J. Org. Chem. **2002,** *67,* 693−702

Photosolvolysis of (*E*)-Styryl(phenyl)iodonium Tetrafluoroborate. Generation and Reactivity of a Primary Vinyl Cation

Roel Gronheid,[†] Gerrit Lodder,*[,†] and Tadashi Okuyama[‡]

Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502,
2300 RA Leiden, The Netherlands, and Faculty of Science, Himeji Institute of Technology, Kamigori,
Hyogo 678-1297, Japan

lodder@chem.leidenuniv.nl

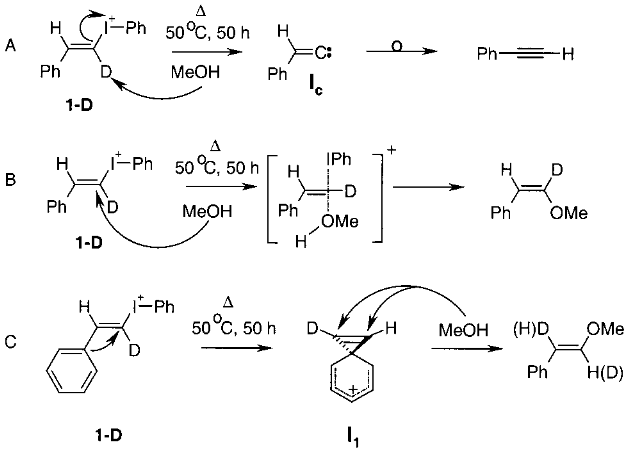
Received July 23, 2001

The photochemistry of (*E*)-styryl(phenyl)iodonium tetrafluoroborate in methanol and 2,2,2-trifluoroethanol as well as in dichloromethane and toluene has been investigated. In all solvents the vinylic C−I bond is more photoreactive than the aromatic C−I bond. Homolysis as well as heterolysis of both bonds occurs, but the latter type of cleavage predominates. In alcoholic solvents, the incipient phenyl cation produces a nucleophilic substitution product. The primary styryl cation gives nucleophilic substitution, elimination, and rearrangement products. The dependence of the photoreaction on the nucleophilicity of the solvent indicates that in the presence of good nucleophiles a 10-I-3 compound is the reactive iodonium species. In this case the reaction proceeds via an S_Ni mechanism. In the absence of good nucleophiles an 8-I-2 species gives photoreaction via an S_N1 mechanism. This is corroborated by the solvent dependence of the UV spectra, and the product composition upon photoreaction with bromide in varying concentration. Photoreaction of the iodonium salt in a chlorinated alkane yields (*E*)- and (*Z*)-*β*-fluorostyrene in a Schiemann-type reaction. Reaction in toluene yields Friedel−Crafts products. The results of the photochemical reactions are compared to those of the thermal ones, and the implications of the differences are discussed.

Introduction

Thermal solvolysis of vinyliodonium salts has been the subject of numerous recent[1] and a few older[2] studies. Owing to the superb leaving group ability of the iodonio group (>10^5 times better than triflate),[3] this class of compounds gives remarkable chemistry such as in-plane vinylic S_N2 substitution[1] and S_N1 substitution via highly unstable (vinylic) carbocations.[3,4] Until recently there were no examples of photochemical solvolysis of vinyliodonium salts.[5] This is in stark contrast to diaryliodonium ions the photochemistry of which has been thoroughly investigated over the past decades.[6−8] Here we present an in-depth study of the photochemical solvolysis of (*E*)-styryl(phenyl)iodonium tetrafluoroborate (**1**). As solvents were used methanol, trifluoroethanol, dichloromethane, and toluene. The results are compared to those of the corresponding thermal reactions.

Scheme 1. Mechanism of Formation of Products in the Thermal Methanolysis of the (*E*)-Styryl(phenyl)Iodonium Ion (1)



Particularly relevant for our investigations is the thermal solvolysis of **1** in methanol and trifluoroethanol.[9] In methanol four products are formed: iodobenzene (the leaving group), phenylacetylene (the elimination product), and (*Z*)- and (*E*)-*β*-methoxystyrene (the substitution products). The mechanism of formation of the products was unraveled, using specifically deuterium-labeled **1** (Scheme 1).

[†] Leiden University.

[‡] Himeji Institute of Technology.

(1) For a recent review see: Okuyama, T. *Rev. Heteroatom Chem.* **1999**, *21*, 257.

(2) (a) Nesmeyanov, A. N.; Tolstaya, T. P.; Petrakov, A. V.; Gol'tsev, A. N. *Dokl. Akad. Nauk SSSR* **1977**, *235*, 425. (b) Nesmeyanov, A. N.; Tolstaya, T. P.; Petrakov, A. V.; Leshcheva, I. F. *Dokl. Akad. Nauk SSSR* **1978**, *238*, 70.

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

(4) (a) Hinkle, R. J.; Thomas D. B. *J. Org. Chem.* **1997**, *62*, 7534. (b) Hinkle, R. J.; McNeil, A. J.; Thomas, Q. A.; Andrews, M. N. *J. Am. Chem. Soc.* **1999**, *121*, 7437.

(5) Gronheid, R.; Lodder, G.; Ochiai, M.; Sueda, T.; Okuyama, T. *J. Am. Chem. Soc.* **2001**, *123*, 8760.

(6) (a) Dektar, J. L.; Hacker, N. P. *J. Org. Chem.* **1990**, *55*, 639. (b) Dektar, J. L.; Hacker, N. P. *J. Org. Chem.* **1991**, *56*, 1838. (c) Hacker, N. P.; Leff, D. V.; Dektar, J. L. *J. Org. Chem.* **1991**, *56*, 2280.

(7) Gu, H.; Zhang, W.; Feng, K.; Neckers, D. *J. Org. Chem.* **2000**, *65*, 3484.

(8) DeVoe, R. J.; Olofson, P. M.; Sahyun, M. R. V. In *Advances in Photochemistry*; Volman, D. H.; Hammond, G. S.; Neckers, D. C., Eds.; John Wiley & Sons: New York, 1992; Vol. 17, p 313.

(9) (a) Okuyama, T.; Ochiai, M. *J. Am. Chem. Soc.* **1997**, *119*, 4785. (b) Okuyama, T.; Ishida, Y.; Ochiai, M. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 163.

10.1021/jo0107397 CCC: $22.00

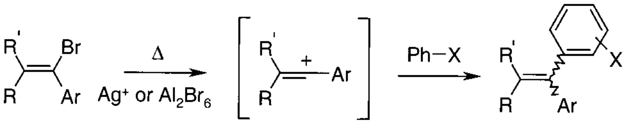
Phenylacetylene is formed by solvent-assisted α-elimination, initially yielding a vinylidene carbene (**I**$_c$) which subsequently rearranges to the alkyne. In this case complete loss of label is observed (route A). Substitution with inversion of configuration proceeds via an in-plane S_N2 substitution, yielding (*Z*)-*β*-methoxystyrene. No scrambling of the label occurs (route B). Substitution with retention of configuration occurs when iodobenzene leaves with anchimeric assistance of the phenyl ring, yielding a vinylenebenzenium ion (**I**$_1$). Nucleophilic attack by the solvent on this ion gives (*E*)-*β*-methoxystyrene with net retention of configuration and complete scrambling of the deuterium label (route C). In 2,2,2-trifluoroethanol (TFE), a solvent which is a much weaker base than methanol, no elimination occurs. Also no vinylic S_N2 substitution takes place, because TFE is also a very poor nucleophile. The only product in this case is (*E*)-*β*-(2,2,2-trifluoroethoxy)styrene, formed via route C.

Upon irradiation of diaryliodonium salts in various solvents, heterolysis of the carbon−iodine bond occurs, predominantly from the first singlet-excited state. Electron transfer within the ion−molecule pair yields the corresponding radical and radical ion. From the triplet-excited state exclusive homolysis is observed.[6b] Considering the iodonio group as a pseudohalide, this behavior is quite different from that of simple halobenzenes in solution. With such compounds, homolytic cleavage of the carbon−halogen bond is the only dissociative pathway for both the singlet and triplet excited state.[10] Apparently the high nucleofugality of the phenyliodonio group also has a large effect on the photochemistry of phenyliodonium compounds.

The effect of the leaving group has earlier been studied in the photochemistry of vinyl halides.[11] The results of these studies were, however, inconclusive. Both increases and decreases in cation/radical ratio upon changing the leaving group (F → Cl → Br → I) have been reported, but the efficiency of the photochemical reaction was shown to increase in all cases. The phenyliodonio leaving group extends this series with a pseudohalide, and efficient formation of a primary vinyl cation from **1** by C−I bond heterolysis is anticipated.[5,12]

The reactivity of vinyl cations has been studied by varying the nucleophilicity of the solvent. For example, irradiation of vinyl bromides such as bromostilbene gives exclusive HBr elimination in diethyl ether and *n*-hexane, but elimination as well as nucleophilic substitution in methanol.[11a,b,13,14] The thermal solvolysis of **1** in an apolar solvent such as chloroform results in reaction of **I**$_1$ with its counterion, yielding (*E*)-*β*-fluorostyrene via a mechanism similar to that in Scheme 1C.[15] We wondered how **1** would react upon photolysis in nonnucleophilic solvents.

Scheme 2



Reaction of photogenerated vinyl cations with aromatic compounds (vinylic photo-Friedel−Crafts reaction) has only been reported for an intramolecular case.[16] Intermolecular vinylation has been performed using thermally generated vinyl cations (Scheme 2)[17] and using the parent vinyl cation $C_2H_3^+$ generated by tritium decay.[18] The thermal solvolysis of a cyclohexenyliodonium compound in benzene also yields Friedel−Crafts type adducts,[19] but in this case the origin of the aromatic moiety is uncertain: is it the leaving group (undergoing *ipso* substitution), or the solvent? We wondered whether intermolecular photochemical vinylation of aromatic compounds would be feasible, using iodonium precursors.

The results of the investigation of **1** reported here provide answers to the following questions: (1) Does photochemistry of vinyl(phenyl)iodonium compounds lead to (primary) vinyl cation-derived products? (2) How does the photochemistry of vinyl(phenyl)iodonium compounds compare with its thermal chemistry? (3) How does **1** photoreact in the absence of external nucleophiles? (4) Does electrophilic aromatic substitution occur upon irradiation of **1** in the presence of aromatic compounds?

Results and Discussion

Alcoholic Solvents. Photoproducts in Methanol. Irradiation of (*E*)-styryl(phenyl)iodonium tetrafluoroborate (**1**) in methanol ($\lambda_{exc} = 248$ nm) results in the reaction mixture depicted in Scheme 3. In marked contrast to its thermal behavior, photoexcited **1** does yield a rearranged vinyl ether (i.e., **7-OMe**) next to two unrearranged ones (i.e., *Z*-**6-OMe** and *E*-**6-OMe**) as vinylic nucleophilic substitution products.

At sufficiently low conversion of **1**, the rates of formation of all photoproducts were shown to be constant at constant light flux, indicating primary photoproducts. In Figure 1, two typical examples are given for the formation of phenylacetylene (**5**) and (*Z*)-*β*-methoxystyrene (*Z*-**6-OMe**), respectively. During the photoreaction, (*Z*)-*β*-iodostyrene is formed in trace amounts. The kinetics of formation of this product show, however, that it is a secondary photoproduct, presumably formed by *E* → *Z* isomerization of (*E*)-*β*-iodostyrene (**2**).

The various primary photoproducts are proposed to be formed via three carbon−iodine bond cleavage pathways (Scheme 4): (1) Heterolytic cleavage of the phenylic

---

(10) Lodder, G.; Cornelisse, J. In *The Chemistry of Functional Groups − Supplement D2: The chemistry of halides, pseudohalides and azides Part 2*; Patai, S; Rappoport, Z., Eds.; John Wiley & Sons: Chichester, 1995; Ch. 16.

(11) (a) Šket, B.; Zupan, M.; Pollak, A. *Tetrahedron Lett.* **1976**, 783. (b) Šket, B.; Zupan, M. *J. Chem. Soc., Perkin Trans. 1* **1979**, 752. (c) Kitamura, T.; Kobayashi, S.; Taniguchi, H. *J. Org. Chem.* **1982**, *47*, 2323. (d) Zupancic, N.; Šket, B. *J. Photochem. Photobiol. A: Chem.* **1991**, *60*, 361. (e) Verbeek, J. M.; Stapper, M.; Krijnen, E. S.; Van Loon, J. D.; Lodder, G.; Steenken, S. *J. Phys. Chem.* **1994**, *98*, 9526.

(12) Gronheid, R.; Zuilhof, H.; Hellings, M. G.; Cornelisse, J.; Lodder, G. Manuscript in preparation.

(13) (a) Op den Brouw, P. M.; Laarhoven, W. H. *J. Org. Chem.* **1982**, *47*, 1546. (b) Krijnen, E. S.; Zuilhof, H.; Lodder, G. *J. Org. Chem.* **1994**, *59*, 8139.

(14) Lodder, G. In *Dicoordinated Carbocations*; Rappoport, Z.; Stang, P. J., Eds.; John Wiley & Sons: Chichester, 1997; Ch.8.

(15) Okuyama, T.; Fujita, M.; Gronheid, R.; Lodder, G. *Tetrahedron Lett.* **2000**, *41*, 5125.

(16) (a) Kitamura, T.; Kobayashi, S.; Taniguchi, H. *Chem. Lett.* **1984**, 547. (b) Kitamura, T.; Kobayashi, S.; Taniguchi, H.; Hori, K. *J. Am. Chem. Soc.* **1991**, *113*, 6240.

(17) (a) Roberts, R. M.; Abdel-Basset, M. B. *J. Org. Chem.* **1976**, *41*, 1698. (b) Stang, P. J.; Anderson, A. G. *Tetrahedron Lett.* **1977**, *17*, 1485. (c) Stang, P. J.; Anderson, A. G. *J. Am. Chem. Soc.* **1978**, *100*, 1520. (d) Kitamura, T.; Kobayashi, S.; Taniguchi, H.; Rappoport, Z. *J. Org. Chem.* **1982**, *47*, 5003.

(18) (a) Fornarini, S.; Speranza, M. *Tetrahedron Lett.* **1984**, 869. (b) Fornarini, S.; Speranza, M. *J. Am. Chem. Soc.* **1989**, *111*, 7402.

(19) Ochiai, M.; Takaoka, Y.; Sumi, K.; Nagao, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 1382.

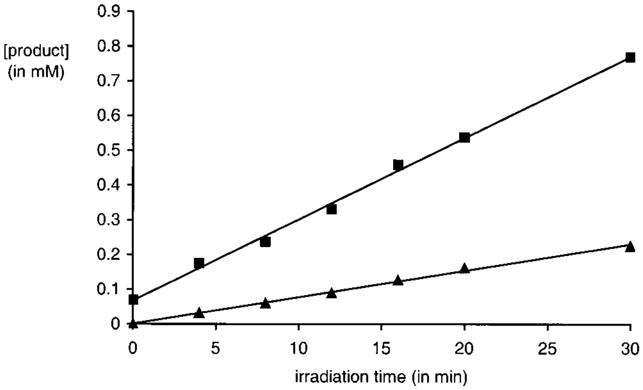
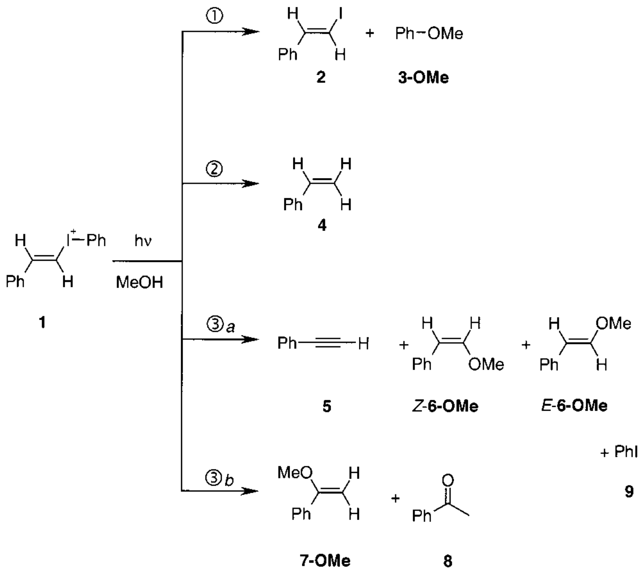


Figure 1. Formation of phenylacetylene (■) and (*Z*)-β-methoxystyrene (▲) upon irradiation of **1** (λ_{exc} = 248 nm) in methanol as a function of time.

Scheme 3



carbon−iodine bond leading to (*E*)-iodostyrene (**2**) and the phenyl cation. Reaction of the latter species with the solvent results in anisole (**3-OMe**). This pathway does not occur in the thermal methanolysis of **1**.[9,20] (2) Homolytic cleavage of the vinylic carbon−iodine bond yielding the styryl radical and the radical cation of iodobenzene. The styryl radical abstracts a hydrogen atom from the solvent to give styrene (**4**). When the iodobenzene radical cation acquires an electron, neutral iodobenzene (**9**) is formed. This type of chemical behavior is also not observed upon thermal solvolysis of **1**.[9] (3a) Heterolytic cleavage of the vinylic carbon−iodine bond resulting in **9** and the open primary styryl cation ($\mathbf{I_2}$). This species can undergo nucleophilic attack by the solvent or loss of a β-hydrogen. These two pathways account for (*E*)- and (*Z*)-β-methoxystyrene (*E*- and *Z*-**6-OMe**) and phenylacetylene (**5**). Both addition of solvent to $\mathbf{I_2}$ and proton loss from $\mathbf{I_2}$ can in principle be preceded by one or more 1,2-phenyl shifts, via the benzenium ion $\mathbf{I_1}$. These shifts are however degenerate, and therefore not included. (3b) Intermediate $\mathbf{I_2}$ can also rearrange by a 1,2-hydride shift, to the secondary styryl cation $\mathbf{I_3}$.[21] Loss of a β-hydrogen from $\mathbf{I_3}$ again yields **5**. Nucleophilic attack by the solvent on $\mathbf{I_3}$ yields α-methoxystyrene (**7-OMe**). Acid-catalyzed hydrolysis of this unstable enol ether yields acetophenone (**8**).

The products expected from the fourth possible mode of C−I bond cleavage, homolytic cleavage of the phenylic carbon−iodine bond, are benzene, formed by hydrogen atom abstraction from the solvent by the initially formed phenyl radical, and **2**, formed from the radical cation of **2** by acquisition of an electron. However, benzene, if present, is obscured by the solvent in the GC-product analysis. Compound **2** is present, but may also be formed by the heterolytic pathway. The occurrence of this homolytic pathway can therefore not be demonstrated, but is by no means excluded.

The pathways of photoreactivity of **1** are comparable to those of diaryliodonium salts[6] in the sense that both heterolytic and homolytic cleavage of C−I bonds occur. The radical-derived products in the photochemistry of diphenyliodonium salts are all formed by hydrogen atom abstraction from the solvent, giving net replacement of the phenyliodonio group by a hydrogen atom. The photogenerated aryl cations give two types of photoproducts: Products derived from nucleophilic attack of the solvent (methanol) or products derived from reaction with the neutral leaving group (iodobenzene) within the solvent cage to give Friedel−Crafts type adducts. Addition of the aryl cation at all positions of iodobenzene is observed: *para*, *meta*, *ortho*, and *ipso*. Products derived from nucleophilic substitution by the solvent methanol obviously are also observed in the photochemistry of **1**, but Friedel−Crafts products (i.e., *p*-, *m*-, or *o*-iodostilbenes) are not. In some experiments traces of (*E*)-stilbene are formed (the product derived from Friedel−Crafts addition at the *ipso* position).

Sensitization Experiments. In diphenyliodononium compounds the multiplicity of the excited state determines whether homolytic or heterolytic photochemical bond cleavage prevails.[6] It is of interest to see whether this is also the case for **1**. Moreover, upon sensitized irradiation of *E*-vinyl halides, only *E*/*Z*-isomerization is observed.[12] In general, *E*/*Z*-isomerization of alkenes is a well-known photochemical process, occurring from the triplet as well as the singlet excited state.[22] *E*/*Z*-Isomerization of **1** to the corresponding *Z*-vinyl(phenyl)iodonium ion is particulary relevant because it presents an alternative mechanism of formation of **5**. Vinyliodonium compounds with a hydrogen atom positioned at the trans-β-position with respect to the phenyliodonio moiety, are known to rapidly react thermally by trans-elimination of iodobenzene and a proton,[23,24] yielding the corresponding alkyne. Therefore, **5** and **9** are the only expected products, if in analogy with vinyl halides, *E*/*Z*-isomerization of **1** is the only mode of reaction from its triplet excited state (Scheme 5).

Irradiation of benzophenone in methanol, in the presence of *E*-**1** was performed at λ_{exc} = 366 nm. At this wavelength no light is absorbed by the iodonium salt (vide infra), so direct excitation of **1** does not occur. The major products (>90%) are phenylacetylene (**5**) and iodobenzene (**9**). Also small amounts of **2**, **4**, and the vinyl

---

[20] Cleavage of the phenylic C−I bond of **1** is observed upon addition of a strong nucleophile see ref 2a.

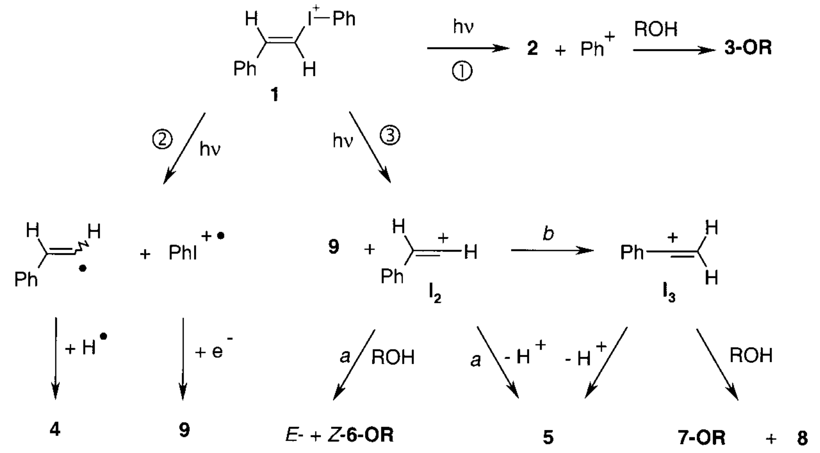
[21] Lee, C. C.; Ko, E. C. F. *J. Org. Chem.* **1975**, *40*, 2132.

[22] See e.g.: Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415.

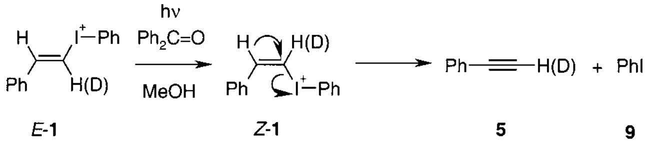
[23] Ochiai, M.; Oshima, K.; Masaki, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 869.

[24] Ochiai, M.; Sumi, K.; Takaoka, Y.; Kunishima, M.; Nagao, Y.; Shiro, M.; Fujita, E. *Tetrahedron* **1988**, *44*, 4095.

Scheme 4. Mechanism of Formation of Photoproducts from 1 in Methanol and TFE



Scheme 5



ethers *E*- and *Z*-**6-OMe** are detected (all formed with about equal efficiency). This indicates that in the sensitized irradiation of *E*-**1**, indeed the elimination product is formed via *E*/*Z*-isomerization of the iodonium salt. This was further tested by sensitized irradiation of selectively deuterated **1**.

When benzophenone was irradiated in the presence of α-deuterated *E*-**1** (*E*-**1-D**), 91.3 (±1.1)% of the elimination product **5** was not scrambled (i.e., 8.7% nondeuterated phenylacetylene was formed) in line with Scheme 5. Thus, although *E*/*Z*-isomerization is not the only reactive pathway of triplet excited **1**, it is certainly the most important one. Upon direct irradiation of *E*-**1-D** in methanol 21.6 (±1.7)% of scrambling was observed. This means that different pathways for elimination are followed upon sensitized and direct photolysis. The larger amount of scrambling in the direct irradiation is in line with initial formation of $\mathbf{I}_2$, followed by rearrangement via the benzenium ion $\mathbf{I}_1$ and proton loss.[12] In an alternative mechanism for isotope scrambling, part of **5** may be formed via loss of the α-hydrogen (or α-deuterium) from $\mathbf{I}_2$, yielding vinylidene carbene $\mathbf{I}_c$ which will rearrange to **5**.[9] Whereas homolysis is the exclusive pathway of reaction upon sensitized photolysis of diphenyliodonium compounds, pathway 2 is at best a minor pathway upon sensitized irradiation of **1**: only trace amounts of **4** are formed. The same is true for the heterolytic pathways 1 and 3, yielding **2** and **6**. Apparently *E*/*Z*-isomerization followed by trans-elimination is the most efficient reaction path from the triplet-excited state.

Clearly, the lowest triplet-excited state is not the origin of most of the products in the direct irradiation of **1**, as shown by the different amounts of isotope scrambling and the relative difference in efficiency in formation of photoproducts (vide infra). The triplet-excited state may be active in the formation of part of **5** and **9**. The singlet-excited state (or a higher triplet state) is responsible for the majority of the products observed upon direct excitation.

Table 1. Quantum Yields of Formation of Products in the Photoreaction of (*E*)-Styryl(phenyl)iodonium Tetrafluoroborate (1) in Methanol and 2,2,2-Trifluoroethanol

	Φ (in methanol; R = CH_3)	Φ (in 2,2,2-trifluoroethanol; R = CH_2CF_3)
2[a]	0.133 ± 0.008	0.168 ± 0.010
3-OR	0.038 ± 0.003	0.046 ± 0.007
4	0.079 ± 0.011	0.012 ± 0.001
5	0.325 ± 0.020	<0.02[b]
Z-**6-OR**	0.121 ± 0.011	0.0066 ± 0.0005
E-**6-OR**	0.398 ± 0.015	0.0065 ± 0.0004
7-OR	0.038 ± 0.007	- -[c]
8	0.010 ± 0.002	0.228 ± 0.037
9	0.756 ± 0.051	0.463 ± 0.054

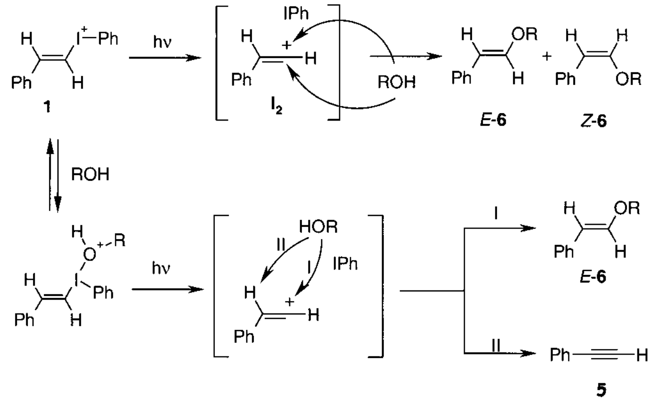
[a] *Z*-**2** was shown to be a secondary photoproduct in the irradiation of *E*-**1** and is added to *E*-**2**. [b] Upper limit estimate, because **1** is contaminated with small amounts of **5** and **9**. [c] Under the workup conditions, α-trifluoroethoxystyrene is not stable and only **8** is observed from path 3b.

Quantum Yields of Product Formation in Methanol and 2,2,2-Trifluoroethanol. In the thermal solvolysis of **1** a large effect on the product distribution is observed upon changing the solvent from methanol to TFE. The photochemical solvolysis has therefore also been performed in TFE. The same products are obtained as described for the irradiation in methanol, with 2,2,2-trifluoroethoxy groups instead of methoxy groups, but the product distribution is quite different. For a quantitative comparison the quantum yields of product formation in the two solvents have been measured (Table 1).

In both solvents the photosolvolysis of **1** is quite efficient. In methanol, the sum of the quantum efficiencies of formation of the leaving groups (iodobenzene and (*E*)-iodostyrene) is 0.89. The total quantum yield of formation of all other photoproducts in methanol equals unity within experimental error. This may indicate that the homolytic C−I bond cleavage pathways producing the radical cations of the leaving groups yield unidentified products. In TFE the quantum yield of the photoreaction, based on the leaving groups, is ~0.6, substantially higher than that based on the other products (~0.3). Cationic polymerization in this excellent cation-stabilizing solvent may well be responsible for the unaccounted products.

In the thermal solvolysis of **1** exclusive cleavage of the vinylic C−I bond is observed. Although this bond is still the most reactive one in the photochemical solvolysis, also considerable cleavage of the phenylic C−I bond is ob-

Scheme 6. Mechanisms of Formation of Enol Ethers 6 and Acetylene 5



served. The ratio of cleavage of the vinylic and phenylic C−I bond changes from 5.7:1 in methanol to 2.8:1 in TFE.

In the photochemical nucleophilic substitution pathways of **1** in methanol and TFE a marked stereochemical difference with its thermal solvolysis is encountered. In the thermal solvolysis the stereoselectivity gets higher on going to weaker nucleophilic solvents.[9] In sharp contrast, in the photochemical reaction the *E*/*Z* selectivity in **6**, observed in methanol, is completely lost in TFE. An explanation for this observation will be presented later in this section.

The photochemical formation of ion-derived products from **1** in methanol and in TFE shows two remarkable differences. First, the relative importance of paths 3a and 3b (see Scheme 4): In methanol, path b (products **5**, **7**, and **8**) is a minor path of reaction, while it is the major one in TFE. For path a (products **5** and **6**), the situation is reversed. Since a much smaller amount of **5** is formed in TFE than in MeOH, path b may be a pathway to form **5**, but it is not as important as path a.

The relative importance of paths a and b is determined by the lifetime of $\mathbf{I_2}$. The primary styryl cation $\mathbf{I_2}$ is known to be a very unstable species.[21,25] On the basis of quantum chemical calculations, rapid rearrangement to $\mathbf{I_3}$ is predicted.[12] Fluorine-substituted alcohols are known to be good cation-stabilizing solvents,[26] so the lifetime of $\mathbf{I_2}$ is expected to be larger in TFE than in methanol. This gives $\mathbf{I_2}$ more time to rearrange to the more stable $\mathbf{I_3}$ in TFE, and this makes path b more important.

In the thermal reaction of **1** no products derived from $\mathbf{I_3}$ (i.e., **7-OR** and **8**) are formed. In this case, the initially formed cationic species is the bridged benzenium ion $\mathbf{I_1}$. This structure already corresponds to a local minimum, and it will react with the solvent before rearrangement to $\mathbf{I_3}$ can occur.

The second remarkable difference between the two solvents is the large difference in the stereoselectivity of the vinyl ethers **6**. In methanol considerable *E*/*Z*-selectivity is observed ($E/Z = 3.3$), i.e., mainly retention of configuration, however, in TFE the *E*/*Z*-ratio in **6** equals 1. A refinement of the mechanism of photoreaction of **1** (proposed in Scheme 4) can explain the solvent dependence of the stereoselectivity on the formation of the vinyl ethers invoking ground-state complexation (Scheme 6).

Hypervalent iodine (8-I-2)[27] compounds are known to coordinate readily with a wide variety of nucleophiles such as halide anions, to give the corresponding tricoordinated 10-I-3 (λ^3-iodane) species.[28] When the solvent is nucleophilic, the overall photochemical behavior of **1** will be a mixture of the photochemistry of the free and the solvent-coordinated iodonium ion.[29] Excitation of the free iodonium ion yields $\mathbf{I_2}$ in an S_N1 mechanism, which gives substitution products in ~1:1 *E*/*Z* ratio, as well as elimination and rearrangement products as depicted in Scheme 4. Excitation of the λ^3-iodane results in formation of $\mathbf{I_2}$, **9** and a solvent molecule within the solvent cage (Scheme 6). Nucleophilic attack of the solvent molecule within the solvent cage will preferentially give retention of configuration and lead to *E*-**6-OR** (path I), by an S_Ni mechanism.[30] The phenomenon is more important in methanol than in TFE, since methanol is a stronger nucleophile than TFE. The *E*/*Z* stereoselectivities for the thermal and the photochemical reaction in methanol and TFE thus have different origins. In the thermal reaction the ratio is determined by the relative importance of S_N1 and S_N2 pathways, and in the photochemical reaction by the occurrence of λ^3-iodanes.

In addition, the mechanism in Scheme 6 (path II) clarifies the higher efficiency of formation of elimination product **5** in methanol than in TFE (Table 1). Upon photolysis of **1** in methanol, $\mathbf{I_2}$ is formed with methanol inside the solvent cage, a cation−molecule pair. The methanol not only acts as a nucleophile, but also as a base. Abstraction of a proton from $\mathbf{I_2}$ yields **5**. In the case of TFE, the proton has to be abstracted by the leaving group (**9**), or by external TFE. Both agents are less basic than methanol, causing a lower efficiency of formation of **5**.

This situation is reminiscent of the product formation upon excitation of (*E*)-β-bromostyrene in methanol.[12] In this case bromide, a stronger base than methanol, is formed with $\mathbf{I_2}$ within a solvent cage, as a cation−anion pair, and exclusive elimination is observed. Complete suppression of the formation of nucleophilic substitution products due to the high kinetic basicity of a halide anion is not uncommon and well documented.[31]

The present interpretation is in line with our recent results on the photochemistry of two *E*/*Z*-isomeric methyl-substituted analogues of **1**.[5] In those cases also preferential retention of configuration was observed in methanol, but not in TFE. Also more rearrangement of the initially formed vinyl cation occurred in TFE, and

---

[25] Apeloig, Y.; Franke, W.; Rappoport, Z.; Schwarz, H.; Stahl, D. *J. Am. Chem. Soc.* **1981**, *103*, 2770.

[26] Steenken, S.; Ashokkumar, M.; Maruthamuthu, P.; McClelland, R. A. *J. Am. Chem. Soc.* **1998**, *120*, 11925.

[27] The *N*−X−*L* notation conveniently describes the nature of a hypervalent compound by the number (*N*) of formally assignable electrons of more than the octet in a valence shell directly associated with the central atom (X) in directly bonding a number (*L*) of ligands (substituents): Akiba, K.-y. In *Chemistry of Hypervalent Compounds*; Akiba, K.-y., Ed.; Wiley-VCH: New York, 1999; Ch. 1.

[28] (a) Ochiai, M.; Oshima, K.; Masaki, Y. *J. Am. Chem. Soc.* **1991**, *113*, 7095. (b) Okuyama, T.; Takino, T.; Sato, K.; Ochiai, M. *Chem. Lett.* **1997**, 955. (c) Okuyama, T.; Takino, T.; Oshima, K.; Imamura, S.; Yamataka, H.; Asano, T.; Ochiai, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 243. (d) Okuyama, T.; Takino, T.; Sato, K.; Ochiai, M. *J. Am. Chem. Soc.* **1998**, *120*, 2275.

[29] Complexation with a nucleophile has previously been proposed to occur photochemically in the nucleophilic photosubstitution of diaryliodonium ions with sulfur nucleophiles: Spyroudis, S. P. *Liebigs Ann. Chem.* **1986**, 947.

[30] For previous examples of the S_Ni mechanism see: (a) March, J. In *Advanced Organic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1992; p 326. (b) Hori, K.; Nishiguchi, T.; Nabeya, A. *J. Org. Chem.* **1997**, *62*, 3081 and references therein.

[31] (a) Thibblin, A. *J. Phys. Org. Chem.* **1992**, *5*, 367. (b) Thibblin, A. *Chem. Soc. Rev.* **1993**, *22*, 427.

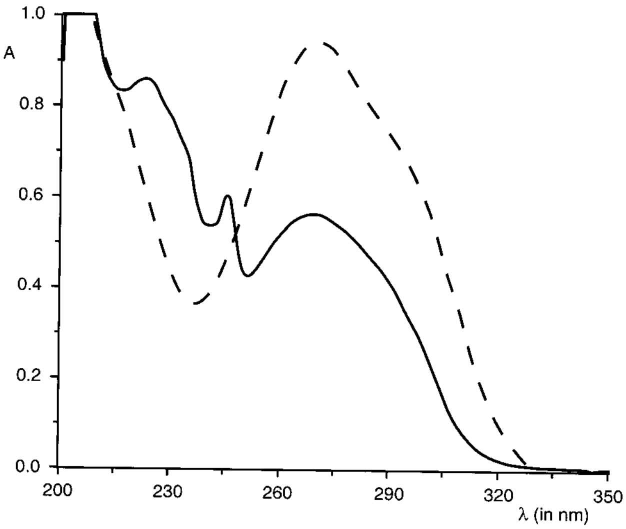


Figure 2. UV absorption spectra of (*E*)-styryl(phenyl)iodonium tetrafluoroborate in methanol ([**1**] = 4.57 × 10^{-5} M; solid line) and TFE ([**1**] = 4.83 × 10^{-5} M; dashed line).

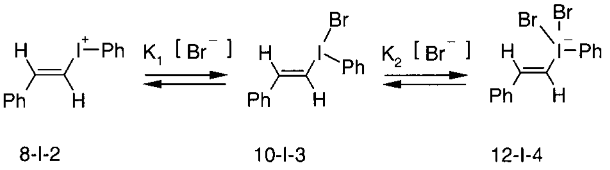
elimination was found to be far more important in methanol than in TFE.

UV Spectra in Methanol and 2,2,2-Trifluoroethanol. Coordination of nucleophiles to iodonium salts leads to significant changes in the iodonium UV absorption spectra.[28c,d,32] The absorption spectra of **1** in methanol and TFE are therefore expected to differ significantly, if formation of λ^3-iodanes of **1** plays a more important role in methanol.

Indeed, the absorption spectra in methanol and TFE are quite different (Figure 2). The extinction coefficient of the large and broad absorption band at $\lambda_{max} = 270$ nm is smaller in methanol ($\epsilon = 12400$ M^{-1} cm^{-1}) than in TFE ($\epsilon = 19500$ M^{-1} cm^{-1}), and in methanol two extra, narrow bands are present at $\lambda_{max} = 245$ nm ($\epsilon = 13300$ M^{-1} cm^{-1}) and $\lambda_{max} = 223$ nm ($\epsilon = 18800$ M^{-1} cm^{-1}). The absorption spectrum of **1** in TFE is similar to its spectrum in acetonitrile, both in shape and intensity (in acetonitrile $\epsilon_{270} \cong 19000$ M^{-1} cm^{-1}).[33] The iodonium ion is not expected to be complexed by these solvents, because of their low nucleophilicity. A ground-state complex is therefore the probable origin for the blue-shifted absorption bands in methanol. The new absorption bands are narrow, which suggests that the **1**–methanol ground state complex is structurally well defined.

The wavelength of irradiation employed ($\lambda_{exc} = 248$ nm) for the photochemical experiments allows direct excitation of the ground-state complex ($\lambda_{max} = 245$ nm). Selective excitation of the noncomplexed species by irradiation at longer wavelengths may result in a lower *E*/*Z*-ratio of the methoxystyrenes **6-OMe** and a larger importance of path 3b. This is however not observed. The *E*/*Z*-ratio and the relative importances of paths 3a and 3b are identical within experimental error, irrespective of employment of $\lambda_{exc} = 248$ nm, or $\lambda_{exc} = 296$ nm. Thus, the solvent dependence of the UV-absorption spectra supports the formation of λ^3-iodanes in methanol and their absence in TFE in line with the mechanism of Scheme 6, but the differences in photochemical behavior of **1** in these solvents do not stem from differences in electronic excitations.

Scheme 7



Effect of Added Bromide on the UV Spectra and the Photochemistry in Methanol. The validity of the reaction mechanism depicted in Scheme 6, involving λ^3-iodanes in the photochemistry of **1**, was further examined by adding varying amounts of tetrabutylammonium bromide to the irradiation mixtures. The effect of added bromide on the thermal chemistry of **1** in acetonitrile has been studied in great detail.[32] The association constants of bromide ions with iodonium compounds in acetonitrile are quite high, resulting in almost complete association to a 10-I-3 bromide–iodonium complex at low concentrations ($K_1 = 2.8 \times 10^3$ M^{-1}; Scheme 7). At higher bromide concentrations a 12-I-4 complex is formed as well, albeit with a far lower association constant ($K_2 = 20$ M^{-1}; Scheme 7).[32] The mechanism presented in Scheme 6 predicts preferential attack of the coordinated nucleophile at the intermediate styryl cation $\mathbf{I_2}$. Added bromide can compete with methanol and give a λ^3-iodane complex with **1**, if $K_1 \times [Br^-]$ is comparable or greater than the association constant of methanol with **1** times the methanol concentration. Photolysis of the **1**–bromide complex, according to Scheme 6, should result in bromide addition to $\mathbf{I_2}$ preferentially giving the *E*-vinyl bromide.

To study the aptitude of bromide to complex with **1** in methanol, UV spectra of **1** at various bromide concentrations were recorded. Other than in acetonitrile,[32] the changes in absorbance in methanol unfortunately are too small to accurately measure the equilibrium constants K_1 and K_2 of Scheme 7.

Evidence that the 10-I-3 association complex is indeed already formed efficiently in methanol at low [Br^-] comes from the photochemistry of **1** in the presence of added bromide ions. Upon irradiation of **1** in a 5 mM Bu_4NBr solution in methanol, (*E*)- and (*Z*)-β-bromostyrene are formed efficiently. Also bromobenzene (formed via path 1; Scheme 4), trace amounts of α-bromostyrene (formed via path 3b; Scheme 4), and the products described earlier in the irradiation of **1** in methanol in the absence of bromide salt (Scheme 3) are produced.

(*E*)- and (*Z*)-β-bromostyrene are formed at the expense of (*E*)- and (*Z*)-β-methoxystyrene. The ratio Φ_{Br}/Φ_{OMe} rises from 2.2 at [Br^-] = 5 mM to ~44 at [Br^-] = 30 mM. Already at [Br^-] = 30 mM, the formation of the methoxystyrenes is suppressed to the extent that only traces of the vinyl ethers are observed. Obviously, bromide ion competes efficiently with methanol in the association to the iodonium ion. From the value of 2.2 at [Br^-] = 5 mM, and the assumption that all β-bromostyrene originates from a **1**–bromide complex, K_1 can be estimated to be ~4 × 10^2 M^{-1}. This high association constant of Br^- with **1** in methanol results in complete suppression of the formation of vinyl ethers at already relatively low [Br^-].

Variation of the bromide concentration affects the ratio of the stereoisomers of β-bromostyrene as well as of β-methoxystyrene (Figure 3).

---

(32) Okuyama, T.; Oka, H.; Ochiai, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1915.

(33) The ϵ-value was calculated from data in ref 32.

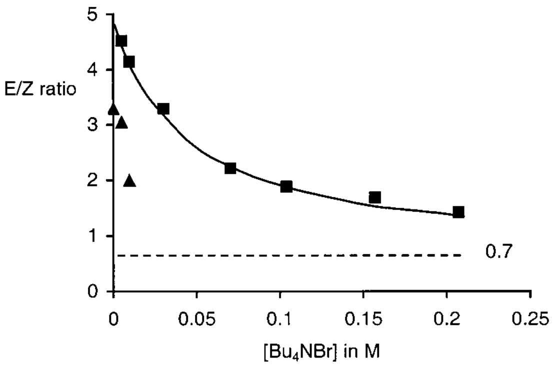


Figure 3. Variation of the *E*/*Z*-ratios of β-bromostyrene (■) and β-methoxystyrene (▲) upon irradiation of **1** ([**1**] = 5 mM) in methanol as a function of $[Br^-]$.

The *E*/*Z*-ratio of β-bromostyrene drops from 4.5 at $[Br^-]$ = 5 mM to 1.4 at $[Br^-]$ = 200 mM. Extrapolation to $[Br^-]$ = 0 M shows that the *E*/*Z*-ratio does not go to infinity (Figure 3), but to 5.0. This indicates that nucleophilic attack of the bromide anion within the solvent cage (Scheme 8; path i) does not exclusively lead to (*E*)-β-bromostyrene. Enough initial structural information is lost in the solvent cage for the bromide anion to be able to attack the primary styryl cation on the opposite side from where it left. The extrapolated *E*/*Z* ratio of 5.0 at infinitely low $[Br^-]$ is close to the *E*/*Z*-ratio for β-methoxystyrene in pure methanol (3.3). This further consolidates the assumption that irradiation of the **1**−bromide and the **1**−methanol complex give equivalent photochemistry.

Obviously, at higher bromide concentrations a second pathway for formation of β-bromostyrene is available which leads to a lower *E*/*Z*-ratio. Nucleophilic attack of uncoordinated bromide at the opposite side of the leaving iodobenzene−bromide moiety is proposed as the mechanism for this pathway (Scheme 8; path ii). At infinitely high bromide concentration the *E*/*Z*-ratio does not drop to zero, but goes to 0.7. This is caused by free bromide anions attacking at the side from which the iodobenzene−bromide moiety is leaving (not depicted in Scheme 8).

On the basis of the mechanism in Scheme 8 and the assumption that the nucleophilic attack of the external bromide ion only occurs at the photolyzed **1**−Br^- complex and not at uncomplexed photolyzed **1**,[34] kinetic eq 1 is derived and fitted to the data of Figure 3. (*R* is the *E*/*Z*

$$R = \frac{k_{E,i} + k_{E,ii}[Br^-]}{k_{Z,i} + k_{Z,ii}[Br^-]} \qquad (1)$$

ratio of β-bromostyrenes formed; $k_{E,i}$ is the rate of formation of the *E*-isomer by path i, etc.) From the fit, $k_{E,i}/k_{Z,i}$ and $k_{E,ii}/k_{Z,ii}$ (i.e., the ratio of (*E*)- and (*Z*)-β-bromostyrene at infinitely low (path i) and infinitely high (path ii) $[Br^-]$) are determined to be 5.0 and 0.7, respectively (as depicted in Scheme 8).

The *E*/*Z*-ratio of β-methoxystyrene could only be determined at the two lowest bromide concentrations used, because at higher $[Br^-]$ the amount of β-methoxystyrene formed is too small (Figure 3). The value for the *E*/*Z* ratio for methoxystyrenes of 3.3 at $[Br^-]$ = 0 mM is included as well. The drop in the *E*/*Z* ratio of the vinyl ethers upon addition of Br^- indicates that external methanol competes with external bromide in the addition to the photolyzed λ^3-iodane complex (depicted as path ii for Br^- addition in Scheme 8).

Chlorinated Alkane as Solvent. Irradiation (λ_{exc} = 248 nm) of the tetrafluoroborate salt of **1** in dichloromethane yields the reaction mixture depicted in Scheme 9. The numbers in parentheses are the quantum yields of formation of the primary photoproducts.

The reaction paths are similar to those in the photochemistry of **1** in alcoholic solvents (Scheme 4). (1) Heterolytic cleavage of the phenylic C−I bond yields **2** and the phenyl cation. Probably from the latter, chlorobenzene (**3-Cl**) is formed by chloride abstraction from the solvent. This kind of reactivity has previously been observed, for instance, in the formation of 1-chlorocycloalkenes from 1-cyclovinyl cations in dichloromethane.[35] Alternatively, the phenyl radical, formed by homolytic cleavage of the phenylic C−I bond, can abstract a chlorine atom from the solvent.[36] (2) Homolytic cleavage of the vinylic C−I bond yields the styryl radical and the iodobenzene radical-cation. The latter species can acquire an electron and yield neutral iodobenzene (**9**). The styryl radical can abstract a hydrogen atom from the solvent and yield styrene (**4**). (3a) Heterolytic cleavage of the vinylic C−I bond yields **9** and the primary styryl cation $\mathbf{I_2}$. The latter species can lose a proton to give **5**. It can also produce products **6-F** by fluoride abstraction from the, nearby, tetrafluoroborate anion. In poor ion-solvating solvents, such as dichloromethane, **1** is known not to be free from its tetrafluoroborate counterion.[15,37] The styryl cation $\mathbf{I_2}$ can also acquire chloride from the solvent to yield (*E*)- or (*Z*)-β-chlorostyrene (**6-Cl**). Alternatively, **6-Cl** may be formed by chlorine atom abstraction from dichloromethane[36] by the styryl radical formed in path 2. (3b) Rearrangement of $\mathbf{I_2}$ by a 1,2-hydride shift gives the styryl cation $\mathbf{I_3}$. Reaction of this far more stable cation with fortuitous water yields acetophenone (**8**). (3c) Heterolytic cleavage via path 3 yields $\mathbf{I_2}$ and iodobenzene in a solvent cage (not depicted in Scheme 4). In-cage recombination at the *ipso*-position of **9** and loss of I^+ gives stilbene (**10**). An analogous reaction has been observed in the photochemistry of diaryliodonium salts.[6] In that case biaryls are produced by heterolysis of the C−I bond and subsequent in-cage recombination of the cation and the neutral leaving group. The *E*-isomer of **10** is formed preferentially, because it is the product of attack at the side from which **9** is leaving.[38] In alcoholic solvents no **10** is formed, since in that medium more efficient pathways of reaction are opened. Moreover, in a medium of low polarity, **1** gives a tighter molecule−ion pair than in, for instance, methanol, leading to efficient Friedel−Crafts addition of $\mathbf{I_2}$ to iodobenzene.

Fluorobenzene, the expected product upon fluoride abstraction by the phenyl cation, generated in path 1 of Scheme 9, is not observed upon photolysis of the tetra-

---

[34] The bromostyrenes being already formed in significant amounts at low $[Br^-]$ favors this assumption, because under those conditions bromide ions cannot compete with the much more abundant methanol as external nucleophile. At higher $[Br^-]$, bromide does compete efficiently, but in this case all **1** is complexed with bromide.

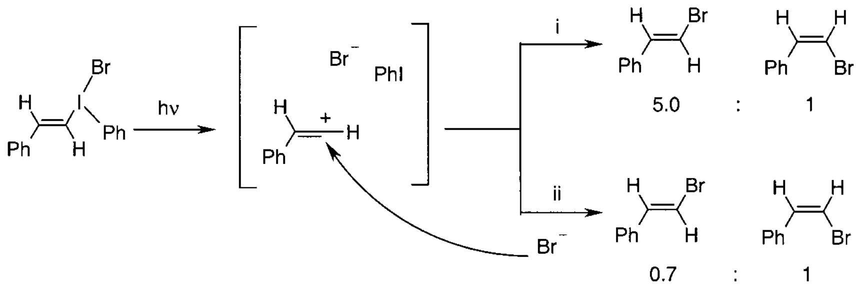
[35] Kropp, P. J.; McNeely, S. A.; Davis, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 6907.

[36] Afanas'ev, I. B.; Mamontova, I. V.; Samokhavlov, G. I. *J. Org. Chem. USSR* **1971**, *7*, 462.

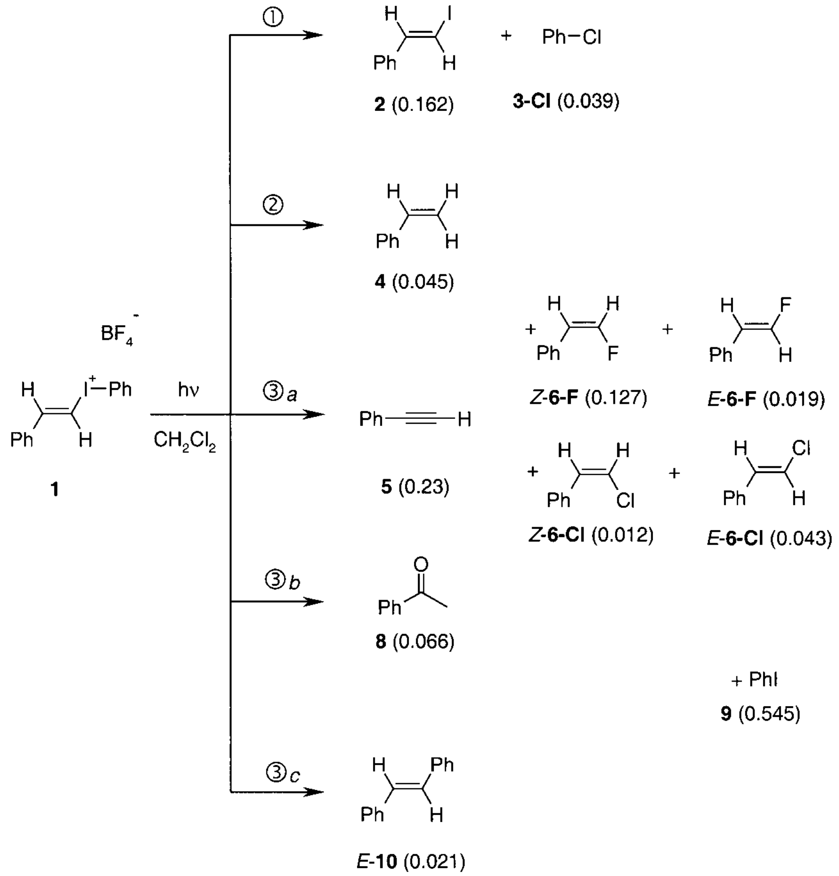
[37] Swain, C. G.; Roger, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 799.

[38] Cf. the S_Ni mechanism of nucleophilic photosubstitution towards **1**.

Scheme 8. Mechanism of Formation of the β-Bromostyrenes



Scheme 9

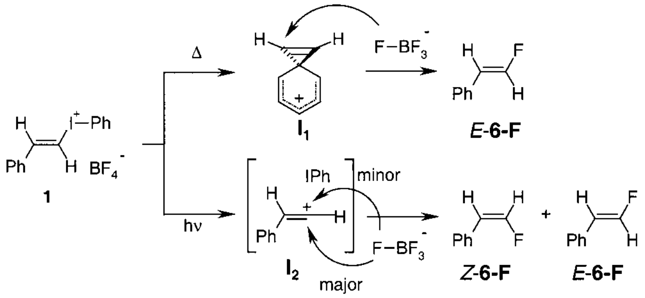


fluoroborate salt of **1** in dichloromethane. This may well be caused by the solvent obscuring fluorobenzene in the GC analysis.

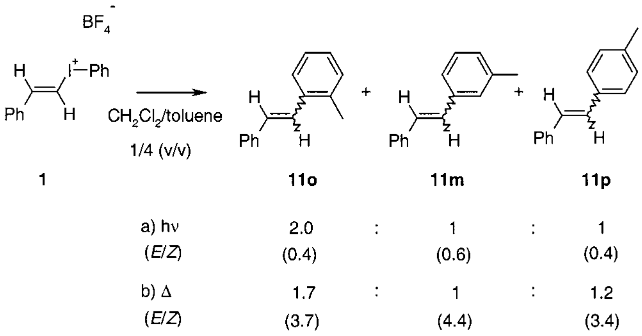
The most interesting products in Scheme 9 are the vinyl fluorides **6-F**. Their formation has a thermal counterpart in the solvolysis of **1** in chloroform, where exclusively *E*-**6-F** is formed, next to the elimination product **5** and **9**.[15] No (*Z*)-β-fluorostyrene is formed, due to the intermediacy of the vinylenebenzenium ion $\mathbf{I_1}$ (Scheme 10).[9] The stereoselectivity in the photochemical formation of **6-F** is remarkable: in contrast with the thermal mode of reactivity, *Z*-**6-F** is formed more efficiently than *E*-**6-F**. Preferential formation of the *Z*-isomer may indicate that the tight ion−molecule pair of $\mathbf{I_2}$ and **9**, formed upon photolysis of **1**, hampers the approach of the fluoride donor to $\mathbf{I_2}$ (Scheme 10).

Attack of a dichloromethane solvent molecule on $\mathbf{I_2}$ will also be hampered by **9** in the tight ion−molecule pair. Thus, preferential formation of (*Z*)-**6-Cl** is expected as well, contrary to the observation. This means that **6-F** and **6-Cl** do not have a common precursor in the photochemical reaction. This is corroborated by the fact that in the thermal reaction, the products **6-F** and **6-Cl** are formed in equal amounts, while in the photochemical reaction **6-F** is formed about three times more efficiently (Scheme 9). A viable candidate via which (part of) **6-Cl** may be formed is the styryl radical from path 2.[36] Steric hindrance by the phenyl group, in the approach of a

Scheme 10. Mechanisms of Formation of β-Fluorostyrenes in the Thermal and Photochemical Reaction of 1



Scheme 11



dichloromethane molecule to this species, explains the preferential formation of (*E*)-**6-Cl**.

The photochemical and thermal[15] formation of vinyl fluorides from vinyl iodonium tetrafluoroborates is unprecedented. Fluoride abstraction from tetrafluoroborates has been reported to occur, however, as a side-reaction in the $AgBF_4$-assisted vinylation of aromatic compounds,[17d,39] in the thermal decomposition of diaryliodonium tetrafluoroborates[40] and in the Balz−Schiemann reaction.[41] The occurrence of cationic intermediates in the latter reaction is widely accepted.[37,42] The vinylic counterpart of this reaction, however, has never been pursued, because of the difficult accessibility of vinylic diazonium salts.[43]

Aromatic Solvent. Upon photolysis of the tetrafluoroborate salt of **1** in dichloromethane, one of the pathways is a Friedel−Crafts reaction, as demonstrated by the formation of **10** (Scheme 9, path 3c). The leaving group is the source of the aromatic moiety introduced. To investigate whether an aromatic medium competes with the leaving group in the addition step to $\mathbf{I_2}$, the tetrafluoroborate salt of **1** was irradiated in toluene ($\lambda_{exc} = 296$ nm; at this wavelength toluene is not excited). Dichloromethane (dichloromethane/toluene = 1/4 (v/v)) was used as a cosolvent.

Indeed Friedel−Crafts type adducts derived from toluene (methylstilbenes **11**) are formed (Scheme 11a) albeit in low yields (~10% of total products). Next to **11** all products are observed that are formed upon photolysis of the tetrafluoroborate salt of **1** in dichloromethane, including stilbene (**10**). The percentage of reaction of $\mathbf{I_2}$ with the aromatic solvent is larger than with the leaving group (**10**/**11** = 0.05). Both *E*- and *Z*-isomers of **11** are formed, the *Z*-isomers somewhat more efficiently ($E/Z = \sim 0.4$). For the sake of comparison the reaction of **1** was also carried out thermally in the same solvent mixture (Scheme 11b). Now mainly (*E*)-methylstilbenes are produced ($E/Z = \sim 3.7$).

For the thermal production of **11**, formation of ion $\mathbf{I_1}$ is proposed as the first step in the reaction mechanism, in analogy with the thermal reaction of **1** in alcoholic solvents and in chloroform (cf. Schemes 1 and 10). Addition of this ion to toluene and subsequent proton abstraction from the σ-complex yields (*E*)-methylstilbenes. Formation of small amounts of the (*Z*)-methylstilbenes next to the *E*-isomers may be due to a secondary (acid-catalyzed) isomerization reaction.

The preferential formation of the *Z*-isomers of the methylstilbenes **11** upon irradiation of **1** in the presence of toluene, resembles the preferential formation of (*Z*)-fluoroalkenes upon its irradiation in pure dichloromethane and can also be explained by assuming the formation of a tight ion−molecule pair, hampering the approach of the nucleophile (i.e., toluene).

In the photochemical as well as in the thermal reaction, products derived from addition to three ring positions of toluene (*ortho*: **11o**, *meta*: **11m**, and *para*: **11p**) are formed. The relative rates of formation of these products is almost identical for both reactions. In the photochemical reaction the ratio is **11o**:**11m**:**11p** = 2.0:1:1,[44] in the thermal reaction **11o**:**11m**:**11p** = 1.7:1:1.2, in both cases invariant to the *E*/*Z*-stereochemistry. These ratios are remarkably close to the relative rates of formation of the regioisomers in the condensed-phase vinylation of toluene by $C_2H_3^+$ (o:m:p = 1.3:1:1.0).[18] The low positional selectivity indicates kinetic control of formation of the σ-complexes, with low activation barriers by the highly unstable carbocations $\mathbf{I_1}$ and $\mathbf{I_2}$.[45] Alternatively, it may be the result of facile migration of the unsaturated styryl moiety over the arene ring in the σ-complex.[18] Evidence against the latter argument is provided by the Friedel−Crafts reaction of α-anisyl substituted vinyl cations with toluene.[17d] These relatively stable vinyl cations show a significantly higher regioselectivity (o:m:p = 3:2:9.3).

Conclusions

Styryl(phenyl)iodonium salt **1** is an excellent precursor for the photochemical generation of the primary styryl cation and allows the study of the reactivity of this ion. The iodonium salt is extremely photoreactive as demonstrated by quantum yields of product formation ranging from 0.65 in 2,2,2-trifluoroethanol to 1.0 in methanol. The yields of ion-derived products are far higher than in the corresponding styryl halides. Moreover, the iodonium salt is more prone to give nucleophilic substitution instead of elimination. The difference in reactivity is due to the formation of a cation−molecule pair in the first case and a cation−anion pair in the latter. The basicity of the anion is high enough to give exclusive elimination. The basicity of the molecule is not, resulting in both elimination and nucleophilic substitution.

There are significant differences between the photochemical and the thermal behavior of **1**. First, in the photochemistry both C−I bonds are cleaved, whereas in the thermal chemistry only the vinylic C−I bond is reactive. Second, the ratios of the products formed upon thermal and photochemical cleavage of the vinylic C−I bond are quite different. In the photochemical reaction rearranged substitution products are formed, which is not the case in the thermal reaction. Also, in the

---

[39] Hammen, G.; Hanack, M. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 614.

[40] Van der Puy, M. *J. Fluorine Chem.* **1982**, *21*, 385.

[41] Balz, G.; Schiemann, G. *Berichte* **1927**, *60*, 1186.

[42] For a review see: Suschitzky, H. In *Advances in Fluorine Chemistry*; Stacey, M.; Tatlow, J. C.; Sharpe, A. G., Eds.; 1965; Vol. 4, p 1.

[43] Bott, K. In *Methoden der Organischen Chemie (Houben-Weyl)*, 4th ed.; Verlag: Stuttgart, 1993; E 15, p 1101. Formation of a vinyl chloride from its vinyldiazonium hexachloroantimonate derivative in dichloromethane or 1,2-dichloroethane has been reported, but the origin of the chloride (from the counterion or the solvent) is uncertain. See: Bott, K. *Chem. Ber.* **1994**, *127*, 933.

[44] Formation of the para-isomer could not be accurately studied due to overlap of its GLC peak with that of another (unidentified) photoproduct and is estimated.

[45] In the reactions of more stable carbocations, such as the *p*-methoxybenzyl cation, towards toluene, far less *meta*-substitution is observed: o:m:p = 19:1:47, see: Olah, G. A.; Tashiro, M.; Kobayashi, S. *J. Am. Chem. Soc.* **1970**, *92*, 6369.

photochemical reaction the ratio substitution/elimination is higher than in the thermal reaction. Third, in the thermal as well as the photochemical reactions there is a large solvent dependence on the product composition. However, decreasing the solvent nucleophilicity leads to more nucleophilic substitution in the thermal and more rearrangement in the photochemical reaction. This is all in line with mechanisms, where assisted cleavage (either by the solvent or the phenyl ring) of the C−I bond occurs in the thermal reaction and unassisted cleavage in the photochemical reaction.

In the poorly nucleophilic solvent TFE, the reaction proceeds from the bare 8-I-2 iodonium species by an S_N1 mechanism. Use of nucleophilic solvents or addition of nucleophiles leads to the formation of 10-I-3 species, which yield nucleophilic photosubstitution products with predominant retention of configuration via S_Ni substitution.

Upon irradiation of **1** in the nonnucleophilic solvent dichloromethane significant reactivity with the counterion is observed, indicating the involvement of ion pairs in such solvents. The vinyl fluoride products are ion-derived, and the stereoselectivity of the addition step is controlled by steric hindrance exerted by the leaving group. Irradiation of **1** in toluene yields photo-Friedel−Crafts products, via reaction of the primary styryl cation with the solvent. The regioselectivity resembles that of the parent vinyl cation $C_2H_3^+$, indicating kinetic control in the addition step.

Experimental Section

Materials. Methanol (Rathburn) and dichloromethane (p.a. grade; Carlo Erba) were checked for UV transparency and used as received. 2,2,2-Trifluoroethanol (Aldrich) was boiled with decolorizing charcoal and subsequently distilled. Toluene and *n*-hexane (Baker) were used as received, as were tetrabutylammonium bromide (Aldrich) and tetrabutylammonium perchlorate (Fluka). All reference compounds and starting materials for the syntheses were obtained from Aldrich or Acros.

The preparation of (*E*)-styryl(phenyl)iodonium tetrafluoroborate (**1**) and its deuterated counterpart *E*-**1-D** have been described in refs 24 and 32, respectively.

All reaction products were characterized by comparison of retention times on analytical GLC and comparison of mass spectra (by GC-MS) with those of authentic samples. For reference compounds, commercial samples were used, when available. The remaining reference compounds were prepared by literature procedures: (*Z*)-*β*-methoxystyrene (**6-OMe**)[46] (contaminated with small amounts of α-methoxystyrene (**7-OMe**)[47]), (*E*)-*β*-iodostyrene (**2**),[48] 2,2,2-trifluoroethoxybenzene (**3-OCH$_2$CF$_3$**),[49] (*E*)-*β*-trifluoroethoxystyrene (**6-OCH$_2$CF$_3$**),[9] (*E*)- and (*Z*)-*β*-fluorostyrene (**6-F**) as a mixture (E:Z = 13:87),[50] and (*E*)-*β*-chlorostyrene (**6-Cl**).[51,52] (*E*)-*p*-Methylstilbene (**11p**) was prepared via the method of Bellucci et al.[53] The *o*- and *m*-methylstilbene isomers were prepared accordingly.[54] In all cases where pure *E*- or *Z*-isomers were obtained, an *E*/*Z*-mixture of the reference compound was prepared by sensitized irradiation in argon purged acetone solutions with a medium-pressure mercury arc through Pyrex.

Photochemistry. For all product studies (both sensitized and direct excitation) and quantum yield experiments the same photochemical setup was used. A high-pressure Hg/Xe arc, from which the IR output was removed by a water filter was used as the light source. The light beam was processed through a model 77250 Oriel monochromator, to select the desired wavelength 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.

In a typical experiment 3 mL of ∼5 mM solution of the iodonium salt, containing ∼1 mM *n*-pentadecanol (in case of TFE) or *n*-hexadecane (in the other solvents) as internal standard, was irradiated at the desired wavelength. At appropriate time intervals 50 μL samples were taken, using a syringe, through the septum and injected in a test tube containing ∼1 mL of water and 100 μL of *n*-hexane. The two layers were mixed vigorously, and the *n*-hexane layer was removed with a pipet and analyzed by GC and/or GC-MS. For all kinetic 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 by means of product appearance, were kept below 15%. All quantum yields were obtained as the average of data from three independent irradiations and calculated from the kinetic data using least-squares treatment and the intensity of the light employed. The intensity of the light used was determined using the chemical actinometer: Actino Chromo 1R (248/334) from Photon Technology International.

Equipment. UV spectra were recorded at room temperature on a double beam Varian DMS 200 spectrophotometer, with pure solvent in the reference cell. ^{1}H NMR spectra were recorded on a JEOL 200, using $CDCl_3$ as solvent. As analytical GC a Hewlett-Packard 6890 series was used, fitted with a CP SIL5-CB column (30 m, ∅ = 0.25 mm) using hydrogen as carrier gas. The flame-ionization detector (FID) was calibrated, using synthesized or commercially available materials. Isomers were assumed to have equal response factors. HP Chemstation was used for analysis of the analytical GC data. Mass spectra were measured using a GC-MS setup consisting of a Packard model 438A GC, fitted with a CP SIL5-CB (30 m, ∅ = 0.25 mm) using helium as carrier gas, coupled with a Finnigan Mat ITD 700 mass spectrometer. Electron impact was used as the ionization method.

Acknowledgment. The authors thank Professor Jan Cornelisse (Leiden University) for continuous interest and helpful discussions.

JO0107397

---

(46) Miller, S. I. *J. Am. Chem. Soc.* **1956**, *78*, 6091.

(47) For previous characterization of **7-OMe** see: Willmore, N. D.; Hoic, D. A.; Katz, T. J. *J. Org. Chem.* **1994**, *59*, 1889.

(48) Wright, G. F *J. Org. Chem.* **1936**, *1*, 457.

(49) Canning, P. S. J.; McCrudden, K.; Maskill; H.; Sexton, B. *Chem. Commun.* **1998**, 1971.

(50) Cox, D. G.; Gurusamy, N.; Burton, D. J. *J. Am. Chem. Soc.* **1985**, *107*, 2811.

(51) Chowdhurry, S.; Roy, S. *J. Org. Chem.* **1997**, *62*, 199.

(52) For previous characterizations of *E*- and *Z*-**6-Cl** see: Dolby, L. J.; Wilkins, C.; Freg, T. G. *J. Org. Chem.* **1966**, *31*, 1110.

(53) Bellucci, G.; Bianchini, R.; Chiappe, C.; Brown, R. S.; Slebocka-Tilk, H. *J. Am. Chem. Soc.* **1991**, *113*, 8012.

(54) For previous characterizations of *E*- and *Z*-**11o** see: Lawrence, N. J.; Muhammad, F. *Tetrahedron* **1998**, *54*, 15361. For *E*- and *Z*-**11m**: Ito, Y.; Uozu, Y.; Doke, T.; Ueda, M.; Matsuura, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 189.