986**, *108*, 1579.

(22) Kevill, D. N.; Kamil, W. A.; Anderson, S. W. *Tetrahedron Lett.* **1982**, *23*, 4635.

Table 4. Solvolysis Rates for Comparison of Leaving Ability

substrate	solvent	temp/°C	k_{obsd}/s^{-1}	ref
1a	60E	50	2.32×10^{-4}	present work
1-c-C_6H_9-OTf	60E	50	2.8×10^{-10}	5
2-Adm-OTf	80E	25	2.13×10^{-2}	a
2-Adm-OTs	80E	25	2.4×10^{-8}	20
1-Adm-OTs	80E	50	5.55×10^{-2}	b
1-Adm-S^+Me_2	80E	50	7.7×10^{-8}	21

[a] Kevill, D. N.; Anderson, S. W. *J. Org. Chem.* **1985**, *50*, 3330. [b] Kevill, D. N.; Kolwyck, K. C.; Weitl, F. L. *J. Am. Chem. Soc.* **1970**, *92*, 7300.

Table 5. Relative Leaving Ability

nucleofuge	relative leaving ability	
$-I^+Ph$	8×10^5	5×10^{17}
$-OTf$	1	6×10^{11}
$-OTs$	$1/(9 \times 10^5)$	7×10^5
$-S^+Me_2$	$1/(6 \times 10^{11})$	1

entropy obtained from the temperature dependence (Table 3) is also characteristic of the reaction of a cationic substrate, as was observed for the solvolysis of sulfonium salts.[21]

The Hammett ϱ value evaluated from three points is about 1.7 (Table 3), implying that the leaving ability of the aryliodonio group increases with an increase in the electron-withdrawing ability of the ring substituent, which destabilizes the positive charge of the iodonio group. This is consistent with the heterolysis mechanism, where the positive charge moves to the cyclohexenyl moiety at the transition state, but not with the homolysis-SET mechanism with the rate-determining homolysis. In the latter mechanism, the developing iodobenzene cation radical would also be destabilized by the electron-withdrawing group and the polar effects would hardly be operative.

The rate for **1a** is compared with that for 1-cyclohexenyl triflate under the same conditions evaluated from the activation parameters;[5] **1a** is nearly 10^6 times more reactive than the triflate. That is, the phenyliodonio group is about 10^6 times as good a nucleofuge as the triflate leaving group, that is about 10^6 times as reactive as the tosylate, and is considered to be one of the best leaving groups.[23,24] The iodonio group is the most efficient leaving group which has ever been determined quantitatively. For the comparison of the leaving abilities of some related nucleofuges, solvolysis rates of pertinent substrates are summarized in Table 4. Some data are evaluated by activation parameters. Relative leaving abilities estimated from the literature values are listed in Table 5. A remarkably high reactivity of the iodonium ion is apparent. By contrast, another positively charged nucleofuge, the sulfonio group, is surprisingly a very poor leaving group.

The relative reactivitiy of about 250 evaluated for **2** compared with **1a** would correspond to the effect of the 2-methyl substitution, since the 4-*tert*-butyl group may have a relatively small influence on the reactivity. This effect of methyl substitution is quite large as compared with a similar effect in the solvolysis of 1-cyclohexenyl triflate observed at 100 °C in the same solvent—2-methyl substitution enhancing the rate only by 13-fold.[5] These results must come from the greater stability of the 2-methylvinyl cation than the vinyl cation. Such stabilizing effects of the 2-methyl group (8 kcal/mol) were theoretically demonstrated for the vinyl cation by the MP/6-31G* calculations.[25]

(1-Cyclopentenyl)phenyliodonium tetrafluoroborate was stable in methanol or TFE at least 2 weeks at 50 °C. A primary alkenyl salt, (1-decenyl)phenyliodonium tetrafluoroborate, was also stable in TFE but undergoes elimination to give alkyne in a more basic media like methanol.[1e] These results reflect instability of the vinyl cations. There has been presented no evidence for generation of cyclopentenyl or primary alkenyl cations. 1-Cyclopentenyl triflate and nonaflate were recovered practically unchanged even after heating in TFE containing triethylamine at 100 °C for 10 days.[8,26] Strongly bent vinyl cations like cyclopentenyl cation are strained too much to be formed as an intermediate.

Experimental Section

IR spectra were recorded on a JASCO IRA-1 spectrometer. ^1H NMR spectra were recorded on a JEOL JNM-FX200 or a JNM-GX400 spectrometer. Chemical shifts are given in ppm downfield from internal Me_4Si. Mass spectra (MS) were obtained on a JEOL JMS-SX102A or an MS-AUTOMASS 150 spectrometer. Analytical gas chromatography was conducted on a Shimadzu GC-14A gas chromatograph with 1% or 20% Silicone GE SF-96 on a Chromosorb W-AWDMCS column (3 m) and on a Shimadzu GC-15A gas chromatograph with an FFS ULBON HR-1, HR-1701, or HR-20M capillary column (0.25 mm × 50 m). Preparative GC was performed on a Shimadzu GC-14A gas chromatograph with 1% Silicone GE SF-96 on a Chromosorb W-AWDMCS column (1 m). Melting points were determined with a Yanaco micro-melting-point apparatus and are uncorrected.

Purification of solvents was carried out under a nitrogen atmosphere. THF was distilled from sodium benzophenone ketyl. Dichloromethane was dried over CaH_2 and distilled. EtOH and MeOH were distilled from sodium. TFE was dried over $CaSO_4$ in the presence of a small amount of $NaHCO_3$ and distilled. BF_3-Et_2O was distilled from CaH_2. Other commercially available chemicals are of the best grade and were used as received.

(4-*tert*-Butyl-1-cyclohexenyl)phenyliodonium Tetrafluoroborate (1a). The BF_3-catalyzed silicon—iodonium exchange reaction between 4-*tert*-butyl-1-(trimethylsilyl)cyclohexene and iodosylbenzene was carried out in the same way as described previously.[2a] The yield of **1a** was 96%.

(4-*tert*-Butyl-1-cyclohexenyl)-*p*-methylphenyliodonium Tetrafluoroborate (1b). To a stirred suspension of *p*-(diacetoxyiodo)toluene[27] (511 mg, 1.52 mmol) and 4-*tert*-butyl-1-(trimethylsilyl)cyclohexene (200 mg, 0.95 mmol) in dichloromethane (11 mL) was added BF_3-Et_2O (216 mg, 1.52 mmol) at 0 °C under nitrogen, and the mixture was stirred for 1 h at 0 °C and for additional 3 h at room temperature. After the addition of a saturated aqueous sodium tetrafluoroborate solution (10 mL), the mixture was stirred for 15 min. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was concentrated under an aspirator vacuum to give an oil, which was washed several times with hexane—diethyl ether by decantation at −78 °C. Further purification using hexane—diethyl ether gave the vinyliodonium salt **1b** (355 mg, 85%) as a white powder: mp 83—84 °C dec. IR (Nujol) 1100—1000, 805 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 0.85 (s, 9H), 1.31—1.54 (m, 2H), 1.82—2.57 (m, 3H), 2.46 (s, 3H), 2.57—2.75 (m, 2H), 6.93—7.03 (m, 1H), 7.33 (d, J = 8.5 Hz, 2H), 7.85 (d, J = 8.5 Hz, 2H). HRMS (FAB): *m/z* obsd 355.0898 [$(M - BF_4)^+$], calcd for $C_{17}H_{24}I$ 355.0923. Anal. Calcd for $C_{17}H_{24}BF_4I$: C, 46.19; H, 5.47. Found: C, 45.99; H, 5.82.

(4-*tert*-Butyl-1-cyclohexenyl)-*p*-chlorophenyliodonium Tetrafluoroborate (1c). To a stirred suspension of *p*-chloroiodosylbenzene[27] (814 mg, 3.20 mmol) and 4-*tert*-butyl-1-(trimethylsilyl)cyclohexene (419 mg, 2.00 mmol) in dichloromethane (8 mL) was added BF_3-Et_2O (454 mg, 3.20 mmol) at 0 °C under nitrogen and the mixture was stirred for 12 h at 0 °C and for 1 h at room temperature. After the addition of a saturated aqueous sodium tetrafluoroborate solution (20 mL), the mixture was stirred for 15 min. The reaction mixture was poured into water and extracted with dichloromethane. The organic

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(23) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85.

(24) Stirling, C. J. M. *Acc. Chem. Res.* **1979**, *13*, 198.

(25) Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496.

(26) (a) Subramanian, L. R.; Hanack, M. *J. Org. Chem.* **1977**, *42*, 175. (b) Hanack, M.; Bentz, H.; Markl, R.; Subramanian, L. R. *Liebigs Ann. Chem.* **1978**, 1894.

(27) Ochiai, M.; Ito, T.; Takaoka, Y.; Masaki, Y. *J. Am. Chem. Soc.* **1991**, *113*, 1319.

layer was concentrated under an aspirator vacuum to give an oil, which was washed several times with hexane–dichloromethane by decantation at −78 °C. Recrystallization from hexane–dichloromethane gave the vinyliodonium salt **1c** (403 mg, 44%) as colorless needles: mp 92–94 °C dec. IR (Nujol) 1100–1000, 820 cm^{-1}. ^{1}H NMR (200 Hz, $CDCl_3$) δ 0.85 (s, 9H), 1.34–1.60 (m, 2H), 1.73–2.03 (m, 2H), 2.17–2.77 (m, 3H), 7.00–7.30 (m, 1H), 7.48 (d, J = 8.5 Hz, 2H), 7.96 (d, J = 8.5 Hz, 2H). HRMS: m/z obsd 375.0339 [(M − BF_4)$^+$], calcd for $C_{16}H_{21}ClI$ 375.0378. Anal. Calcd for $C_{16}H_{21}BClF_4I$: C, 41.55; H, 4.58. Found: C, 41.19; H, 4.77.

(2-Methyl-1-cyclohexenyl)phenyliodonium Tetrafluoroborate (2). To a stirred suspension of iodosylbenzene (244 mg, 1.11 mmol) and 2-methyl-1-(trimethylstannyl)cyclohexene[7] (180 mg, 0.70 mmol) in dichloromethane (6 mL) was added BF_3–Et_2O (158 mg, 1.11 mmol) at 0 °C under nitrogen over 1 min. The mixture turned to a yellow clear solution during the addition of BF_3–Et_2O. After the addition of a saturated aqueous sodium tetrafluoroborate solution (6 mL), the mixture was stirred for 0.5 min. The organic layer was concentrated under an aspirator vacuum at 0 °C to give an oil, which was washed several times with diethyl ether by decantation at −78 °C to yield the highly labile vinyliodonium salt **2** (174 mg, 65%) as a white powder. The salt was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$, −20 °C) δ 1.70–1.82 (m, 4H), 2.22 (s, 3H), 2.48–2.58 (br s, 2H), 2.74–2.83 (br s, 2H), 7.54 (t, J = 7.8 Hz, 2H), 7.70 (t, J = 7.8 Hz, 1H), 7.93 (d, J = 7.8 Hz, 2H). MS (FAB): m/z 299 [(M − BF_4)$^+$].

Product Analysis. (a) Solvolysis of 1a in 60:40 (v/v) Ethanol–Water. The Vinyliodonium tetrafluoroborate **1a** (30 mg) was dissolved in 60:40 (v/v) ethanol–water (8 mL) under nitrogen. The solution was kept under the conditions described in Table 1. Products were extracted with pentane, and the yields were determined by analytical GC: for 4-*tert*-butylcyclohexanone (**3K**) and iodobenzene (**4a**) with 20% Silicone GE SF-96 (150 °C, tetradecane as the internal standard) and for (4-*tert*-butyl-1-cyclohexenyl)iodobenzenes (**5a**) with 1% Silicone GE SF-96 (150 °C, icosane as the internal standard). The isomeric distribution of **5a** was determined by capillary GC (FFS ULBON HR-20M) at 230 °C. Preparative GC afforded pure 2-(4-*tert*-butyl-1-cyclohexenyl)iodobenzene (**5a–o**) and a mixture of 3- (**5a–m**) and 4-(4-*tert*-butyl-1-cyclohexenyl)iodobenzene (**5a–p**). **5a–o**: IR (neat) 2950, 2865, 1665, 1470, 1360, 1020, 769 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (s, 9H), 1.34–1.42 (m, 2H), 1.91–1.98 (m, 2H), 2.18–2.29 (m, 3H), 5.56–5.58 (m, 1H), 6.91 (dt, J = 1.5, 8.0 Hz, 1H), 7.13 (dd, J = 1.5, 8.0 Hz, 1H), 7.28 (dt, J = 1.0, 8.0 Hz, 1H), 7.82 (dd, J = 1.0, 8.0 Hz, 1H). MS: m/z (rel intensity) 340 (65, M$^+$), 284 (24), 283 (22), 217 (28), 156 (22), 129 (37), 115 (45), 57 (100). HRMS: m/z obsd 340.0698 (M$^+$), calcd for $C_{16}H_{21}I$ 340.0688. **5a–m** and **5a–p**: IR (neat) 2950, 2865, 1370, 800 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (s, total 9H), 1.25–1.35 (m, total 2H), 1.91–1.99 (m, total 2H), 2.12–2.43 (m, total 3H), 6.09–6.16 (m, total 1H), 7.03 (t, J = 7.8 Hz, 1H for **5a–m**), 7.12 (d, J = 8.3 Hz, 2H for **5a–p**), 7.33 (br d, J = 7.8 Hz, 1H for **5a–m**), 7.53 (br d, J = 7.8 Hz, 1H for **5a–m**), 7.61 (d, J = 8.3 Hz, 2H for **5a–p**), 7.72 (t, J = 1.0 Hz, 1H for **5a–m**). MS for **5a–m**: m/z (rel intensity) 340 (15, M$^+$), 284 (10), 217 (16), 129 (100), 89 (14), 57 (78). MS for **5a–p**: m/z (rel intensity) 340 (32, M$^+$), 269 (13), 217 (23), 129 (100), 57 (54). HRMS for **5a–m**: m/z obsd 340.0701 (M$^+$), calcd for $C_{16}H_{21}I$ 340.0688. HRMS for **5a–p**: m/z obsd 340.0698 (M+), calcd for $C_{16}H_{21}I$ 340.0688. Protodeiodination of **5a–o** with butyllithium in THF at −78 °C for 4.5 h gave 4-*tert*-butyl-1-phenylcyclohexene[2a] in high yield.

(b) Solvolysis of 1a in Methanol and TFE. The vinyliodonium salt **1a** (30 mg) was dissolved in methanol or TFE (8 mL) under nitrogen and the solution was kept under the conditions described in Table 1. After addition of 10% aqueous HCl (8 mL), the mixture was stirred for 1 h at room temperature and extracted with pentane. The yields of the products[28] and the isomeric distribution of **5a** were determined by analytical GC. Formation of **6** was not detected in the solvolysis of **1a** in methanol by analytical capillary GC.

(c) Solvolysis of 1a in the Presence of 1,4-Cyclohexadiene. The iodonium salt **1a** (30 mg, 0.07 mmol) and 1,4-cyclohexadiene (561 mg, 7.00 mmol) were dissolved in methanol (7 mL) in nitrogen and the solution was stirred for 7 h at 50 °C. After addition of 10% aqueous HCl (7 mL), the mixture was stirred for 4 h at room temperature and extracted with pentane. Analytical capillary GC using an FFS ULBON HR-1 column (100 °C) with undecane as the internal standard showed the formation of **3K** (56%), **6** (1%), and **4a**. The structures were determined by comparison of spectral data (GC-MS and/or ^{1}H NMR) of these products with those of the authentic samples. An authentic sample of **6**[29] was prepared from the tosylhydrazone of **3K** by the reaction with butyllithium.[30] **6**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.86 (s, 9H), 1.02–1.30 (m, 3H), 1.60–2.10 (m, 4H), 5.57–5.77 (m, 2H); MS m/z (rel intensity) 138 (5, M$^+$), 123 (4), 95 (10), 80 (53), 67 (61), 57 (100).

(d) Solvolysis of 1a in 2-Propanol. The iodonium salt **1a** (30 mg) was dissolved in 2-propanol (7 mL) in nitrogen and the solution was stirred for 17.5 h at 50 xalC. After addition of 10% aqueous HCl (7 mL), the mixture was stirred for 4 h at room temperature and extracted with pentane. Analytical capillary GC showed the formation of **3K** (51%), **6** (1%), and **4a**.

(e) Solvolysis of 1b in 60:40 (v/v) Ethanol–Water. The iodonium salt **1b** (30 mg) was dissolved in 60:40 (v/v) ethanol–water (8 mL) under nitrogen. The solution was kept under the conditions described in Table 1. Products were extracted with pentane, and the yields were determined by analytical GC: for **3K** and *p*-iodotoluene (**4b**) with 20% Silicone GE SF-96 (150 °C, tetradecane as the internal standard) and for (4-*tert*-butyl-1-cyclohexenyl)iodotoluenes (**5b**) with 1% Silicone GE SF-96 (150 °C, nonadecane as the internal standard). The isomeric distribution of **5b** was determined by capillary GC (FFS ULBON HR-20M) at 230 °C. Preparative GC afforded 3-(4-*tert*-butyl-1-cyclohexenyl)-4-iodotoluene (**5b–o**) and 2-(4-*tert*-butyl-1-cyclohexenyl)-4-iodotoluene (**5b–m**). **5b–o**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (s, 9H), 1.29–1.44 (m, 2H), 1.88–1.99 (m, 2H), 2.15–2.35 (m, 3H), 2.28 (s, 3H), 5.53–5.58 (m, 1H), 6.74 (dd, J = 2.0, 8.0 Hz, 1H), 6.96 (d, J = 2.0 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H). MS: m/z (rel intensity) 354 (81, M$^+$), 298 (51), 231 (39), 170 (100), 143 (85), 128 (64), 115 (35), 57 (89). HRMS: m/z obsd 354.0817 (M$^+$), calcd for $C_{17}H_{23}I$ 354.0845. **5b–m**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (s, 9H), 1.25–1.40 (m, 2H), 1.87–1.98 (m, 2H), 2.13–2.30 (m, 3H), 2.21 (s, 3H), 5.54–5.57 (m, 1H), 6.89 (d, J = 8.0 Hz, 1H), 7.41 (d, J = 2.0 Hz, 1H), 7.43 (dd, J = 2.0, 8.0 Hz, 1H). MS: m/z (rel intensity) 354 (80, M$^+$), 298 (54), 231 (24), 171 (48), 143 (100), 128 (86), 115 (42), 57(97). HRMS: m/z obsd 354.0863 (M$^+$), calcd for $C_{17}H_{23}I$ 354.0845.

(f) Solvolysis of 1b in Methanol and TFE. The iodonium salt **1b** (30 mg) was dissolved in methanol or TFE (8 mL) under nitrogen and the solution was kept under the conditions described in Table 1. After addition of 10% aqueous HCl (8 mL), the mixture was stirred for 1 h at room temperature and extracted with pentane. The yields of the products and the isomeric distribution of **5b** were determined by analytical GC.

(g) Solvolysis of 2 in Aqueous Ethanol. The iodonium salt **2** (86 mg) was dissolved in 60:40 (v/v) ethanol–water (22 mL) at −20 °C. The cooling bath was removed and the solution was stirred for 5 h. After the addition of 10% hydrochloric acid solution (22 mL) at room temperature, the reaction mixture was stirred for 1 h and extracted with pentane. Analytical capillary GC using an HR-1701 column (100 °C) with dodecane as the internal standard showed the formation of 2-methylcyclohexanone (**7**, 61%), cyclopentyl methyl ketone (**8**, 10%), and **4a**. The structures were determined by comparison of spectral data (GC-MS and ^{1}H NMR) of these products with those of the authentic samples.

(h) Solvolysis of 2 in TFE. The iodonium salt **2** (9.3 mg) was dissolved in TFE (6 mL) at 0 °C under nitrogen. After **2** was completely dissolved, the mixture was allowed to warm up to room temperature with stirring. After 5 h, 10% HCl was added under ice-cooling and the mixture was stirred for 1 h. The products were extracted with pentane and dodecane was added as an internal standard. The GC analysis showed formation of **7** (40%), **8** (34%), and **4a**.

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(28) Variable ratios of **3E**, **3K**, and **3A** were observed in unbuffered alcohols but more than 80% yield of **3E** was obtained from reaction in the presence of a base, e.g., pyridine. The total solvolysis products were usually determined as **3K** after acid hydrolysis.

(29) (a) Sicher, J.; Sipos, F.; Tichy, M. *Collect. Czech. Chem. Commun.* **1961**, *26*, 847. (b) Lambert, J. B.; Wang, G.; Finzel, R. B.; Teramura, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 7838.

(30) (a) Shapiro, R. H. *Org. React.* **1976**, *23*, 405. (b) Chamberlin, A. R.; Bloom, S. H. *Org. React.* **1990**, *39*, 1.

Kinetic Measurements. Rates of solvolysis of **1** were measured by monitoring the decrease in absorbance at 245 (for **1a**) or 250 nm (for **1b** and **1c**) at temperatures in the range 30–70 °C on a Shimadzu UV-2200 spectrophotometer. The reaction temperature was controlled by a CPS-240A controller and accurate to within ±0.1 °C. A stock solution of the substrate **1** was prepared by weighing and dissolving in dioxane (0.01–0.03 M) and stored in a refrigerator. The reaction solvents were prepared by volume at room temperature and unbuffered. To 3.0 mL of the solvent in a quartz cuvette inserted in a cell compartment of the spectrophotometer and equilibrated at the reaction temperature was added 10 μL of the stock solution of **1** from a microsyringe. The absorbance change was fed to a computer NEC PC-9801FA through an interface and processed by a pseudo-first-order kinetics program. The reaction followed pseudo-first-order kinetics for at least 4 half-lives and the pseudo-first-order rate constants k_{obsd} were calculated.

Kinetics of the solvolysis of **2** were also carried out in the same way at 25 °C by monitoring at 240 nm. The stock solution was prepared by dissolving an appropriate amount of the salt in ethanol at −20 °C under nitrogen and the cold solution was introduced from a microsyringe to 3.0 mL of the reaction solvent equilibrated at 25 °C in the cell compartment of the spectrophtometer.

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