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# Photochemical Generation of Highly Destabilized Vinyl Cations: The Effects of α- and β-Trifluoromethyl versus α- and β-Methyl Substituents

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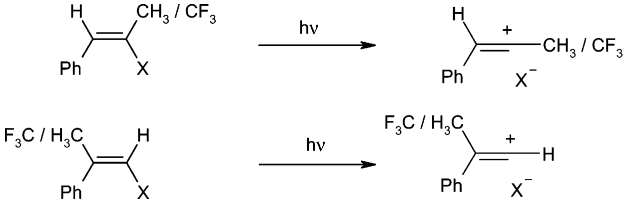

The photochemical reactions in methanol of the vinylic halides **1**−**4**, halostyrenes with a methyl or a trifluoromethyl substituent at the α- or β-position, have been investigated quantitatively. Next to *E*/*Z* isomerization, the reactions are formation of vinyl radicals, leading to reductive dehalogenation products, and formation of vinyl cations, leading to elimination, nucleophilic substitution, and rearrangement products. The vinyl cations are parts of tight ion pairs with halide as the counterion. The elimination products are the result of β-proton loss from the primarily generated α-$CH_3$ and α-$CF_3$ vinyl cations, or from the α-$CH_3$ vinyl cation formed from the β-$CH_3$ vinyl cation via a 1,2-phenyl shift. The β-$CF_3$ vinyl cation reacts with methanol yielding nucleophilic substitution products, no migration of the phenyl ring producing the α-$CF_3$ vinyl cation occurs. The α-$CF_3$ vinyl cation, which is the most destabilized vinyl cation generated thus far, gives a 1,2-fluorine shift in competition with proton loss. The experimentally derived order of stabilization of the vinyl cations photogenerated in this study, α-$CF_3$ < β-$CF_3$ < β-$CH_3$ < α-$CH_3$, is corroborated by quantum chemical calculations, provided the effect of solvent is taken into account.

## Introduction

Substituent effects on carbocations have received tremendous attention over the years.[1] Recent interest has focused on alkyl cations bearing electron-withdrawing substituents, including CN, $CF_3$, and $C_2F_5$, mainly at the α-position.[2] For these substituents next to their α-effects also their β-effects have been studied, leading to measures of relative (de)stabilization by α- and β-substituents.[3] Compared to alkyl cations, vinyl cations are more elusive and the range of substituents studied is smaller. Vinyl cations bearing various electron-donating substituents have been prepared both thermally and photochemically.[4,5] The number of vinyl cations with electron-withdrawing substituents, however, is quite limited: only the formation of the α-CH=O and α-CN species by photochemical means from vinyl halides[6] and the α-$CO_2C_2H_5$ species by thermal means from vinyl diazonium compounds[7] have been reported thus far. Also, β-stannyl vinyl cations with α-electron-withdrawing groups are proposed as intermediates in the preparation of alkynyl iodonium salts.[8]

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[1] (a) *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1968, Vol. I; 1970, Vol. II; 1972, Vol. III; 1973, Vol. IV; 1976, Vol. V. (b) Vogel, P. *Carbocation Chemistry*; Elsevier: Amsterdam, The Netherlands, 1985. (c) *Advances in Carbocation Chemistry*; Creary, X., Ed.; JAI Press Ltd.: London, England, 1989; Vol. I.

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[4] (a) *Dicoordinated Carbocations*; Rappoport, Z., Stang, P. J. , Eds.; Wiley: Chichester, UK, 1997. (b) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. *Vinyl Cations*; Academic Press: New York, 1979.

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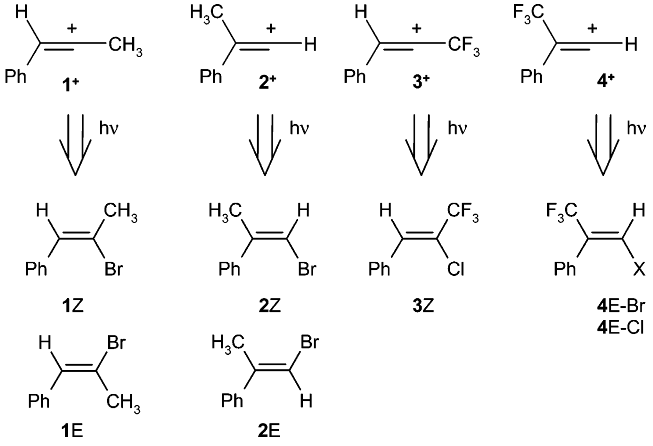


**FIGURE 1.** Compounds under study.

Quantum chemical studies on the effects of a range of α-substituents R on the stability of the vinyl cations $H_2C{=}C(+)\text{-}R$ predict that the α-$CF_3$ substituent is considerably more destabilizing than the substituents mentioned above.[9]

In this study we report the photogeneration of the vinyl cations $\mathbf{3}^+$ and $\mathbf{4}^+$ substituted at the α- and β-position, respectively, by a trifluoromethyl group and thus the production of highly destabilized vinyl cations (see Figure 1). By virtue of these species being vinyl cations and the presence of a $CF_3$ group these species are doubly destabilized carbocations.[2b,10] For comparison also the corresponding α- and β-methyl-substituted vinyl cations $\mathbf{1}^+$ and $\mathbf{2}^+$ are photogenerated, which allows the assessment of the effects of the $CF_3$ substituent compared to the $CH_3$ group at both the α- and β-position on the (in)stability and reactivity of the vinyl cations. To generate these species the halostyrene precursors **1**−**4** have been synthesized and their photochemistry in methanol has been studied.

## Results and Discussion

**Photochemistry of 1**. Irradiation of **1***E* or **1***Z* in methanol yields the same three types of products for both stereoisomers (Scheme 1). Next to the *E*/*Z*-isomerization products, commonly observed in the photochemistry of C═C containing materials, two products are formed in which the bromine atom is replaced by a hydrogen atom (**5***E* and **5***Z*) as well as two compounds that have been formed by loss of HBr from the starting materials (**6** and **7**). No nucleophilic substitution products in which the bromine is replaced by a methoxy group are formed. The quantum yields of appearance of the products are given in Table 1.

**SCHEME 1**

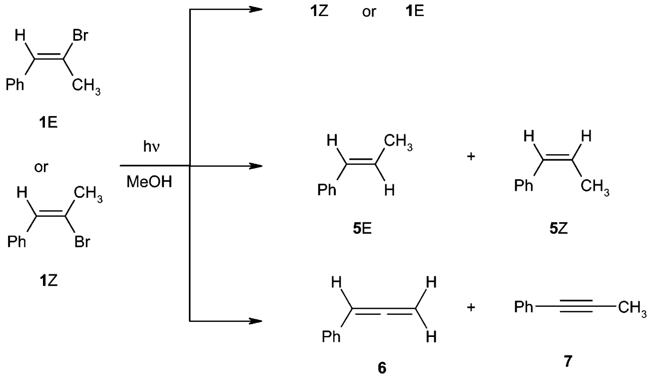
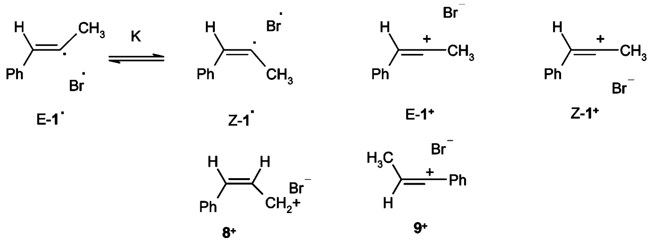


**TABLE 1. Quantum Yields (×10$^{-2}$) of Formation of 5*E*, 5*Z*, 6, and 7 upon Irradiation ($\lambda_{exc}$ = 248 nm) of 1 in Methanol**[a]

| | $\Phi_{5E}$ | $\Phi_{5Z}$ | $\Phi_6$ | $\Phi_7$ |
|---|---|---|---|---|
| **1***E* | 9.7 | 3.4 | 15.7 | 23.1 |
| **1***Z* | 9.7 | 4.1 | 16.0 | 14.5 |

[a] Owing to problems with the GC separation of **1***Z* and **1***E* no reliable quantum yields for the *E*/*Z*-isomerization could be obtained.

**SCHEME 2. Possible Reactive Intermediates Produced upon Photolysis of 1**



The reductive dehalogenation products **5***E* and **5***Z* are typical vinyl radical-derived products, formed by abstraction of a hydrogen atom from the solvent. Even though the intermediate α-methyl-substituted vinyl radicals *E*- and *Z*-$\mathbf{1}^\bullet$ (Scheme 2) are bent,[11] both stereoisomeric products **5***E* and **5***Z* are formed from either of the stereoisomeric starting materials, since *E*/*Z*-isomerization in the radicals $\mathbf{1}^\bullet$ is fast compared to hydrogen abstraction.[12] This means that each of the initially formed vinyl radicals equilibrates to a mixture of *E*/*Z*-vinyl radicals that yields **5***E* and **5***Z* in a ratio of about 2.5:1 after hydrogen abstraction, almost regardless of the stereochemistry of **1**. The incomplete stereoconvergence can be ascribed to the intervention of radical pairs.[13,14] The preponderance of **5***E* over **5***Z* is due to the facts that the hydrogen atom transfer from the solvent methanol to $\mathbf{1}^\bullet$

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(5) (a) Kropp, P. J. *CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Song, P.-S., Eds.; CRC Press: Boca Raton, FL, 1995; Chapter 84. (b) Kitamura, T. *CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Song, P.-S., Eds.; CRC Press: Boca Raton, FL, 1995; Chapter 85. (c) Lodder, G.; Cornelisse, J. *The Chemistry of Functional Groups*: *Supplement D2*; Patai, S., Rappoport, Z., Eds.; Wiley, Chichester, UK, 1995; Chapter 16. (d) Okuyama, T.; Lodder, G. *Adv. Phys. Org. Chem.* **2002**, *37*, 1−56.

(6) (a) Krijnen, E. S.; Lodder, G. *Tetrahedron Lett.* **1993**, *34,* 729−732. (b) Krijnen, E. S.; Van Alem, K.; Van der Vlugt, D. H. J.; Zuilhof, H.; Lodder, G. Manuscript in preparation.

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(9) (a) Apeloig, Y.; Biton, R.; Zuilhof, H.; Lodder, G. *Tetrahedron Lett.* **1994**, *35*, 265−268. (b) Van Alem, K.; Lodder, G.; Zuilhof, H. *J. Phys. Chem. A* **2002**, *106*, 10681−10690.

(10) Allen, A. D.; Tidwell, T. T. *J. Org. Chem.* **2001**, *66*, 7696−7699 and references therein.

(11) (a) Singer, L. A.; Wong, N. P. *Tetrahedron Lett.* **1966**, 2089−2094. (b) Singer, L. A.; Wong, N. P. *J. Am. Chem. Soc.* **1966**, *88*, 5213−5219.

(12) Goumans, T. P. M.; Van Alem, K.; Lodder, G. Manuscript in preparation.

is a highly exothermic process,[15] and that the rates of hydrogen atom transfer from the small H-donor methanol to the two isomeric radicals are about equal. This implies[16] that the product ratio is determined by the equilibrium constant $K$ for inversion between the *trans*- and the *cis*-vinyl radical $E$-**1**$^\bullet$ and $Z$-**1**$^\bullet$ (Scheme 2), which will be less than unity, leading to a ratio of >1:1 of **5*E*** versus **5*Z***.[12]

The elimination products **6** and **7** are formed from the vinyl cation **1**$^+$, which is generated by C−Br bond heterolysis, via loss of a proton from either the methyl group or the $\beta$-vinylic carbon. Allenic structures such as **6** have also been observed as products of cation **1**$^+$ thermally generated from a vinyl triflate precursor, and of various photochemically generated 1-methylethenyl cations.[17] Acetylene derivatives, such as **7**, also have been observed in vinyl cation chemistry before, if a $\beta$-vinylic hydrogen is present in the vinyl cation. Abstraction of that proton can compete with or even completely overwhelm the formation of nucleophilic substitution products.[6,18] The vinyl cations **1**$^+$ that are formed upon irradiation of **1*E*** and **1*Z*** are most probably not free cations, but parts of tight ion pairs with bromide as counterion.[13,14] The $\beta$-protons are abstracted by Br$^-$ within the ion pairs. This abstraction is facile because of the high kinetic basicity of the bromide anion, and apparently faster than nucleophilic addition of the solvent.[14] The ion pairs formed in the irradiations of **1*E*** and **1*Z*** are not only tight but also different, since the stereoisomeric starting materials **1** give different **6**/**7** ratios. This indicates that the locations of the bromide ion in the initially formed ion pairs within the solvent cage are not the same and that proton transfer is faster than equilibration of the position of the bromide anion within the ion pair.

The allylic cation **8**$^+$ and the vinylic cation **9**$^+$ [19] (Scheme 2) are isomers of **1**$^+$, which can be formed via a 1,2-hydride shift toward the C=C bond and a 1,2-hydride shift across the C=C bond, respectively.[4,17a] No allylic or vinylic ether, the solvent addition products of these cations, has been detected. The former 1,2-shift of **1**$^+$ is thermodynamically feasible because it forms a more stable allylic cation (**8**$^+$), but kinetically it is not because the barrier for this process has been shown both experimentally and computationally to be quite high (in the order of 18 to 20 kcal/mol).[20−22] 1,2-Hydride shifts across the C=C bond, to convert **1**$^+$ into **9**$^+$, are quite facile, but either this migration cannot compete with the proton transfer to the bromide anion within the tight ion pair [**1**$^+$, Br$^-$] or the ion pair [**9**$^+$, Br$^-$], if formed, exclusively loses its $\beta$-proton to yield acetylene **7** (see also Scheme 4).

**SCHEME 3**

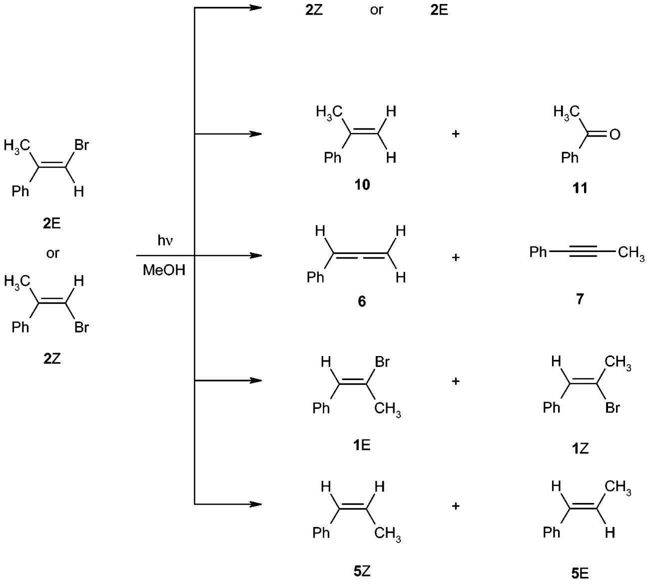

**TABLE 2. Quantum Yields (×10$^{-2}$) of *E*/*Z*-Isomerization of 2 and Formation of 10 + 11, 6, 7, 1*E*, 1*Z*, 5*E* + 5*Z* upon Irradiation ($\lambda_{exc}$ = 248 nm) of 2 in Methanol**

| | $\Phi_{E/Z}$ | $\Phi_{10+11}$ | $\Phi_6$ | $\Phi_7$ | $\Phi_{1E}$ | $\Phi_{1Z}$ | $\Phi_{5E+5Z}$ |
|---|---|---|---|---|---|---|---|
| **2*E*** | 29.8 | 18.6 | 1.1 | 2.1 | 0.07 | 0.05 | trace |
| **2*Z*** | 19.4 | 11.6 | 2.0 | 2.0 | 0.10 | 0.09 | trace |

In principle, compounds **6** and **7** may also have been formed from the vinyl radical **1**$^\bullet$, via loss of a hydrogen atom from the methyl group or the $\beta$-vinylic carbon. This was demonstrated not to be the case by preparing **1**$^\bullet$ independently from **1**, using tri-*n*-butyltin hydride and AIBN as initiator.[23] At over 90% conversion the only products were **5*E*** and **5*Z***, and no **6** or **7** was detected.

**Photochemistry of 2.** Irradiation of **2*E*** or **2*Z*** in methanol yields five types of products, as compared to three in the case of **1** (Scheme 3 and Table 2). Next to the *E*/*Z*-isomerization products **2*Z*** and **2*E*** and the reductive dehalogenation products **10** and **11**, the products observed in the irradiation of **1** are found (**5*Z***, **5*E***, **6**, and **7**), and even **1*E*** and **1*Z*** themselves. The latter six products must have been formed after a rearrangement. Study of the generation of the photoproducts as a function of time shows that all products are primary products of **2** and no significant secondary photochemistry occurs at the low percentage of conversion (<5%) studied.

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[13] Recombination of the radical pairs [**1**$^\bullet$, Br$^\bullet$], as well as recombination of the ion pairs [**1**$^+$, Br$^-$], in principle, may yield *E*/*Z*-isomerized starting materials. Isotope effect studies, however, indicate that internal return within radical or ion pairs is not an important pathway for photochemical *E*/*Z* isomerization of vinylic halides.[14]

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[15] The C−H bond dissociation energies of ethene and methanol are 108 and 92.6 kcal/mol, respectively, according to: Egger, K. W.; Cocks, A. T. *Helv. Chim. Acta* **1973**, *56*, 1516−1536.

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[19] (a) Kernaghan, G. F.P.; Hoffmann, H. M. R. *J. Am. Chem. Soc.* **1970**, *92*, 6988−6990. (b) Reich, I. V.; Haile, C. L.; Reich, H. J. *J. Org. Chem.* **1978**, *43*, 2402−2410.

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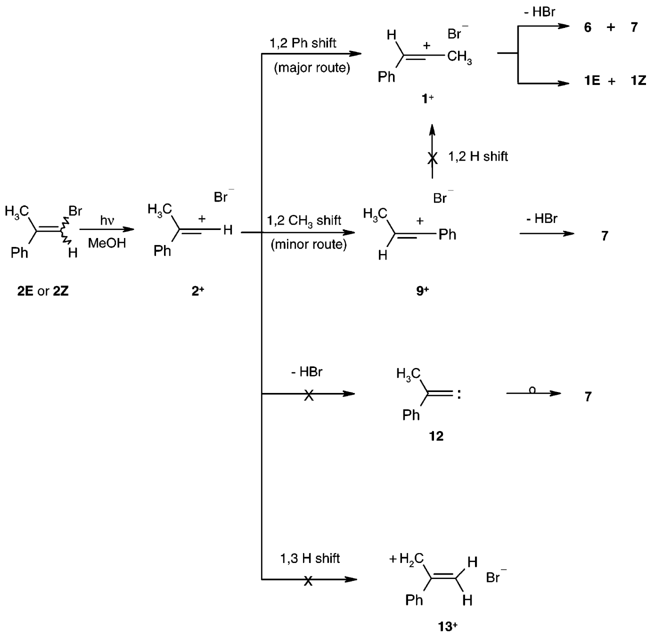
[22] McAllister, M.; Tidwell, T. T.; Peterson, M. R.; Csizmadia, I. G. *J. Org. Chem.* **1991**, *56*, 575−580.

[23] Neumann, W. P. *Synthesis* **1987**, 665−683.

**SCHEME 4. Mechanism of Formation of Ion-Derived Photoproducts from 2**



The unrearranged compounds **10** and **11** are vinyl radical-derived products formed via abstraction of a hydrogen atom from the solvent, yielding **10**, or via reaction with traces of oxygen, producing **11**.[24] Compound **11** is formed despite flushing with argon prior to and during the irradiation. The ratio of **10** to **11** analyzed at set times during separate irradiations was never constant, which is likely the result of slight variations in the oxygen concentration. The sum of **10** and **11**, however, always was constant, which demonstrates their common precursor.

We propose that all rearranged products (**6**, **7**, **1*E*/*Z***, and **5*E*/*Z***) are vinyl cation derived. 1,2-Phenyl rearrangements across the C═C bond are a common feature of substituted vinyl cations.[4] Aryl shifts occur forming a more stable cation,[25] but also degenerate 1,2-aryl shifts have been observed.[26] Also 1,2-alkyl shifts across the C═C bond do occur in vinyl cations.[4,21,27] but they are expected to be slower than phenyl rearrangements.[28] On the other hand, in substituted vinyl radicals phenyl rearrangements have never been observed,[29] suggesting that the rearranged products of Scheme 3 do not originate from such processes. Supposedly the initially formed primary vinyl cation $\mathbf{2}^+$ rearranges to the more stable α-methyl-substituted vinyl cation $\mathbf{1}^+$ via a 1,2-phenyl shift (Scheme 4). This phenyl shift is apparently faster than the nucleophilic addition of the solvent. Intermediate $\mathbf{1}^+$ subsequently forms **6** and **7** by losing a proton from either the methyl group or the vinylic position, or alternatively **1*E*** and **1*Z*** by recombination with the bromide anion. The formation of **1*E*/*Z*** in the photochemistry of **2** shows the involvement of a tight ion pair [$\mathbf{1}^+$, $\mathrm{Br}^-$]: even after the phenyl shift the counterion is still present in the solvent cage, allowing internal return to be more effective than reaction with the external nucleophile, the solvent methanol.

Next to a phenyl shift, a methyl shift is also possible in $\mathbf{2}^+$, yielding the even more stable α-phenyl-substituted vinyl cation $\mathbf{9}^+$.[19] Evidence that predominantly the phenyl group migrates rather than the methyl group is found in the quantum yields of appearance of **6** and **7** upon irradiation of **1** and **2**. The **6/7** ratios are 0.5 and 1.0 in the irradiation of **2*E*** and **2*Z*** and 0.7 and 1.1 in that of **1*E*** and **1*Z***, respectively. If the methyl shift in $\mathbf{2}^+$ would play an important role a much lower **6/7** ratio is expected for **2** than for **1**, since upon the irradiation of **2** only **7** can be formed directly from the methyl-shifted vinyl cation $\mathbf{9}^+$. Indirectly, formation of **6** from $\mathbf{9}^+$ might take place after a 1,2-hydrogen shift yielding $\mathbf{1}^+$, but such a shift is energetically not feasible because $\mathbf{9}^+$ is more stable than $\mathbf{1}^+$ (Scheme 4).

The similar **6/7** ratios found for **1** and **2** also exclude the possibility that **7** is generated via loss of the α-proton from $\mathbf{2}^+$, followed by rearrangement of the resulting vinylidene carbene **12**. In conclusion, **6** and **7** are formed via the same intermediate ($\mathbf{1}^+$) generated in the photochemistry of both **1** and **2**.

Another potential pathway of vinyl cation $\mathbf{2}^+$ is a 1,3-hydrogen shift yielding the more stable allylic cation $\mathbf{13}^+$. The barrier for this process is calculated to be less substantial than that for the corresponding 1,2 H shift in $\mathbf{1}^+$ (11 instead of 18 kcal/mol)[22] but is apparently still too high for the reaction to compete with the 1,2-phenyl (and 1,2-methyl) shift. No nucleophilic recombination or solvent addition products of $\mathbf{13}^+$ are observed.

The primary vinyl cation $\mathbf{2}^+$ has also been prepared by photolytic cleavage of the C−I bond of *E*- and *Z*-2-phenyl-1-propenyl(phenyl)iodonium tetrafluoroborate.[30] In that case the leaving group is iodobenzene and a cation molecule pair [$\mathbf{2}^+$, PhI] is produced instead of the cation−anion pair [$\mathbf{2}^+$, $\mathrm{Br}^-$] for **2**. This neutral, nonbasic counterpart in the solvent cage allows addition of the solvent to compete with proton transfer. For example, upon irradiation of the iodonium analogue of **2** in trifluoroethanol, the main products are the vinyl ethers derived from the phenyl-shifted and methyl-shifted vinyl cations $\mathbf{1}^+$ and $\mathbf{9}^+$.

In principle, the rearranged reductive dehalogenation products **5*E*** and **5*Z*** can be formed via a phenyl shift in $\mathbf{2}^\bullet$, yielding $\mathbf{1}^\bullet$. However, 1,2-rearrangements across the C═C bond do not occur in vinyl radicals.[29] Therefore **5*E*** and **5*Z*** must be formed via cationic intermediates. The formation of these products provides strong evidence for

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[24] (a) The product of addition of oxygen to a vinyl radical has been observed with time-resolved spectroscopy. (b) Verbeek, J. M.; Stapper, M.; Krijnen, E. S.; Van Loon, J.-D.; Lodder, G.; Steenken, S. *J. Phys. Chem.* **1994**, *98*, 9526−9536.

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[26] Kitamura, T.; Kobayashi, S.; Taniguchi, H.; Fiakpu, C. Y.; Lee, C. C.; Rappoport, Z. *J. Org. Chem.* **1984**, *49*, 3167−3170.

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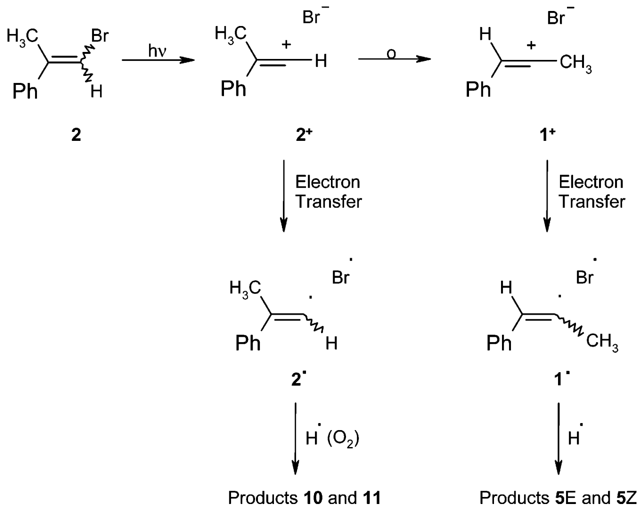
**SCHEME 5. Mechanism of Formation of Radical-derived Products from 2**



**SCHEME 6**

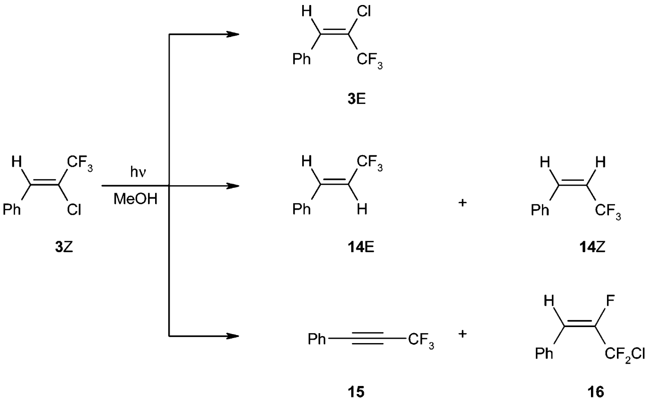


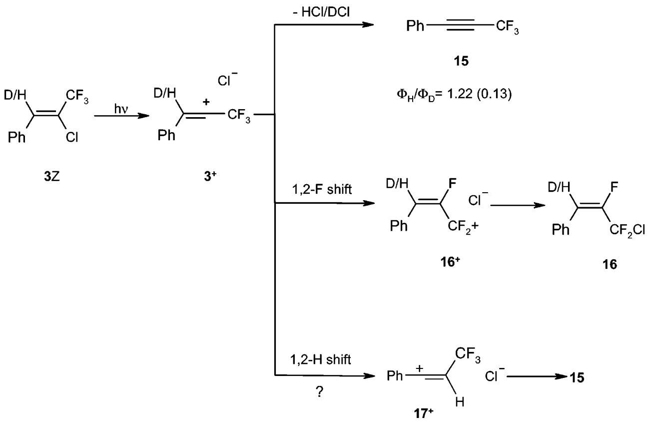
**TABLE 3. Quantum Yields ($\times 10^{-2}$) of Formation of Products 3*E*, 14*E*, 14*Z*, 15, and 16 upon Irradiation ($\lambda_{exc}$ = 254 nm) of 3*Z* in Methanol**

| | $\Phi_{3E}$ | $\Phi_{14E}$ | $\Phi_{14Z}$ | $\Phi_{15}$ | $\Phi_{16}$ |
|---|---|---|---|---|---|
| 3*Z* | 25 | 1.8 | 1.3 | 0.22 | 0.2 |

the mechanism displayed in Scheme 5. Electron transfer within ion pair $\mathbf{1}^+$ yields a radical pair $\mathbf{1}^\bullet$, from which subsequently **5*E*** and **5*Z*** are formed. Such a mechanism where initially an ion pair is photoproduced from which either electron transfer or product formation can take place has already been proposed for (*E*)-*β*-bromostyrene.[14] If electron transfer to the α-methyl-substituted $\mathbf{1}^+$ from the counterion is feasible, this is also the case for the less stable α-H-substituted $\mathbf{2}^+$. Electron transfer to $\mathbf{2}^+$ leads to $\mathbf{2}^\bullet$, which yields **10** and **11**.

**Photochemistry of 3.** Upon irradiation of **3*Z*** (85:15 *Z*/*E*, see experimental details) in methanol five products are formed (Scheme 6 and Table 3): **3*E***, the stereoisomer of the starting material, the radical-derived products **14*E*** and **14*Z***, the elimination product **15**, and the constitutional isomer of the starting material **16**. As in the case of the α-methyl-substituted vinyl radicals $\mathbf{1}^\bullet$, α-$CF_3$ vinyl radicals $\mathbf{3}^\bullet$ are presumably bent, and have a low barrier of interconversion. As discussed above, this leads to a mixture of stereoisomeric hydrogen-abstraction products, with **14*E*** dominating.

**SCHEME 7. Mechanism of Formation of Ion-Derived Products from 3**



Acetylene **15** is the analogue of **7** and is presumably formed via *β*-proton loss from the α-$CF_3$-vinyl cation $\mathbf{3}^+$ (Scheme 7). To demonstrate that **15** is indeed generated via an α-$CF_3$-substituted vinyl cation and not for instance via concerted HCl loss, the isotope effect on its formation was measured with 2-chloro-3,3,3-trifluoro-1-phenyl-1-deuteriopropene as substrate (Scheme 7).[31] The value of 1.22 found is typical for *β*-secondary isotope effects in reactions proceeding through carbocations[32] and shows clearly that **15** is produced via a stepwise and not via a concerted process, and proceeds via an intermediate, of which the *β*-C−H bond is still intact and the C−Cl bond is broken to a significant extent, i.e. $\mathbf{3}^+$. The magnitude of the isotope effect resembles the value of 1.25 observed for the thermal generation at 75 °C of a vinyl cation in the solvolysis of (Z)-2-buten-2-yl-3-deuterio triflate.[33]

The formation of **16** supports the notion of the intermediacy of $\mathbf{3}^+$ in the irradiation of **3*Z***. Product **16** is thought to be formed via a novel 1,2-fluorine shift in the primarily formed cation $\mathbf{3}^+$, generating the more stable allylic cation $\mathbf{16}^+$, followed by recombination with the counter chloride ion (Scheme 7). Fluorine shifts are well-documented for alkyl carbocations in the gas phase,[34] but virtually without precedent for carbocations in solution.[35] Unlike the corresponding 1,2-hydride shift toward the C=C bond in cation $\mathbf{1}^+$ (vide supra) the analogous 1,2-fluorine shift in the α-$CF_3$-substituted vinyl cation $H_2C{=}C^+{-}CF_3$ to the more stable allylic cation $H_2C{=}CF{-}CF_2^+$ has been calculated to have a low activation barrier (6 kcal/mol) in vacuo.[22] In a dielectric medium mimicking methanol the barrier of activation is MP4 calculated to be 11.9 kcal/mol (vide infra). No indication for the formation of the product generated by nucleophilic attack of the solvent methanol at the rearranged cation $\mathbf{16}^+$ is found. Internal return within the ion pair [$\mathbf{16}^+$, $Cl^-$] is apparently faster than reaction with the external nucleophile methanol.

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(31) The rather large error in the kinetic isotope effect is mainly due to the detection method, flame ionization, used. The deviation also appeared to be concentration dependent.

(32) Melander, L.; Saunders: W. H. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1980; Chapter 6.

(33) Stang, P. J.; Hargrove, R. J.; Dueber, T. E. *J. Chem. Soc., Perkin Trans. 2* **1974**, 843−847.

(34) Shaler, T. A.; Morton, T. H. *J. Am. Chem. Soc.* **1994**, *116*, 9222−9226 and references therein.

(35) Ferraris, D.; Cox, C.; Anand, R.; Lectka, T. *J. Am. Chem. Soc.* **1997**, *119*, 4319−4320 and references therein.

**SCHEME 8**

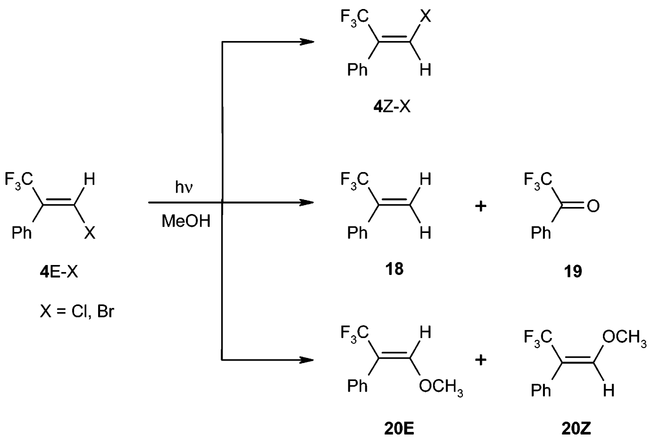


**TABLE 4. Quantum Yields ($\times 10^{-2}$) of Formation of Products 4*Z*, 18 + 19, and 20*E* and 20*Z* upon Irradiation ($\lambda_{exc}$ = 248 nm) of 4*E*-X in Methanol**

| | $\Phi_{4Z}$ | $\Phi_{18+19}$ | $\Phi_{20E}$ | $\Phi_{20Z}$ |
|---|---|---|---|---|
| 4*E*-Br | 25.4 | 25.4 | 4.7 | 2.2 |
| 4*E*-Cl | 20.5 | 4.5 | 1.1 | 1.8 |

A 1,2-H shift across the C=C bond in **3**$^+$, yielding **17**$^+$, either cannot compete with proton loss within the tight ion pair [**3**$^+$, Cl$^-$] or if it can and **17**$^+$ is formed, that species only loses its $\beta$-proton, yielding **15**. Computationally **3**$^+$ indeed rearranges to **17**$^+$.

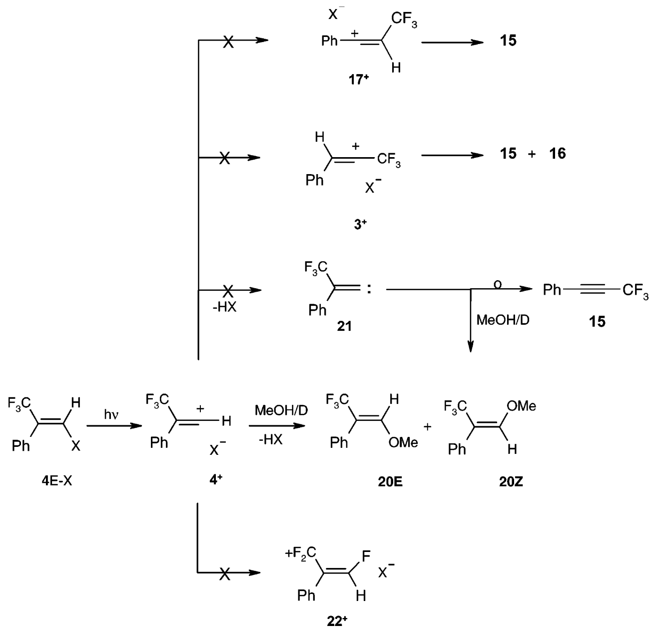
**Photochemistry of 4.** The nature of the halogen leaving groups used in the study of the $\beta$-CF$_3$-substituted compounds **4*E*-Br** and **4*E*-Cl** has no effect on the type of photoproducts but a distinct effect on the product distribution (Scheme 8 and Table 4). Next to the *E*/*Z*-isomerization products **4*Z*-X** and the radical-derived products **18** and **19**, now two vinyl ethers (**20*E*** and **20*Z***) are produced. No elimination products are formed.

Presumably, the substitution products **20*E*** and **20*Z*** are formed via reaction of the initially formed vinyl cation **4**$^+$ with the solvent methanol (Scheme 9). The possibility that the vinyl ethers are alternatively formed via insertion of carbene **21**, formed by α-proton loss from **4**$^+$, in the OH bond of methanol is excluded on the basis of the lack of deuterium incorporation in **20** upon irradiation of **4*E*-Cl** in methanol-OD. The absence of **15** in the reaction mixture also indicates that **21** is not formed. If no carbene intermediate is formed from **4**$^+$, certainly no carbene is generated from **2**$^+$, which bears a less acidic α-proton than **4**$^+$.

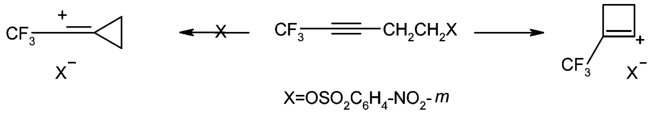
In contrast to compound **2**, for which rearrangement followed by elimination is faster than nucleophilic capture by the solvent, here nucleophilic substitution products are the only cation-derived products. This means that **4**$^+$ undergoes neither a 1,2-phenyl shift to **3**$^+$, which would yield **15** and **16**, nor a 1,2-CF$_3$ shift to **17**$^+$, which would yield **15**. The conversion of **4**$^+$ into **3**$^+$ is energetically not feasible, because according to MO calculations (vide infra) an α-CF$_3$ group is considerably more destabilizing than an $\beta$-CF$_3$ group *in solution*. The 1,2-CF$_3$ shift needed to convert **4**$^+$ into **17**$^+$ would be unprecedented.

The $\beta$-CF$_3$-substituted vinyl cation **4**$^+$ not converting to the α-CF$_3$-substituted **3**$^+$ is reminiscent of results for

**SCHEME 9. Mechanism of Formation of the Ion-Derived Products from 4**



**SCHEME 10**



CF$_3$C≡CCH$_2$CH$_2$X (Scheme 10). The rearrangement of this homopropargyl sulfonate in trifluoracetic acid only yields products derived from the $\beta$-CF$_3$ vinyl cation and none from the α-CF$_3$ species.[36] Also, α-CF$_3$-substituted alkyl cations have been found to be less stable than their $\beta$-CF$_3$-substituted analogues.[3a,b]

Unlike in the case of **3**, for **4** no photoproducts which are constitutional isomers of the starting materials are observed. These products could be formed via a 1,3-F shift in **4**$^+$ producing the allylic cation **22**$^+$, followed by recombination with the counterion. Such a 1,3-fluorine shift in $CF_3CH{=}C^+{-}H$ yielding $^+CF_2CH{=}CHF$ has been predicted to have a (very) low activation barrier (ranging from 10.8 to 0.3 kcal/mol, depending on the level of theory) in vacuo.[22] In methanol the barrier is PM4 calculated (vide infra) to be 6.1 kcal/mol. Apparently the 1,3-F shift in **4**$^+$ cannot compete with addition of methanol.

**Open vs bridged cations.** The above discussion shows that compounds **1**−**4** produce vinyl cations upon photolysis. However, the precise structures of the photogenerated vinyl cations, open or bridged, have not yet been clarified. In the thermal solvolysis of phenyl-substituted vinyl derivatives indications for bridged cations, phenonium ions, and open vinyl cations as intermediates have been found, as well as indications for bridged ions as transition states.[4,37]

Compound **2** gives 1,2-phenyl rearrangement products, which demonstrates the involvement of the vinylidene

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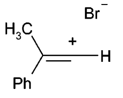
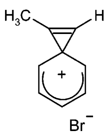
(36) Hanack, M.; Bocher, S.; Herterich, I.; Hummel, K.; Voett, V. *Liebigs Ann. Chem.* **1970**, *733*, 5−26.

(37) Yamataka, H.; Biali, S. E.; Rappoport, Z. *J. Org. Chem.* **1998**, *63*, 9105−9108.

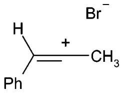
benzenium ion $23^+$, either as a transition state in the rearrangement from $2^+$ to $1^+$ or as an energy miminum. As already discussed, in the irradiation of **1** and **2** the same intermediate is present, forming **6** and **7**. So either the initially formed vinyl cations $1^+$ and $2^+$ both rearrange to $23^+$ or $2^+$ rearranges to $1^+$ from which **6** and **7** are formed. Whether **6** and **7** are formed via $1^+$ or from $23^+$ is unclear. Cation $23^+$ has been generated thermally from $\beta$-alkyl-$\beta$-phenyl vinyl precursors,[30,38] and in those cases proton abstraction from $23^+$ was not considered to occur. However, here we deal with the first example where next to $1^+$, or $23^+$, a relatively strong base ($Br^-$) is present in an ion pair.



$2^+$



$23^+$

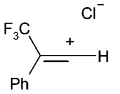


$1^+$

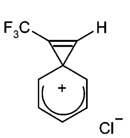
The formation of **1***E* and **1***Z* in comparable yields in the photochemistry of **2** shows that at least these products are produced via the open vinyl cation $1^+$, since reaction via $23^+$ would yield only the *E*-isomer as is observed in the thermal chemistry of $\beta$-phenyl vinyl-(phenyl)iodonium salts.[30,38,39] The formation of products **1***E* and **1***Z* via $1^+$ makes it likely that **6** and **7** are also produced from the *open* linear cation $1^+$.

For compound **3**, the situation is less clear. No rearrangement and nucleophilic substitution products typical for phenonium ions are observed, but in principle, the elimination product **15** can be formed by proton abstraction from $24^+$ rather than from $3^+$. However, the *open* vinyl cation $3^+$ must be formed initially, on the basis of the measured isotope effect, which rules out phenyl group participation. An isotope effect much closer to 1.0 would be expected, in case the phenyl ring would help to break the C−Cl bond, due to the charge delocalization onto the phenyl ring.

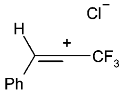
The results for **4** give an unambiguous answer: the formation of two stereoisomeric vinyl ethers (the products formed by nucleophilic attack of methanol on the vinyl cation) demonstrates that the product-forming intermediate is the *open* vinyl cation $4^+$. Were the intermediate bridged, i.e. $24^+$, only one isomer (the *Z*-isomer, with the phenyl group and the methoxy substituent trans to each other, i.e. **20***Z* (cf. Scheme 8)) would be formed.



$4^+$



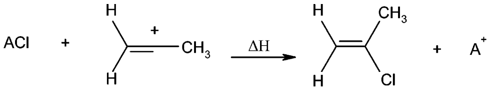
$24^+$



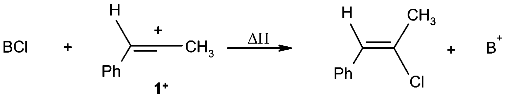
$3^+$

In conclusion, all cation-derived products are produced from the *open* vinyl cations. For **4** this is absolutely clear, and for **3** the best circumstantial evidence is the isotope effect, for **2** and **1** the type of products formed. The photochemistry of **1**−**4** yielding open vinyl cations is in agreement with the results of previous studies of $\beta$-phenyl-substituted vinyl halides and $\beta$-phenyl-substituted vinyl iodonium salts.[14,30] For these compounds it was shown that the photoheterolytic cleavage of the vinylic C−X bond occurs unassisted via an $S_N1$ mechanism, with no participation of the $\beta$-phenyl group.

**Quantum Chemical Calculations. (a) Stabilities of the Cations.** The effects of α- and $\beta$-methyl versus α- and $\beta$-trifluoromethyl substituents on the stability of vinyl cations were assessed by using the chloride transfer isodesmic reaction eq 1. The MP4 calculated stabilities ($\Delta H$) of the parent vinyl cations $A^+$ in vacuo and in methanol are presented in Table 5. In addition, the differences in heats of formation ($\Delta H$) of the α- and $\beta$-$CH_3$, and of the α- and $\beta$-$CF_3$ ions, are given. Furthermore, for the relevant cases the relative stabilities of the various $\beta$-phenyl-substituted vinyl cations $B^+$ in this study were B3LYP computed with eq 2.



(1)



(2)

As expected the $CF_3$-substituted parent vinyl cations are considerably less stable than the $CH_3$-substituted ones. For the $CF_3$ substituents, the difference in stability of the cations with the group at the α- or $\beta$-position in vacuo is quite small ($\Delta H = 0.1$ kcal/mol), as observed previously.[22] This is, however, not the case in the dielectric medium mimicking methanol, in which the α-$CF_3$ species is calculated to be 5.0 kcal/mol less stable than the $\beta$-$CF_3$ species. This is likely due to the smaller steric bulk near the formally positively charged carbon atom in the $\beta$-$CF_3$ species, which allows stronger interaction with this carbon atom. In addition, the α-$CF_3$ moiety in the α-$CF_3$ species carries a significantly smaller NPA charge than the highly approachable α-H atom in the $\beta$-$CF_3$ species. This will also make the overall solvation enthalpy more negative for the α-$CF_3$ species. Thus, rearrangement of the $\beta$-$CF_3$ cation $4^+$ to the α-$CF_3$ cation $3^+$ (Scheme 9) is energetically not feasible in solution. For the α- and $\beta$-methyl-substituted ions the difference in stability is much larger, but also solvent dependent. In methanol the $\beta$-$CH_3$ species is calculated to be 13.1 kcal/mol less stable than the α-$CH_3$ species, which provides the driving force for the experimentally observed rearrangement of $2^+$ into $1^+$ (Scheme 4).

Similar results regarding the relative substituent effects of α/$\beta$-$CH_3$ and α/$\beta$-$CF_3$ as for the parent vinyl cations $A^+$ are obtained for the $\beta$-phenyl-substituted vinyl cations $B^+$ ($1^+$−$4^+$), as long as symmetry restrictions ($C_s$) are applied to prevent spontaneous 1,2-shift rearrangements (data not shown). If these symmetry restrictions are lifted, full optimization at the B3LYP/6-311+G(d,p) level of calculations shows that the cations $2^+$, $3^+$, and $4^+$ are not minima on the potential energy surface. Cation $1^+$ is a minimum and so are the bridged ions $23^+$ and $24^+$. In the calculations cation $2^+$ rearranges to the bridged vinyl cation $23^+$ via a partial 1,2-phenyl shift. In vacuo cation $23^+$ is calculated to be 3.0 kcal/mol more

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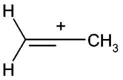
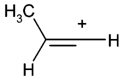
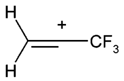
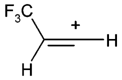
[38] Hinkle, R. J.; Thomas, D. B. *J. Org. Chem.* **1997**, *62*, 7534−7535.

[39] Okuyama, T.; Ochiai, M. *J. Am. Chem. Soc.* **1997**, *119*, 4785−4786.

**TABLE 5. Vinyl Cations, Their Relative Stabilities (Δ*H*) Calculated by Using Eqs 1 and 2, and the Relative Stabilities within a Substituent Series (Δ*H*, Data in Italics), in Vacuo, and in Methanol**

| $A^{+\,a}$ = |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| in vacuo: | 0.0 kcal/mol | *19.1* | 16.9[b,c]<br>16.9[d] | 42.1 | *0.1* | 43.2<br>40.2[d] |
| in MeOH: | 0.0 kcal/mol | *13.1* | 11.7<br>11.6[d] | 35.6 | *5.0* | 33.2<br>30.7[d] |
| $B^{+\,e}$ = | **1**$^+$ | **23**$^+$ | **2**$^{+b}$ | **3**$^{+b}$ | **24**$^+$ | **4**$^{+b}$ |
| in vacuo: | 0.0 kcal/mol | -3.0[f]<br>-3.4[g] |  |  | 16.3<br>12.0[g] |  |
| in MeOH: | 0.0 kcal/mol | 0.4<br>0.1[g] |  |  | 15.0<br>10.8[g] |  |

[a] Values obtained with MP4(SDQ)/6-311+G(d,p) single-point energies (corrected for zero-point energies) at MP2/6-311G(d,p) optimized geometries. [b] No minimum at the level of calculation. [c] Computed with the $H_3C-C{=}C$ angle constrained at 120°. [d] Value in the case of *Z*-alkene precursor. [e] Values obtained with B3LYP/6-311+G(d,p) energies corrected for zero-point energies. [f] Negative values indicate a stabilization compared to the reference compound. [g] Value in the case of *E*-alkene precursor.

stable than **1**$^+$ but in methanol the two ions are of comparable stability (0.4 kcal/mol). Thus, the experimentally observed conversion of **2**$^+$ to **1**$^+$ (Scheme 4) via **23**$^+$ as intermediate is quite feasible.

Cation **3**$^+$ rearranges via a 1,2-hydrogen shift to the α-phenyl-substituted vinyl cation **17**$^+$. This computational result is compatible with the experimental data because product **15** may be formed by loss of the *β*-proton directly from **3**$^+$ or indirectly from **17**$^+$ (see Scheme 7). Cation **4**$^+$ rearranges via a partial 1,2-phenyl shift to the bridged ion **24**$^+$, a result that does not correlate with the experimental data. The formation of both an *E*- and a *Z*-substituted vinyl ether **20** as photosubstitution product of **4** suggests the open cation **4**$^+$ and not the bridged cation **24**$^+$ as product-forming intermediate (Scheme 9). The calculations, however, regard stabilities of free ions in the gas phase and methanol while experimentally tight ion pairs are involved rather than free ions. The counterion in the ion pairs is expected to have a large effect on the relative stabilities of the vinyl cations. It will stabilize the open, more localized vinyl cations more than the bridged ones, and possibly even change the order of stability, making the open ions more stable than the vinylidene benzenium ions. Inclusion of counterions in calculations on carbocations is known to lead to different geometries and stabilities.[40]

**(b) Fluorine Shifts.** Next to the geometries and energies of the parent vinyl cations of **3**$^+$ and **4**$^+$ also the geometries and energies of the transition structures for their 1,2- and 1,3-fluorine shift, respectively, were MP4 calculated, both in vacuo and in methanol (Scheme 11).

Transition state (1,2-F shift) **3**$^+$ is rather early in terms of the lengths of the C−F bond broken and formed (1.473 and 1.745 Å). The largest change compared to the starting material is in the C−C−F bond angle of the migrating F atom. Transition state (1,3-F shift) **4**$^+$ is very early, the C−F bonds broken and formed are 1.461 and 1.998 Å. Comparison of these bond lengths with the corresponding distances in the starting material shows that the transition state depends largely on a decrease of the $C-C{=}C$ bond angle, rather than on C−F bond lengthening.

The activation barrier for the 1,2-fluorine shift is MP4 calculated to be 9.1 kcal/mol in the gas phase and 11.9 kcal/mol in methanol. For the 1,3-fluorine shift the barrier is 4.7 kcal/mol in vacuo and 6.1 kcal/mol in methanol. The barriers in solution are expected to be higher, as the charge is less localized in a polar solvent than in vacuo.

The values of the calculated activation barriers indicate that both the 1,2-fluorine shift discussed for **3**$^+$, yielding **16**$^+$ (Scheme 7), and the 1,3-fluorine shift discussed for **4**$^+$, yielding **22**$^+$ (Scheme 9), are kinetically feasible. A photoproduct resulting from the 1,2-F shift is indeed formed (i.e. **16**), a product resulting from the 1,3-F shift is not.

**Efficiencies of Photoproduct Formation.** For two (limited) series of vinyl halides the efficiency of photoformation of vinyl cation-derived products has been found to increase with the electron-donating ability of the α-substituent and thus with the stability of the photogenerated vinyl cations.[18b,24b] Analysis of the quantum yields of formation of the cation-derived products from **1**−**4** (Table 6) also shows an evident effect of the stability of the α-substituted vinyl cations **1**$^+$ and **3**$^+$: the most stabilized (α-$CH_3$ substituted) vinyl cation **1**$^+$ is formed with the highest efficiency, and the α-$CF_3$-substituted vinyl cation **3**$^+$ is hardly formed at all. The dependence of the efficiencies of formation of the vinyl cations on the nature of the α-substituents is less prominent than that in thermal reactions. For example, replacement of the α-$CH_3$ group with an α-$CF_3$ group in benzylic- and allylic-type cations decreases their rate of formation in $S_N1$ solvolysis reactions by a factor of $10^6$ to $10^9$.[41] In the photochemical reaction the transition states in the bond heterolysis reaction are quite early (see also ref 24b). The *β*-$CF_3$-substituted vinyl cation **4**$^+$ is generated with a

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[40] Fărcaşiu, D.; Norton, S. H.; Hâncu, D. *J. Am. Chem. Soc.* **2000**, *122*, 668−676 and references therein.

[41] (a) McClelland, R. A.; Cozens, F. L.; Steenken, S.; Amyes T. L.; Richard, J. P. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1717−1722 and references therein. (b) Poulter, C. D.; Wiggins, P. L.; Le, A. T. *J. Am. Chem. Soc.* **1981**, *103*, 3926−3927 and references therein.

**SCHEME 11**

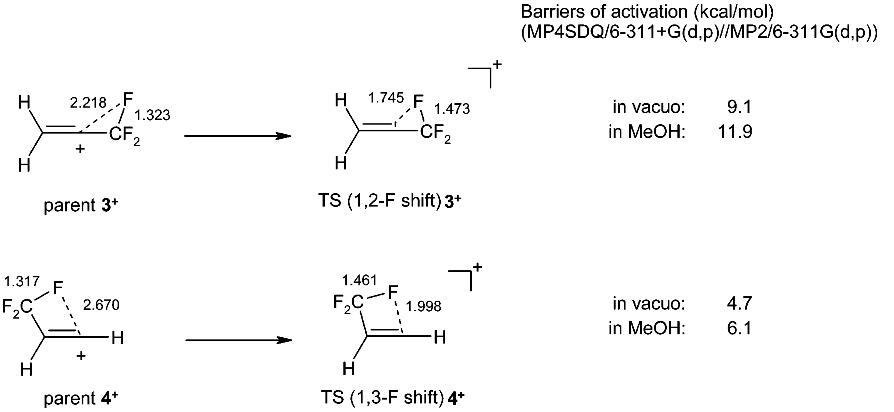
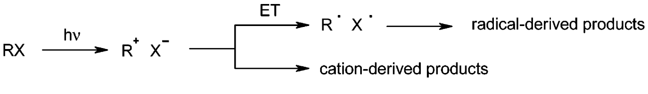


**TABLE 6. Quantum Yields of Cation-Derived Products and Ratios of Cation- to Radical-Derived Products in the Photolysis of 1−4**

| | $\Phi_{ion}$ | | $R^+/R^\bullet$ | |
|---|---|---|---|---|
| | *E* | *Z* | *E* | *Z* |
| **1** | 0.4 | 0.3 | 3.0 | 2.2 |
| **2** | 0.03 | 0.04 | 0.18 | 0.36 |
| **3** | | 0.004 | | 0.14 |
| **4**-Cl | | 0.03 | | 0.64 |
| **4**-Br | | 0.07 | | 0.27 |

higher quantum yield than its α-$CF_3$ isomer $\mathbf{3}^+$, in agreement with $\mathbf{4}^+$ being more stable than $\mathbf{3}^+$ according to the results of the MO calculations for the solution phase. Likewise, the $\beta$-Me-substituted vinyl cation $\mathbf{2}^+$ is generated with lower quantum efficiency than its α-Me-isomer $\mathbf{1}^+$, in agreement with their relative stabilities. The $\beta$-Me- and $\beta$-$CF_3$-substituted vinyl cations $\mathbf{2}^+$ and $\mathbf{4}^+$, however, are produced with similar efficiencies. This is remarkable since on the basis of their relative stability a less efficient formation of the $\beta$-$CF_3$-substituted vinyl cation $\mathbf{4}^+$ is expected. Of course, in the interpretation of quantum yields, next to the pathway to the vinyl cation also other deactivation pathways of the electronically excited vinyl halides have to be considered and the rates of these pathways may well be significantly affected by the substituents.

A more useful probe than quantum yields is the ratio of cation-derived to radical-derived products ($R^+/R^\bullet$ ratios) found in the photochemistry of compounds **1**−**4** (Table 6). Their analysis gives a further understanding of the processes involved in the formation of products and allows assessment of the stabilities of the vinyl cations. With the assumption that the mechanism, as shown below, proposed for **2** (Scheme 5), holds also for **1**, **3**, and **4**, the cation/radical-derived product ratios should reflect the relative stabilities of the ion pairs and radical pairs involved.



The initially produced vinyl cation−halide anion ion pair can react via two different pathways: (a) via electron transfer yielding a radical pair and subsequent abstraction of a hydrogen atom from the solvent by the vinyl radical and (b) via either loss of a proton or nucleophilic addition, yielding a (possibly rearranged) cation-derived product. The cation/radical product ratio thus depends on the relative rates of the competing reactions. In the following sections first the effect of the *E*- vs *Z*-stereochemistry on the ratios will be discussed, followed by the effect of Cl vs Br and finally the influence of the position and the nature of the $CH_3$ and $CF_3$ substituents.

**(a) *E*- vs *Z*-Isomer.** The $R^+/R^\bullet$ ratios for **1*E*** and **1*Z*** are distinctly different, which indicates that the rate of the electron-transfer step, or the rate of the proton loss, is different for the two stereoisomers. The quantum yield of formation of **7** is higher for **1*E*** than for **1*Z***, which is rationalized by assuming that in the case of **1*E*** the counterion is located in the vicinity of the $\beta$-proton in the ion pair in the solvent cage and in the case of **1*Z*** more on the other side of the molecule. The quantum yields of formation of the radical-derived products **5*E*** and **5*Z*** are almost invariant with the stereochemistry (0.13 and 0.14 for **1*E*** and **1*Z***, respectively, Table 1). The quantum yield of formation of **6** is also the same for both isomers. The higher cation/radical ratio for **1*E*** thus can be ascribed to the faster $\beta$-proton abstraction by the bromide ion in the ion pair from **1*E*** compared to that in the ion pair from **1*Z*** (thus yielding more cation-derived product), while the rate of electron transfer is not affected.

For **2*E*** and **2*Z*** a smaller $R^+/R^\bullet$ ratio is observed for the *E*-isomer. The yield of radical derived-product from **2*E*** is higher than that for **2*Z*** (0.19 vs 0.12), and the yield of cation-derived products is lower (0.03 vs 0.04). Assuming that a tight ion pair is formed, for the shift of the phenyl group to occur the bromide ion has to move further away in **2*Z***, where the Br substituent is located on the same side as the phenyl group, than in **2*E***, where the Br substituent is positioned trans to the phenyl group. Due to this larger distance the rate of electron transfer will be decreased, which leads to less radical- and more cation-derived product, and thus to a higher ratio for **2*Z*** than for **2*E***.

**(b) Cl vs Br as Leaving Group.** For **4*E***-Br the $R^+/R^\bullet$ ratio is lower than that for **4*E***-Cl. Such a leaving group effect has been observed previously in the photosolvolysis of α-H- and α-$CH_3$-substituted precursors of vinyl cations,[42] and is in line with the proposed mechanism. The

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[42] (a) Kitamura, T.; Kobayashi, S.; Taniguchi, H. *J. Org. Chem.* **1982**, *47*, 2323−2328. (b) Sket, B.; Zupan, M. *J. Chem. Soc., Perkin Trans. 1* **1979**, 752−756. (c) Kitamura, T.; Kobayashi, S.; Taniguchi, H. *J. Am. Chem. Soc.* **1986**, *108*, 2641−2645.

electron affinity of Cl is higher than that of Br (EA(Cl) = 83.2 kcal/mol, EA(Br) = 77.4 kcal/mol).[43] This makes the electron transfer in the ion pair $4^+$-$Cl^-$ more endothermic than in the ion pair $4^+$-$Br^-$, which increases the cation/radical-derived ratio for **4*E***-Cl relative to **4*E***-Br. The rate of nucleophilic addition of the solvent is not much affected by the nature of the counterion.

**(c) Position of Substituent. (i) 1 vs 2:** The $R^+/R^•$ ratios are much larger for **1** than for **2**. This large effect of the position of the methyl group is caused by the higher rate of electron transfer in $\mathbf{2}^+$-$Br^-$ than in $\mathbf{1}^+$-$Br^-$, since the $\beta$-$CH_3$-substituted cation $\mathbf{2}^+$ is less stable than the $\alpha$-$CH_3$ vinyl cation $\mathbf{1}^+$. This is also the case for $\mathbf{2}^•$ and $\mathbf{1}^•$ but that difference is expected to be smaller (Scheme 5). Also the different rates of formation of the cation-derived products influence the $R^+/R^•$ ratio. For formation of **6** and **7** from $\mathbf{2}^+$ initially a phenyl shift must take place, which is slow compared to the loss of a proton to form **6** and **7** from $\mathbf{1}^+$.

**(ii) 3 vs 4:** The position of the $CF_3$ group also leads to a large difference in the $R^+/R^•$ ratios (**3*Z*** and **4*E***-Cl, 0.14 and 0.64, respectively). In this case, however, the α-substituted compound yields less cation-derived product than the $\beta$-isomer. Since in vinyl cation–halide anion ion pairs proton abstraction is faster than nucleophilic addition (compounds **1**, **2**, and **3** do not give nucleophilic substitution products), the lower ratio for **3*Z*** has to be ascribed to a faster electron-transfer rate in $\mathbf{3}^+$-$Cl^-$ than in $\mathbf{4}^+$-$Cl^-$. This higher rate points to a larger instability of the $\alpha$-$CF_3$-substituted vinyl cation $\mathbf{3}^+$ than the $\beta$-$CF_3$-substituted $\mathbf{4}^+$ (assuming the differences in stability in radicals $\mathbf{3}^•$ and $\mathbf{4}^•$ are smaller). Indeed, $\mathbf{4}^+$ is predicted to be less destabilized than $\mathbf{3}^+$ by our quantum chemical MP4SDQ/6-311+G(d,p) calculations in solution (vide supra).

**(d) Nature of Substituent. (i) 1 vs 3:** The large destabilizing effect of an $\alpha$-$CF_3$ compared to an $\alpha$-$CH_3$ group leads to a larger driving force of the electron transfer in the former and this is reflected in the much lower $R^+/R^•$ ratio observed for **3*Z*** than for **1**, even more so if one takes the different leaving groups into account (Cl as a leaving group gives more cation-derived product than Br as a leaving group: 0.64 vs 0.36 for **4*E***-Cl and **4*E***-Br, respectively).

**(ii) 2 vs 4:** The effect of the $\beta$-$CH_3$ vs the $\beta$-$CF_3$ group is best studied by comparing the results for **2*Z*** and **4*E***-Br, both compounds with the Br substituent positioned cis to the phenyl ring. The lower ratio for **4*E***-Br (0.27 vs 0.36 for **2*Z***) is the result of a combination of the slower reaction of nucleophilic addition of the solvent compared to phenyl migration and faster electron transfer in $\mathbf{4}^+$-$Br^-$ than in $\mathbf{2}^+$-$Br^-$, due to the destabilizing effect of the $\beta$-$CF_3$ substituent compared to $\beta$-$CH_3$.

In conclusion, the $R^+/R^•$ ratios observed are in line with the proposed reaction mechanism. The various effects can be explained in terms of the relative stabilities of the vinyl cations involved and the positions of the counterion within the ion pairs.

## Concluding Remarks

The irradiation of compounds **1**–**4** in methanol produces the same types of products in all cases: *E*/*Z*-isomerization-, radical-, and cation-derived products. In the case of **1** and **3** the cation-derived products are formed via $\beta$-proton loss from the primarily generated $\alpha$-$CH_3$- and $\alpha$-$CF_3$-substituted vinyl cation, in the case of **2** from a vinyl cation formed by phenyl migration. The proton loss gives an acetylene product (for **1**, **2**, and **3**) and a substituted allene product (for **1** and **2**). For compound **3** in competition with proton loss an 1,2-F shift occurs, followed by recombination of the allylic cation with the halide ion present in the solvent cage. The corresponding 1,2-H shift for **1** does not occur. Compound **4** yields nucleophilic substitution products from the $\beta$-$CF_3$ vinyl cation, and no migration of the phenyl ring producing the $\alpha$-$CF_3$ vinyl cation takes place. For compounds **2** and **4** no indications for the occurrence of a 1,3-H shift or 1,3-F shift, respectively, have been found. The radical-derived products are all formed via abstraction of a hydrogen atom from the solvent, or by reaction with $O_2$, by the vinyl radical.

All cation-derived products are produced via an open vinyl cation, and not via a bridged phenonium ion. The strongest indications are the formation of both the *E*- and *Z*-isomer of the nucleophilic substitution product **1*E*** and **1*Z*** from **2**, and **20*E*** and **20*Z*** from **4**. Involvement of vinylidene carbene intermediates, formed via α-proton loss from vinyl cations $\mathbf{2}^+$ and $\mathbf{4}^+$, is excluded on the basis of the lack of deuterium incorporation upon irradiation in MeOD and of the lack of formation of an acetylene in the irradiation of **4**.

The formation of rearranged radical-derived products, the $\beta$-secondary isotope effect on the quantum yield of formation of **15**, and the leaving group effect are all in line with the proposed mechanism: upon photolysis initially a vinyl cation is formed, which either gives cation-derived products or accepts an electron from the halide anion in the ion pair. This yields a radical pair that abstracts a hydrogen atom from the solvent.

The ratios of cation- to radical-derived product reflect the rates of the partitioning steps in the ion pairs leading to the photoproducts. The rate of the electron-transfer step leading to the radical-derived products decreases with increasing stability of the vinyl cations involved. The amount of cation-derived products formed depends on the rates of the subsequent proton loss, phenyl rearrangement, or nucleophilic substitution in competition with electron transfer.

Of the vinyl cations photogenerated in this study the $\alpha$-$CF_3$-substituted one is the least stable: it is also the most destabilized vinyl cation generated thus far. The experimentally derived order of stabilization of the photogenerated vinyl cations is $\alpha$-$CF_3$ < $\beta$-$CF_3$ < $\beta$-$CH_3$ < $\alpha$-$CH_3$. The quantum chemical calculations performed on these vinyl cations give the same order of stabilization, provided the effect of solvent is taken into account.

## Experimental Details

**Irradiation Procedure.** The UV purity of the methanol used in the irradiations was always checked before use. The irradiations at $\lambda_{exc} = 254$ nm were carried out in a cylindrical Pyrex vessel with a content of 160 mL, in which a quartz tube was immersed containing a Hanau TNN-15/32 low-pressure mercury arc and demineralized water. The whole setup was cooled in an ice bath. The irradiations at $\lambda_{exc} = 248$ nm were carried out in a 1-cm quartz cuvette that was positioned in front of a monochromator and a xenon arc. In both setups the

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[43] *CRC Handbook of Chemistry and Physics*, 62nd ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1981; Table E-64.

oxygen was removed by bubbling through Argon during the irradiations and prior to them for either 20 ($\lambda_{exc} = 254$ nm) or 5 min ($\lambda_{exc} = 248$ nm).

The formation of the photoproducts was studied as a function of time. This was done by removing aliquots (0.5 mL for irradiations at $\lambda = 254$ nm and 50 $\mu$L for irradiations at $\lambda = 248$ nm) at regular time intervals. The samples were analyzed at least in duplicate on a gas chromatograph equipped with a flame ionization detector and monitored by using a internal standard (decane or dodecane). Due to the low conversion during the irradiations the disappearance of starting material could not be reliably measured. All irradiations were performed in triplicate. The quantum yields were calculated from the kinetic data obtained in the irradiations by using least-squares treatment and the intensity of light at the wavelength used. The intensity of the light employed was determined by using a chemical actinometer: Actino Chromo 1R (248/334) from Photon Technology International.

**Generation of Vinyl Radicals.** Vinyl radicals **1**$^{\bullet}$ were thermally generated from 1 mM **1***Z*:**1***E* (60:40) with 2 mM *n*-$Bu_3SnH$ in refluxing toluene under an argon atmosphere and a trace of 2,2′-azobis(2-methylpropionitrile) (AIBN) as initiator.[23] Oxygen was removed from the solvent prior to addition of the reagents by refluxing the toluene overnight under argon. According to GC and GC-MS at about 95% conversion the only products were the methylstyrenes **5***E* and **5***Z*. No products resulting from loss of HBr (i.e. **6** or **7**) were formed.

**Quantum Chemical Calculations.** The computations were performed with the Gaussian 03 program, version B3.[44] Calculations of the compounds under study were performed with the B3LYP functional method[45] as implemented in G03 and the Møller−Plesset fourth-order perturbation theory. The total energies were corrected with zero-point energies, obtained at the level of optimization.

**Synthesis of Starting Materials.** The syntheses and spectroscopic characterizations of **1***E*, **1***Z*, **2***E*, **2***Z*, **3***Z*, and $\mathbf{3_d}$*Z* are reported in the Supporting Information.

**(*E*)-1-Bromo-3,3,3-trifluoro-2-phenylpropene (4*E*-Br):** $CH_3I$ (50 mmol, 7.1 g) was added slowly to a chilled solution of 50 mmol of $Ph_3P$ (13.1 g) in THF. The reaction mixture was stirred for 1 h and filtered, and the residue was washed with THF and dried overnight in a vacuum stove, yielding $(Ph)_3PCH_3I$ in 98% yield (49 mmol, 19.8 g). Of this product 29 mmol was dissolved in THF. To this solution, cooled to −78 °C, a solution of 29 mmol *t*-BuOK (3.2 g) in *t*-BuOH was added dropwise. After the solution was stirred for 15 min, 29 mmol of α,α,α-trifluoroacetophenone (5.0 g) was added in one portion. The reaction mixture was stirred for a half hour and warmed to room temperature. The solvent was evaporated and petroleum ether 40/60 was added, the mixture was filtered, and the filtrate was dried over $MgSO_4$ and concentrated. A 29-mmol sample of the product, 3,3,3-trifluoro-2-phenylpropene **(18)** (5.0 g), was dissolved in 30 mL of $CCl_4$ at 0 °C and 32 mmol of $Br_2$ (5.1 g) was added dropwise. After the addition was complete, the reaction mixture was stirred at room temperature for 1 h. The solvent was evaporated. The residue was dissolved in 100 mL of *t*-BuOH together with 32 mmol of *t*-BuOK (3.6 g) and refluxed for 1 h. $H_2O$ (100 mL) was added and the mixture was extracted 3 times with 75 mL of diethyl ether. The combined ether layers were washed with $H_2O$ and brine and dried over $MgSO_4$. Evaporation and column chromatography with silica/petroleum ether 40/60 afforded **4***Z*-Br in an overall yield of 43% (12 mmol, 3.1 g) with an *E*/*Z* ratio of 85:15. This stereoisomeric mixture[46] was used as such for the irradiations. $^{19}$F NMR $\delta$ −63.43 (d, $J_{HF} = 1.2$ Hz). $^1$H NMR $\delta$ 7.36 (m, 6H). MS *m*/*z* (rel intensity) 252, 250 ($M^+$, 100, 95), 171 ($M^+ - Br$, 30), 151 ($M^+ - HBrF$, 40), 102 ($M^+ - CF_3Br$, 50). High-resolution MS *m*/*z* 249.9648 ($C_9H_6F_3Br$ requires 249.9605). UV $\lambda_{max} = 266$ nm ($\epsilon = 6.6\ 10^3$ L/mol·cm).

**(*E*)-1-Chloro-3,3,3-trifluoro-1-phenylpropene (4*E*-Cl):** To a solution, cooled to −78 °C, of 23 mmol of $(Ph)_3PCH_2ClI$[47] (10.1 g) in THF was added a solution of *t*-BuOK in THF (23 mmol, 23 mL of a 1 M solution) dropwise. The solution was stirred at room temperature for 15 min, after which 23 mmol of α,α,α-trifluoroacetophenone (4.0 g) was added in one portion. The reaction mixture was stirred for half an hour. The solvent was evaporated, petroleum ether 40/60 was added, the mixture was filtered, and the filtrate was dried over $MgSO_4$ and concentrated. The product was purified by column chromatography (silica/petroleum ether:diethyl ether 10:1), yielding 9 mmol of **4***E*-Cl (38%, 1.8 g) in an *E*/*Z* ratio of 87:13. This stereoisomeric mixture[48] was used as such for the irradiations. $^1$H NMR $\delta$ 6.59 (s, 1H), $\delta$ 7.38 (m, 5H). MS *m*/*z* (rel intensity) 208, 206 ($M^+$, 30, 100), 171 ($M^+ - Cl$, 40), 151 ($M^+ - HFCl$, 40), 102 ($M^+ - CF_3Cl$, 80). High-resolution MS *m*/*z* 206.0117 ($C_9H_6F_3Cl$ requires 206.0110). UV $\lambda_{max} = 265$ nm ($\epsilon = 5.8\ 10^3$ L/mol·cm).

**Identification of Products.** All photoproducts were identified by GLC co-injection and GC-MS analysis of reference compounds. In all cases the *E*/*Z*-isomeric products of the starting material were obtained during the synthesis of the starting materials. Products **5**(*E*), **10**, **11**, and **19** are commercially available. Product **18** is an intermediate in the synthesis of **4***E*-Br. All other reference compounds were synthesized independently, mainly according to literature procedures. The methods of syntheses and the spectral listings for **3***E*, **4***Z*-Br, **4***Z*-Cl, **5***Z*, **6**, **7**, **14***E*, **14***Z*, **15**, **16**, and **18** are reported in the Supporting Information.

**3,3,3-Trifluoro-1-methoxy-2-phenylpropene (20*E* and 20*Z*):** To 4.7 mmol of 3,3,3-trifluoro-2-phenylpropene (**18**) (0.80 g), obtained via a Wittig reaction as described in the synthesis of **4***E*-Br, in 30 mL of $CH_2Cl_2$ was slowly added 5.1 mmol of $BH_3{\cdot}Et_2O$ (5.1 mL of a 1 M solution in diethyl ether) under $N_2$ via a syringe. The reaction mixture was stirred at 0 °C for 2 h, after which the diethyl ether was evaporated. The reaction mixture was slowly added to a solution of 100 mmol of PCC (21.8 g) in 50 mL of $CH_2Cl_2$. After the initial vigorous reaction had subsided, the reaction mixture was refluxed for 2 h. Diethyl ether (50 mL) was added, the mixture was filtered, and the filtrate was concentrated. The thus obtained 3,3,3-trifluoro-2-phenylpropionaldehyde was used without purification in the next step. $HC(OCH_3)_3$ (4.2 mmol, 0.45 g), 3.5 mmol of 3,3,3-trifluoro-2-phenylpropionaldehyde (0.65 g), and a catalytic amount of *p*-toluenesulfonic acid were dissolved in methanol. The reaction was distilled until no more $HCOOCH_3$ was collected. The resulting mixture was dried over $MgSO_4$ and concentrated. The products were purified and separated by column chromatography with silica/petroleum ether:diethyl

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ether 10:1, yielding **20*E*** as well as **20*Z***. **20*E***: $^1$H NMR $\delta$ 3.81 (s, 3H), $\delta$ 6.40 (q, $J_{HF} = 1.7$ Hz, 1H), $\delta$ 7.29 (m, 5H). MS *m/z* (rel intensity) 202 (M$^+$, 80), 187 (M$^+$ $-$ CH$_3$, 25), 159 (M$^+$ $-$ C$_2$H$_3$O, 40), 146 (M$^+$ $-$ C$_3$H$_4$O, 15), 109 (M$^+$ $-$ C$_3$F$_3$, 100). High-resolution MS *m/z* 202.0604 ($C_9H_7F_3$ requires 202.0605). **20*Z***: $^1$H NMR $\delta$ 3.78 (s, 3H), $\delta$ 6.90 (q, $J_{HF} = 2.1$ Hz, 1H), $\delta$ 7.35 (m, 5H). MS *m/z* (rel intensity) 202 (M$^+$, 100), 187 (M$^+$ $-$ CH$_3$, 25), 159 (M$^+$ $-$ C$_2$H$_3$O, 40), 146 (M$^+$ $-$ C$_3$H$_4$O, 15), 109 (M$^+$ $-$ C$_3$F$_3$, 100). High-resolution MS *m/z* 202.0603 ($C_9H_7F_3$ requires 202.0605).

**Supporting Information Available:** Experimental procedures for the preparation of starting materials **1*E***, **1*Z***, **2*E***, **2*Z***, **3*Z***, and **3$_\mathbf{d}$*Z*** and spectroscopic characterization data for these compounds as well as for the photoproducts **3*E***, **4*Z*-Br**, **4*Z*-Cl**, **5*Z***, **6**, **7**, **14*E***, **14*Z***, **15**, **16**, and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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