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Thermal and Photochemical Solvolysis of (*E*)- and (*Z*)-2-Phenyl-1-propenyl(phenyl)iodonium Tetrafluoroborate: Benzenium and Primary Vinylic Cation Intermediates

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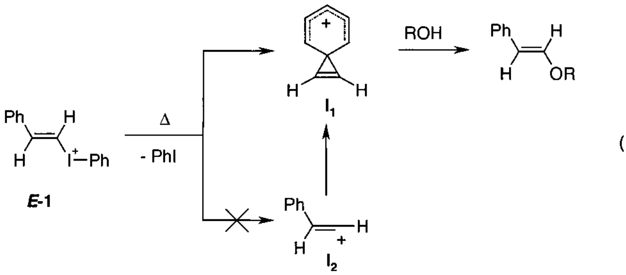
Abstract: The thermal and photochemical solvolysis of the two stereoisomeric 2-phenyl-1-propenyl(phenyl)-iodonium tetrafluoroborates has been investigated in alcoholic solvents of varying nucleophilicity. The product profiles and rates of product formation in the thermal reaction are all compatible with a mechanism involving cleavage of the vinylic C−I bond assisted by the group in the trans position (methyl or phenyl), always leading to rearranged products. Depending on the nucleophilicity of the solvent, the primarily formed cations may or may not further rearrange to more stable isomers. The less reactive *Z* compound also yields some unrearranged vinyl ether product in the more nucleophilic solvents via an in-plane S_N2 mechanism. The mechanism of the photolysis involves direct, unassisted cleavage of the vinylic, and aromatic, C−I bond in an S_N1 mechanism. This produces a primary vinyl cation, which is partially trapped prior to rearrangement in methanol. The unrearranged vinyl ethers are mainly formed with retention of configuration via a λ^3-iodonium/solvent complex in an S_Ni mechanism. Thermal and photochemical solvolyses of iodonium salts are complementary techniques for the generation of different cation intermediates from the same substrate.

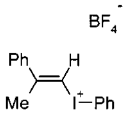
Introduction

The (*E*)-styryliodonium salt *E*-**1** undergoes thermal solvolysis through a vinylene benzenium ion $\mathbf{I_1}$ as intermediate.[1] The departure of the iodonio leaving group has been suggested to proceed with anchimeric assistance of the β-phenyl group.[1,2] That is, the benzenium ion is formed directly without intervention of the primary vinylic cation $\mathbf{I_2}$ (eq 1).

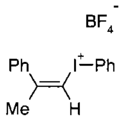


(1)

Stereoelectronic effects require that the participation of the β-phenyl group in this reaction occurs in an anti-periplanar fashion. This implies that only the *E* isomer of substrate **1** can undergo phenyl participation but the *Z* isomer (*Z*-**1**) cannot. It is therefore interesting to examine effects of the β-phenyl group in the reactions of *Z*-**1**. Unfortunately, *Z*-**1** is too unstable to be isolated as a salt owing to its very facile anti-β-elimination.[3] We therefore studied the solvolysis reactions of the *E* and *Z* isomers of the methyl-substituted derivative, 2-phenyl-1-propenyl(phenyl)iodonium tetrafluoroborate (*E*-**2** and *Z*-**2**).



***E*-2**



***Z*-2**

The solvolysis reactions were performed thermally as well as photochemically. Irradiation of β-phenyl-substituted vinyl halides is known to be an excellent entry to vinyl cations.[4] Information about the photochemistry of vinyl iodonium compounds, which are pseudo-vinyl halides, was not available, but formation of vinyl cations by direct C−I bond cleavage was anticipated. This was based on the knowledge of the photochemical behavior of diaryliodonium salts, which do yield aryl cations[5] and the leaving group effects in photochemistry of vinyl halides,[6] where more heterolytic photocleavage occurs with better leaving groups. In this paper, the results of the thermal

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Table 1. Product Distributions (in percent yields) in the Thermal Solvolysis of **2** at 60 °C

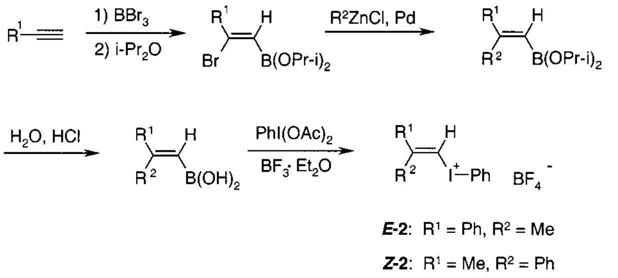
	substrate						
	E-**2**	*Z*-**2**	*E*-**2**	*E*-**2**	*Z*-**2**	*E*-**2**	*Z*-**2**
solvent	MeOH	MeOH	MeOH[a]	AcOH	AcOH	TFE	TFE
time/h	1	95	0.5	1	122	0.5	170
3 (*E*/*Z*)[b]	0	5.8 (5.8/0)	0	0	12.8 (5.2/7.6)	0	0
4 (*E*/*Z*)[c]	29 (15/0)	0	0	42 (35/7)	0	20	0
5 (*E*/*Z*)[d]	0	4.9	0	8.1 (3.1/5.0)	56 (20/36)	11	14
6	28	81	95	35	30	17	6.7
7	30	0	0	7.3	0	6.4	0
8	97	87	86	97	92	85	22

[a] In the presence of 0.05 M of sodium acetate. A similar result was obtained by using *Z*-**2** as substrate. [b] Total yield of **3** and the yields of *E*-**3** and *Z*-**3** in parentheses. [c] Total yield of **4** and **4C** and the yields of *E*-**4** and *Z*-**4** in parentheses. [d] Total yield of **5** and **5C** and the yields of *E*-**5** and *Z*-**5** in parentheses.

and photochemical solvolysis reactions of the stereoisomeric iodonium salts **2** are compared and shown to yield mutually supportive information about mechanisms and the nature of the reactive intermediates.

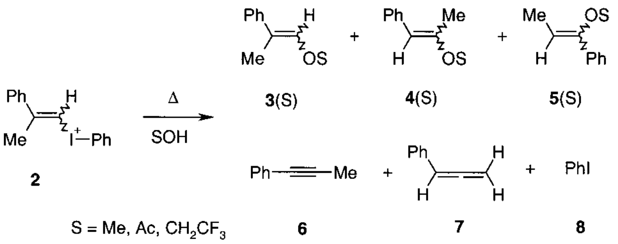
Results

Preparation. The tetrafluoroborate salts of the stereoisomeric 2-phenyl-1-propenyliodonium ions, *E*-**2** and *Z*-**2**, were prepared stereoselectively from phenyl- and methylacetylene, respectively, by bromoboronation[7] and methylation/phenylation[8] followed by treatment with (diacetoxyiodo)benzene[9] (eq 2). Both isomers are stereochemically >98% pure according to ^{1}H NMR.



(2)

Thermal Solvolysis. The thermal solvolysis of **2** was carried out in various alcohols, acetic acid, and aqueous alcoholic solvents at 60 °C. The reaction of *E*-**2** was complete within 1 h in all solvents but that of *Z*-**2** was much slower, taking over a week for completion in TFE. The products obtained in methanol, acetic acid, and TFE were identified on the basis of their gas chromatographic retention times and MS spectra compared with those of independently prepared authentic samples (eq 3).



(3)

Table 2. Rate Constants ($10^4 k_{\mathrm{obsd}}/\mathrm{s}^{-1}$) and Rate Ratios for the Thermal Solvolysis of **2** in Various Solvents at 60 °C

solvent	*E*-**2**	*Z*-**2**	*E*-**2**/*Z*-**2**
MeOH	17.1	0.82	21
EtOH	16.3	1.10	15
80E[a]	15.7	0.8[d]	20
60E[a]	15.3	0.5[d]	30
40E[a]	16.0	0.4[d]	40
20E[a]	16.3	0.6[d]	27
50ET[b]	45.0	1.5	30
AcOH	19.9	0.42	47
TFE	80.4	0.02[e]	4000
AcONa/MeOH[c]	226	823	0.27

[a] Aqueous ethanol containing a specified volume percent of ethanol. [b] 50 vol % EtOH−TFE. [c] Sodium acetate (0.05 M) in methanol, reaction at 25 °C. [d] Approximate value, see text. [e]Obtained from the calculated infinite absorbance.

The product yields were determined using gas chromatography with tetradecane as an internal standard and are summarized in Table 1. The data show that in each of the solvents the product distribution derived from *E*-**2** and *Z*-**2** is quite different. From *E*-**2** two elimination products, 1-phenylpropyne (**6**) and phenylpropadiene (**7**), are formed, as well as a phenyl-migrated (**4**(S)) and a methyl-migrated (**5**(S)) substitution product, and their hydrolysis products 1-phenylpropanone (**4C**) and propiophenone (**5C**), accompanied by iodobenzene (**8**). The *Z* isomer *Z*-**2** gave mainly methyl-migrated products, **5** and **6**, also accompanied by **8**. In the more nucleophilic solvents, methanol and acetic acid, in addition a small amount of unrearranged substitution product **3**(S) was obtained. However, no phenyl-migrated products, **4** and **7**, were found.

In the presence of a base, sodium acetate, in methanol, the very rapid reaction gave 1-phenylpropyne (**6**) and **8** as the exclusive products, irrespective of the substrate structure.

Rate constants for the solvolysis of **2** were determined spectrophotometrically in both alcoholic and aqueous alcoholic solutions using freshly distilled solvent containing 1 mM trifluoroacetic acid to maintain the reproducibility of the results.[1b] The (pseudo-)first-order rate constants k_{obsd} are summarized in Table 2. For the slow reactions of *Z*-**2** in aqueous alcoholic solutions, no good first-order kinetics were observed, and approximate rate constants were evaluated from the change in absorbance during the initial two half-lives.

Photochemical Solvolysis. The photochemical solvolysis of **2** was carried out in methanol and TFE at 20 °C by irradiation

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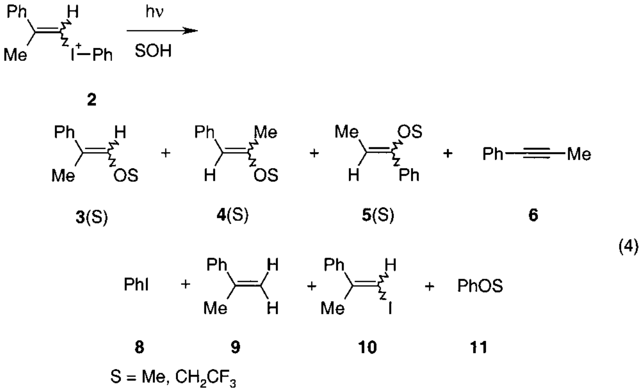
Table 3. Product Distributions (in Percentages) in the Photochemical Solvolysis of **2**[a]

	substrate			
	E-**2**[a]	*Z*-**2**[a]	*E*-**2**[a]	*Z*-**2**[a]
solvent	MeOH	MeOH	TFE	TFE
E-**3**	34.1	14.8	0	0
Z-**3**	13.4	38.5	0	0
E-**4**	6.5	7.5	32.6	11.0
Z-**4**	0	0	4.4	2.2
4C	0	0	9.9	<2[b]
E-**5**	8.2	10.8	36.6	54.1
Z-**5**	8.6	11.5		
5C	0	0	10.2	10.4
6	15.3	16.7	<2[b]	<2[b]
8	66.3	71.5	81.8	70.5
9	10.8	5.7	0	0
E-**10**	33.7	0[c]	18.2	0[c]
Z-**10**	0[c]	28.5	0[c]	29.5
11	6.5	7.1	5.2	8.6

[a] Relative amounts of photoproducts, normalized to **8** + **10** = 100%. [b] The amount of product **6** at the end of the photoreaction does not significantly exceed the initial amount. An upper limit for the efficiency of its formation is given. [c] *Z*-**10** was shown to be a secondary photoproduct in the irradiation of *E*-**2** and is added to *E*-**10**, and similarly *E*-**10** is added to *Z*-**10** for the photoproducts of *Z*-**2**.

at $\lambda_{\mathrm{exc}} = 248$ nm. The relative efficiencies of formation of the photoproducts were determined as a function of the time of irradiation, and all products were found to be primary photoproducts. In both solvents *E*-**2** yields the same photoproducts as *Z*-**2** (eq 4).

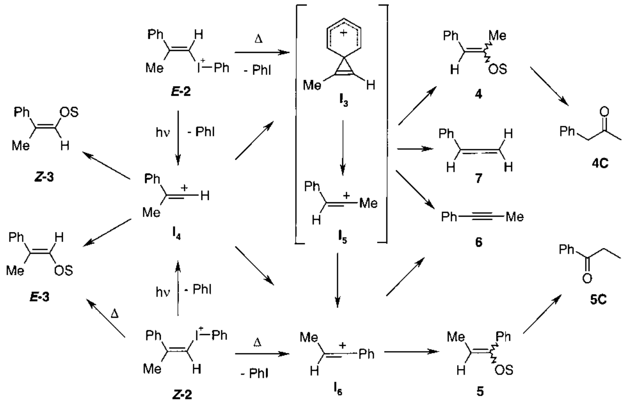


(4)

The products **3**, **4**, **5**, **6**, and **8** are the result of heterolytic cleavage of the vinylic C−I bond, but no **7** is formed. In addition, a product of homolytic cleavage of this bond is formed, 2-phenylpropene (**9**) as well as products of heterolytic cleavage of the phenylic C−I bond: (*E*)- and (*Z*)-1-iodo-2-phenylpropene (**10**) and anisole or 2,2,2-trifluoroethoxybenzene (**11**).

The relative efficiencies of formation are summarized in Table 3. The photochemical experiments in TFE are hampered by the enhanced thermal reactivity of *E*-**2**, making the reported product distributions in this solvent less reliable. In methanol, two unrearranged vinyl ethers **3** as well as one rearranged vinyl ether **4** and two rearranged vinyl ethers **5** are formed. The *E*/*Z* ratios of the unrearranged substitution products **3** depend on the stereochemistry of the starting material, and retention of configuration is favored. The 1,2-phenyl- and 1,2-methyl-shifted products **4** and **5** are formed from *E*-**2** as well as from *Z*-**2**. The product distributions are similar irrespective of the geometrical structure of the starting material (**3**/(**4** + **5**) = 2.0 and 1.8 from *E*-**2** and *Z*-**2**, respectively). The *E*/*Z* ratios are also similar: 1/0 in the case of **4** and 1/1.3 in the case of **5**. The 1,2-methyl-shifted products **5** are formed more efficiently than the 1,2-phenyl-shifted products **4** (**5**/**4** = 2.6 and 3.0 from *E*-**2** and *Z*-**2**, respectively).

Scheme 1. Mechanism of the Thermal and Photochemical Solvolysis of **2**



The unrearranged vinyl ethers **3** are the major products in methanol but are not formed in TFE. However, as in the case of methanol, products **5** are formed more efficiently than products **4**. The apparently smaller **5**/**4** ratio for *E*-**2** than for *Z*-**2** is most probably caused by considerable thermal reaction for *E*-**2** during the photoreaction, yielding **4**.

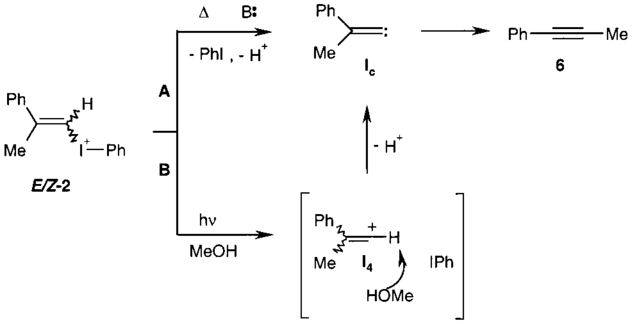
Discussion

The products of the thermal reactions of **2** all derive from heterolysis of the vinylic C−I bond and indicate extensive rearrangement. The product profiles are contrastingly different for the isomeric substrates, *E*-**2** and *Z*-**2**. The *E* substrate *E*-**2** gives mainly the β-phenyl-shifted product **4** while *Z*-**2** gives the β-methyl-shifted product **5**. That is, the main rearranged products are those of migration of the β-substituent trans to the leaving iodonio group. Thus, the product distribution is best rationalized by assuming participation of the β-phenyl group for *E*-**2** and participation of the β-methyl group for *Z*-**2**. The solvolysis of *Z*-**2** gives only **5** and **6** as the rearranged products, but not **4** or **7**, in any of the solvents used. In contrast, *E*-**2** gives all the possible rearranged products **4**−**7** in TFE and AcOH, but **5** is not produced in MeOH.

The formation of the products is explained within the framework of Scheme 1. All products are formed from intermediate ions $\mathbf{I_3}$−$\mathbf{I_6}$. The β-phenyl participation of *E*-**2** affords benzenium ion $\mathbf{I_3}$[1] and subsequently α-methyl cation $\mathbf{I_5}$, which lead to **4** by solvent addition as well as to **6** and **7** by deprotonation. A further, 1,2-hydride, shift in $\mathbf{I_5}$ yields $\mathbf{I_6}$, which gives **5** and **6**. More rearrangement of $\mathbf{I_5}$ to $\mathbf{I_6}$ occurs in the less nucleophilic/basic solvents, AcOH and TFE, but MeOH may rapidly trap $\mathbf{I_5}$ (or even $\mathbf{I_3}$) prior to the 1,2-hydride shift. The only rearranged products obtained from *Z*-**2** are those derived from $\mathbf{I_6}$, which may be formed by trans β-methyl participation. This is reasonable because the α-phenyl cation $\mathbf{I_6}$ is more stable than $\mathbf{I_5}$ and conversion from $\mathbf{I_6}$ to $\mathbf{I_5}$ is not possible. The primary vinylic cation $\mathbf{I_4}$ is not involved in the thermal solvolysis of *E*-**2** or *Z*-**2**. This cation should lead to both $\mathbf{I_5}$ (via $\mathbf{I_3}$) and $\mathbf{I_6}$ by phenyl and methyl migration, respectively, as indicated by the photochemical reactions (see below). Also the stereochemical difference in the substrate structures would be essentially lost upon formation of the linear cation $\mathbf{I_4}$.

The unrearranged vinyl ether *E*-**3** was obtained only from *Z*-**2** in the more nucleophilic solvents, MeOH and AcOH, but not from *E*-**2** or in TFE. This product is likely to be formed by

Scheme 2. Thermal (**A**) and Photochemical (**B**) Formation of 1-Phenylpropyne (**6**) via α-Elimination



direct nucleophilic substitution (in-plane vinylic S_N2).[10] Also noticeable is the formation of a large amount of **6** from *Z*-**2** in methanol. This product may largely be formed via α-elimination (Scheme 2A) in this basic solvent.[1b] The latter reaction can compete with the slow β-methyl-participating reaction of *Z*-**2**.

The higher reactivity of *E*-**2** than *Z*-**2** is also compatible with the participation mechanism. Phenyl participation stabilizes the transition state for *E*-**2** more effectively than methyl participation for *Z*-**2**. This difference induces a rate ratio of 20−40 in the more nucleophilic alcoholic and aqueous alcoholic solvents, but a rate ratio of 4000 in the less nucleophilic TFE (see data in Table 2). Nucleophilic participation of the solvent in the ionization step[11] may diminish the effect of the anchimeric assistance.

For the formation of acetylene **6** in the presence of base, a reverse relative reactivity of the isomeric substrates was observed (i.e., *Z*-**2** more reactive than *E*-**2** as is seen in the last entry of Table 2).[12] This is in line with a reaction via α-elimination, where participation is not important. The higher reactivity of *Z*-**2** than *E*-**2** may be partially due to the ground-state instability of *Z*-**2**.

The solvolysis of (*E*)- and (*Z*)-1-methyl-2-phenyl-1-propenyl triflate in TFE was previously investigated, and the anchimeric assistance by the neighboring phenyl group in the geometrically favorable *E* triflate was found to be ∼70.[13a] The larger enhancement (4000-fold) for the present system **2** in TFE probably is due to the presence of an unsubstituted α-carbon in **2**, compared to the α-methyl-substituted carbon in the triflate compound. In saturated systems, the rate enhancement due to β-phenyl assistance is usually small.[13b,c] The relative rates of acetolysis of *trans*- and *cis*-2-phenylcyclopentyl tosylates (trans/cis = 0.25) are affected by other factors besides phenyl assistance.[13c,d] The results show that the rate enhancement by neighboring group participation is greatly dependent on the stability of the carbocation which would be formed in the unassisted reaction.

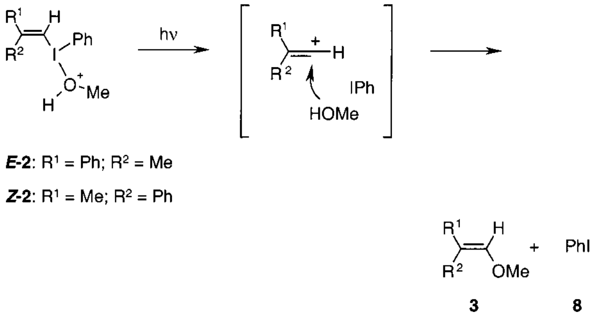
The effects of solvent on the rates of the thermal solvolysis of *E*-**2** and *Z*-**2** are different: for *E*-**2**, EtOH < AcOH < TFE; for *Z*-**2**, EtOH > AcOH > TFE. The order for *E*-**2** is similar to that observed for the S_N1 solvolysis of a 1-cyclohexenyliodonium salt,[14] while that for *Z*-**2** is similar to that for *E*-**1**.[1b] These observations are compatible with our proposal that the solvolysis of *E*-**2** occurs via phenyl participation while *Z*-**2** and *E*-**1** partially undergo α-elimination and in-plane S_N2 substitution in more basic solvents.

The product profiles of the photochemical reactions of **2** are fundamentally different from those of the thermal reactions. Photochemistry of compounds **2** exhibits heterolytic (products **3**−**8**) as well as homolytic (product **9**) cleavage of the vinylic C−I bond. In TFE, no homolytic cleavage of the vinylic C−I bond occurs. Apparently the larger ion-solvating power of this solvent favors heterolytic cleavage. Cleavage of the aromatic C−I bond only occurs in the photochemical reaction. The process is heterolytic (products **10** and **11**), but homolytic cleavage is not excluded, since the expected reaction product from this path (benzene) may be obscured by the solvent in our GC analyses.

Most interesting are the products resulting from heterolytic cleavage of the vinylic C−I bond. Their formation is explained within the framework of Scheme 1 by assuming initial formation of the primary vinylic cation **I$_4$** via an S_N1 mechanism and ensuing rearrangements to the more stable vinylic cations **I$_3$**, **I$_5$**, and **I$_6$**, which in turn give **4** and **5**, respectively. The thermal and photochemical solvolysis of iodonium salts thus are complementary techniques for the formation of different cationic intermediates from the same substrate.

In methanol, the ratios of unrearranged to rearranged vinyl ethers and of phenyl- to methyl-shifted vinyl ethers do not depend on the stereochemistry of the starting material. This strongly indicates that these products are formed via a common intermediate, i.e., **I$_4$**. Unexpectedly, the methyl shift in **I$_4$** is favored over the phenyl shift, in contrast with the favorable phenyl participation in the thermal reaction of *E*-**2** compared to the methyl participation of *Z*-**2**. Preference of a phenyl over a methyl shift was also observed in rearrangements of alkyl cations.[15] Probably **I$_4$** yields both **I$_5$** and **I$_6$** in (almost) barrierless processes. Since the phenyl ring has to rotate out of the plane of the C═C bond prior to rearrangement, it migrates less efficiently than the methyl group, which needs no rotation before migration. It is not clear why no allene **7** is formed from **I$_5$** in the photochemical reactions.

Preferential formation of the stereochemically retained products **3** from **I$_4$** is unexpected in view of the seemingly sterically controlled formation of **4** and **5** from **I$_3$**/**I$_5$**, and **I$_6$**. The very unstable, short-lived **I$_4$** must be trapped by a coordinated methanol molecule of a λ^3-iodane complex before reorganization in an S_Ni-type reaction (eq 5).[16] Upon photolysis of the λ^3-complex, **I$_4$** is formed within a solvent cage with a methanol molecule. Stereochemical information is retained and the methanol molecule preferentially attacks with retention of configuration. However, the migratory tendencies of the β-methyl and β-phenyl groups are not affected by the original geometry, which implies a linear structure of the positively charged vinylic carbon.



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(12) A similar higher reactivity of *Z*-**2** has been observed in the direct nucleophilic substitution by bromide ion (unpublished results).

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In TFE, all vinyl ethers are formed after rearrangement of the initial cation $\mathbf{I_4}$ to $\mathbf{I_5}$ (or $\mathbf{I_3}$) and $\mathbf{I_6}$, but no products **3** are formed. The lower nucleophilicity of the solvent gives the incipient cations more time for rearrangement. The lack of unrearranged vinyl ether products is caused not only by the lower reactivity of TFE compared to methanol toward $\mathbf{I_4}$ but also by the reduced efficiency of formation of a λ^3-complex in less nucleophilic solvents.[17] Finally, it should be noted that in TFE hardly any elimination product **6** is formed. This may be due to the reduced basicity of TFE compared to methanol. It indicates that in methanol the solvent plays an active role in the abstraction of the α-proton from $\mathbf{I_4}$,[18] probably within the solvent cage resulting upon photolysis of the λ^3-complex. This leads to the alkylidenecarbene $\mathbf{I_c}$ and finally to **6** (Scheme 2B).

Concluding Remarks

In this study, we have demonstrated that the thermal and photochemical solvolysis of the vinyl(phenyl)iodonium salts **2** occurs via complementary pathways. Thermal cleavage of the C−I bond proceeds either with neighboring-group participation of the moiety (methyl or phenyl) trans to the leaving group or with assistance of the solvent in an S_N2 mechanism. Photochemical cleavage on the other hand proceeds unassisted in an S_N1 manner. Therefore, in the thermal reaction initially (bridged) secondary vinyl cations are formed and in the photochemical reaction initially a primary vinyl cation is formed. The stereochemistry of the photochemically produced nucleophilic substitution products indicates that the reaction proceeds via the iodonium ion in a solvent of low nucleophilicity but via a solvent-coordinated λ^3-iodane complex (S_Ni mechanism) in a solvent of high nucleophilicity.

Experimental Section

Instruments: NMR, JEOL EX400; GC, Shimadzu GC-14A (0.25 mm × 30 m DB-1 column), Hewlett-Packard 6890 series (0.25 mm × 30 m CP SIL5-CB column); GC−MS, Shimadzu GC-17A/JEOL JMS-AMII, Packard 438A/Finnigan Mat ITD 700; IR, Jasco IRA-1; UV, Shimadzu UV 2200.

Starting Materials. (*E*)-2-Phenyl-1-propenyl(phenyl)iodonium (*E*-2) Tetrafluoroborate. To a solution of (*E*)-2-phenyl-1-propenylboronic acid[7,8,19] (162 mg, 1 mmol) in dichloromethane (10 mL) was added BF_3-Et_2O (170 mg, 1.2 mmol) at 0 °C under nitrogen, and the mixture was stirred for 15 min. A solution of (diacetoxyiodo)benzene (387 mg, 1.2 mmol) in dichloromethane (10 mL) was added at 0 °C, and the mixture was stirred for 4.5 h. After the addition of a saturated aqueous solution of sodium tetrafluoroborate, the mixture was stirred for 15 min at 0 °C. Extraction with dichloromethane, filtration, and then concentration gave an oil, which was washed several times with hexane−diethyl ether by decantation at −78 °C to give the salt (301 mg, 74%): colorless crystals; mp 89−90 °C (recrystallized from dichloromethane−hexane−diethyl ether); λ_{max} (MeOH) 260 nm (log ϵ 4.12); IR (KBr) 1566, 1444, 1060 (br), 738 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, J = 7.3 Hz, 2H), 7.64 (t, J = 7.3 Hz, 1H), 7.55−7.35 (7H), 7.13 (s, 1H), 2.61 (s, 3H); HRMS (FAB) calcd for $C_{15}H_{14}I$ [$(M - BF_4)^+$] 321.0140, found 321.0143. Anal. Calcd for $C_{15}H_{14}BF_4I$: C, 44.15; H, 3.46. Found: C, 44.02; H, 3.50.

(*Z*)-2-Phenyl-1-propenyl(phenyl)iodonium (*Z*-2) Tetrafluoroborate was prepared by a method similar to that for the *E* isomer in 61% yield: colorless crystals; mp 81−82 °C (recrystallized from dichloromethane−hexane−diethyl ether); λ_{sh} (MeOH) 220 nm (log ϵ 4.2); IR (KBr) 1443, 1060 (br), 741 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, J = 7.9 Hz, 2H), 7.58 (t, J = 7.9 Hz, 1H), 7.47−7.42 (m, 3H), 7.38 (t, J = 7.9 Hz, 2H), 7.22−7.25 (m, 2H), 7.01 (q, J = 1.4 Hz, 1H), 2.50 (d, J = 1.4 Hz, 3H); HRMS (FAB) calcd for $C_{15}H_{14}I$ [$(M - BF_4)^+$] 321.0140, found 321.0144. Anal. Calcd for $C_{15}H_{14}BF_4I$: C, 44.15; H, 3.46. Found: C, 44.21; H, 3.52.

Solvents were distilled just before use and kept in a quartz flask if necessary.

Products. 2-Phenylpropanal (**3C**), 1-phenylpropanone (**4C**), propiophenone (**5C**), tetradecane, and hexadecane obtained commercially were used without further purification. 1-Phenylpropyne (**6**)[20a] and phenylpropadiene (**7**)[20b] were samples prepared previously.

Methoxyphenylpropenes, **3**(Me)−**5**(Me), were prepared from the corresponding carbonyl compounds via dealkoxylation of the intermediate acetal.[21]

1-Methoxy-2-phenylpropene (**3**(Me))[21] was obtained in the ratio of *E*/*Z* = 60/1: ^{1}H NMR (400 MHz, $CDCl_3$) δ *E*, 1.93 (s, 3H), 3.66 (s, 3H), 6.35 (s, 1H), 7.34 (5H); *Z*, 1.86 (s, 3H), 3.60 (s, 3H), 6.06 (s, 1H), 7.34 (5H). MS 148 (M^+, 89), 133 (17), 117 (6.6), 115 (6.6), 105 (100), 103 (22), 79 (27), 77 (35), 51 (13).

2-Methoxy-1-phenylpropene (**4**(Me))[21,22] was prepared as an isomeric mixture of *E*/*Z* = 8/1: ^{1}H NMR (400 MHz, $CDCl_3$) δ *E*, 2.05 (s, 3H), 3.70 (s, 3H), 5.63 (s, 1H); *Z*, 2.09 (s, 3H), 3.74 (s, 3H), 5.36 (s, 1H). MS 148 (M^+, 86), 133 (12), 117 (19), 105 (100), 91 (24), 79 (21), 77 (23), 63 (12), 51 (16).

1-Methoxy-1-phenylpropene (**5**(Me))[21] was obtained in the isomeric ratio of *E*/*Z* = 3/7: ^{1}H NMR (400 MHz, $CDCl_3$) δ *E*, 1.68 (d, J = 6.8 Hz, 3H), 3.61 (s, 3H), 4.79 (q, J = 6.8 Hz, 1H), 7.22−7.45 (5H); *Z*, 1.78 (d, J = 6.8 Hz, 3H), 3.52 (s, 3H), 5.36 (q, J = 6.8 Hz, 1H), 7.22−7.45 (5H). MS 148 (M^+, 58), 147 (100), 117 (46), 115 (35), 105 (27), 91 (25), 77 (46), 51 (20).

Acetoxyphenylpropenes, **3**(Ac)−**5**(Ac), were prepared from the corresponding carbonyl compounds in the same way as that described for **4**(Ac).[23]

1-Acetoxy-2-phenylpropene (**3**(Ac)) was obtained in the isomeric ratio of *E*/*Z* = 10/1: ^{1}H NMR (400 MHz, $CDCl_3$) δ *E*, 2.08 (s, 3H), 2.17 (s, 3H), 7.50 (s, 1H); MS 176 (M^+, 7.6), 134 (100), 133 (28), 105 (43), 91 (14), 77 (17), 51 (6.2).

2-Acetoxy-1-phenylpropene (**4**(Ac))[23] was obtained in the isomeric ratio of *E*/*Z* = 1/20: ^{1}H NMR (400 MHz, $CDCl_3$) δ *E*, 2.13 (s, 3H), 2 (s, 3H), 6.25 (s, 1H); *Z*, 2.18 (s, 3H), 2 (s, 3H), 5.95 (s, 1H). MS 176 (M^+, 4.0), 134 (100), 133 (25), 119 (8.8), 117 (8.8), 105 (14), 91 (69), 77 (15), 51 (6.5).

1-Acetoxy-1-phenylpropene (**5**(Ac))[24] was obtained in the ratio of *E*/*Z* = 1/23: ^{1}H NMR (400 MHz, $CDCl_3$) δ *E*, 1.79 (d, J = 6.8 Hz, 3H), 2.13 (s, 3H), 5.51 (q, J = 6.8 Hz, 1H); *Z*, 1.70 (d, J = 6.8 Hz, 3H), 2.29 (s, 3H), 5.88 (q, J = 6.8 Hz, 1H). MS 176 (M^+, 8.5), 134 (86), 133 (100), 115 (11), 105 (52), 91 (7.5), 77 (35), 51 (14).

(*E*)-1-Iodo-2-phenylpropene (**10**) was prepared according to a literature method,[25] and an *E*/*Z* mixture was obtained by sensitized irradiation in argon-purged acetone through Pyrex glass.

Thermal Solvolysis. A typical thermal reaction was carried out as follows. About 1 mg of salt **2** dissolved in 3 mL of solvent was kept at 60 °C for the specified reaction time. The reaction mixture was extracted with pentane containing tetradecane as an internal standard. The pentane layer was analyzed by GC and GC−MS.

Kinetic Measurements. Reaction rates for the solvolysis of **2** were determined by monitoring the decrease in absorbance at 270 nm at 60

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(±0.1) °C as described previously.[1b,14] Freshly distilled solvents were used for all the kinetic determinations, and alcoholic solvents contained 10^{-3} M CF_3CO_2H. The (pseudo-)first-order rate constants k_{obsd} recorded are usually averages of three determinations.

Photosolvolysis. In a typical photochemical experiment, 3 mL of a ~5 mM solution of the iodonium salt, containing ~1 mM hexadecane as internal standard, was irradiated at 20 °C. As light source, a high-pressure Hg/Xe arc, from which the IR output was removed by a water filter was used. The light beam was processed through a model 77250 Oriel monochromator, and the 248-nm wavelength was selected and aimed at a 3-mL quartz cell, containing the sample, equipped with a glass stopper with Teflon septum. All samples were saturated with argon prior to irradiation, and argon bubbling was continued during the irradiations. At appropriate time intervals, 50-μL samples were taken and injected in a test tube containing ~1 mL of water and 100 μL of hexane. The two layers were mixed vigorously, and the hexane layer was removed with a pipet and analyzed by GC, GC−MS, or both. For all experiments, at least six samples per irradiation were taken to study the appearance of photoproduct as a function of the irradiation time. Conversions of starting material, as determined on the basis of product appearance, were kept below 15%. The product distributions recorded are averages of two or three determinations.

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