crude product was purified by flash chromatography eluting with 1:1 hexane/CH_2Cl_2 increasing to CH_2Cl_2 and then to 1:19 ether/CH_2Cl_2 followed by fractional precipitation from CH_2Cl_2 into 1:3 propan-2-ol/acetone to give **21** as a colorless foam: yield 58%; IR 1600, 1470, 1360, and 1170 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.48–1.64 (m, 15 H, CH_3 and CH_2), 2.07 (s, 3 H, CH_3), 2.12–2.17 (m, 6 H, CH_2), 3.78 (br s, 6 H, CH_2O from core), 4.85 and 4.93 (each br s, 372 H, PhCH_2O), 6.36–6.69 (m, 276 H, Ar′- and Ar″*H*), 6.82 and 6.95 (ABq, 24 H, J = 8 Hz, Ar*H*), 7.06 (B of ABq, 6 H, J = 8 Hz, Ar′*H*), and 7.26–7.35 (m, 480 H, Ph*H*); ^{13}C NMR ($CDCl_3$) δ 26.83, 27.90, and 44.67 (CH_3, and CH_2), 31.66 (CH_3), 50.09 and 53.71 (CCH_3), 69.81 and 69.91 (CH_2O), 101.48, 106.28, 113.44, 114.07, 127.45, 127.88, 128.45, 129.49, 136.70, 139.15, 139.50, 141.58, 142.03, 156.54, 156.96, 159.94, and 160.02 (aromatic *C*). Anal. Calcd for $C_{1373}H_{1188}O_{189}$: C, 79.62; H, 5.78. Found: C, 79.49; H, 5.93.

[G-4]$_{12}$-[C] 22. A mixture of [G-4]-Br **19** (1.56 g, 0.46 mmol), (HO)$_{12}$-[C] **18** (80 mg, 0.031 mmol), potassium carbonate (300 mg, 2.2 mmol), and 18-crown-6 (20 mg, 0.08 mmol) was heated at reflux in dry acetone (150 mL) for 96 h. After it was cooled, the mixture was evaporated to dryness and partitioned between water (200 mL) and CH_2Cl_2 (200 mL). The water layer was extracted with CH_2Cl_2 (2 × 200 mL), and the combined extracts were dried and evaporated to dryness. The crude product was purified by flash chromatography eluting with CH_2Cl_2 followed by fractional precipitation from CH_2Cl_2 into 1:3 propan-2-ol/acetone to give **22** as a colorless foam: yield 51%; IR 1600, 1470, 1360, and 1170 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.45–1.70 (m, 45 H, CH_3 and CH_2), 2.00–2.15 (m, 21 H, CH_2 and CH_3), 3.72–3.78 (br s, 18 H, CH_2O from core), 4.84 and 4.91 (each br s, 744 H, PhCH_2O), 6.30–6.70 (m, 576 H, Ar′- and Ar″*H*), 6.80–6.96 (m, 48 H, Ar- and Ar′*H*), and 7.20–7.40 (m, 960 H, Ph*H*); ^{13}C NMR ($CDCl_3$) δ 26.95, 29.10, 44.51, 53.54 (aliphatic *C*, some peaks too small to observe), 69.92 (CH_2O), 101.51, 106.31, 113.49, 127.47, 127.88, 128.48, 129.49, 136.73, 139.18, 142.33, 156.76, 159.96, and 160.05 (aromatic *C*). Anal. Calcd for $C_{2777}H_{2412}O_{381}$: C, 79.64; H, 5.80. Found: C, 79.42; H, 5.82.

[G-4]$_{24}$-[C] 22. A mixture of [G-4]-Br **19** (1.486 g, 0.44 mmol), (HO)$_{24}$-[C] **24** (80 mg, 0.014 mmol), potassium carbonate (300 mg, 2.2 mmol), and 18-crown-6 (20 mg, 0.08 mmol) was heated at reflux in dry acetone (150 mL) for 96 h. After it was cooled, the mixture was evaporated to dryness and partitioned between water (200 mL) and CH_2Cl_2 (200 mL). The water layer was extracted with CH_2Cl_2 (2 × 200 mL), and the combined extracts were dried and evaporated to dryness. The crude product was purified by flash chromatography eluting with CH_2Cl_2 increasing to 1:19 ether/CH_2Cl_2 followed by fractional precipitation from CH_2Cl_2 into 1:19 propan-2-ol/acetone to give **22** as a colorless foam: yield 61%; IR 1600, 1470, 1360, and 1170 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.45-1.85 (m, 105 H, CH_3 and CH_2), 2.00–2.20 (m, 45 H, CH_2 and CH_3), 3.70–3.82 (br s, 42 H, CH_2O), 4.80–5.00 (m, 1488 H, PhCH_2O), 6.40–6.75 (m, 1080 H, Ar″*H*), 6.90–7.05 (m, 180 H, Ar- and Ar′*H*), and 7.25–7.50 (m, 1920 H, Ph*H*); ^{13}C NMR ($CDCl_3$) δ 29.10, 44.51, 53.54 (aliphatic *C*, some peaks too small to observe), 69.80 (CH_2O), 101.54, 106.47, 127.41, 127.78, 128.43, 136.71, 142.13, 159.90, and 160.10 (aromatic *C*). Anal. Calcd for $C_{5585}H_{4860}O_{765}$: C, 79.65; H, 5.82. Found: C, 79.45; H, 6.03.

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Photoreactivity of Some α-Arylvinyl Bromides in Acetic Acid. Selectivity toward Bromide versus Acetate Ions as a Mechanistic Probe

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Abstract: The photochemical reactions of four α-anisyl-β,β-diarylvinyl bromides (**1a–1d**), three α-phenyl-β,β-diarylvinyl bromides (**1e–1g**), and 9-(α-bromo-*p*-methoxybenzylidene)anthrone (**2**) in acetic acid in the presence of sodium acetate and tetraethylammonium bromide (labeled with ^{82}Br) have been studied quantitatively. Bromide exchange, acetate formation, E/Z isomerization, an anisyl 1,2-shift, stilbene-type cyclization to phenanthrenes, reductive debromination, and oxidation are observed as primary pathways. For all compounds **1**, nucleophilic substitution, accompanied by E/Z isomerization in both starting material and product with **1b,c** and **1f,g** and an anisyl 1,2-shift in **1e** but not in **1f,g**, is quite efficient and by far the most important process. (Quantum yields range from 0.1 to 0.3 as compared to 0.01–0.02 for cyclization and 0.001–0.01 for reduction). The α-anisylvinyl bromide **2** is virtually inert for photosubstitution. The selectivity constants toward bromide and acetate ions, corrected for their temperature dependence, the amounts of E/Z isomerized starting material and product, the occurrence or nonoccurrence of an anisyl 1,2-shift, and the nature of the capturing nucleophile in the acetolysis are all in quantitative agreement with the corresponding data for the thermal reactions of **1** in the same medium. The results strongly support a mechanism for the nucleophilic vinylic photosubstitution reactions that involves the generation of a product-forming intermediate, which is exactly the same as the intermediate formed in the thermal reaction, a "cold" (thermally relaxed) linear free vinyl cation.

Introduction

Interest in the photochemical behavior of vinyl halides has surged since it was discovered[1] that, upon irradiation of such compounds in appropriate media, nucleophilic substitution and rearrangement products are formed in addition to reductive dehalogenation products.[2-7] A nucleophilic vinylic photosubstitution

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reaction can be thought to occur via one of the four types of mechanisms depicted in Scheme I, in analogy with the mechanisms found for nucleophilic aromatic photosubstitution reactions.[8]

Scheme I[a]

$$\mathrm{VinX}^{\#} \xrightarrow[-\mathrm{X}^-]{} [\mathrm{Vin}]^+ \xrightarrow{\mathrm{Y}^-} \mathrm{VinY} \qquad \mathrm{S_N1}$$

$$\mathrm{VinX}^{\#} \xrightarrow{\mathrm{Y}^-} [\mathrm{VinXY}]^- \xrightarrow[-\mathrm{X}^-]{} \mathrm{VinY} \qquad \mathrm{S_N2}$$

$$\mathrm{VinX}^{\#} \xrightarrow[-e^-]{} [\mathrm{VinX}]^{\bullet +} \xrightarrow[-\mathrm{X}^-]{\mathrm{Y}^-} \mathrm{VinY} \qquad \mathrm{S_{R^+N}1}$$

$$\mathrm{VinX}^{\#} \xrightarrow{e^-} [\mathrm{VinX}]^{\bullet -} \xrightarrow[-\mathrm{X}^-]{} \mathrm{Vin}^{\bullet} \xrightarrow{\mathrm{Y}^-} \mathrm{VinY} \qquad \mathrm{S_{R^-N}1}$$

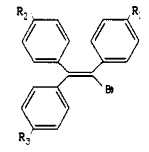
[a] The symbol # idicates the electronically excited state.

For most vinyl halides studied thus far, it is reported that the reaction occurs via the vinyl cation S_N1 route, in analogy with the mechanism proposed for nucleophilic photosubstitution reactions of alkyl halides.[2b] In at least one case though, the reaction is believed to occur via the radical anion $S_{R^-N}1$ route[9] (see also ref 6b). Considering the "intermediate position which the vinylic system holds between saturated and aromatic systems"[10] and the multitude of mechanistic pathways for thermal nucleophilic substitution reactions of vinyl halides,[10] it is quite intriguing that photosubstitution reactions of vinylic systems would follow just one general pathway and that it is the pathway that is least often observed for aromatic systems.[2a,8]

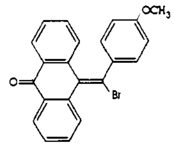
As to the nature of a vinyl cation generated in a photochemically induced S_N1 reaction, comparison with the photochemistry of alkyl halides sets no example.[2,11-15] For some photosolvolysis reactions of alkyl halides, indications have been found for the intermediacy of so-called "cold" carbocations, thermally relaxed species with the same properties as the cations produced in the corresponding ground-state reactions.[2,11-13] In other instances, the results indicate that such photosolvolyses involve the generation of so-called "hot" carbocations, not—or not appreciably—solvated species with properties quite distinct from those of the thermally generated ions.[2,11,14,15]

A time-honored method to probe for the occurrence of a certain intermediate in a photochemical reaction and to establish its nature is to study reactions that are characteristic of such intermediates and that can be used as diagnostic tools for their nature. In the case of a cationic intermediate, characteristic reactions are reactions with nucleophiles, rearrangements, and—in the case of vinyl cations—*E*/*Z* isomerization; the corresponding diagnostic tools are selectivity toward different nucleophiles, degree of rearrangement, and degree of *E*/*Z* isomerization. Comparison of such data for photochemical reactions with those for corresponding thermal reactions under as much as possible the same reaction conditions allows conclusions as to the intermediacy/nonintermediacy of such a species in the photochemical reaction and the similarities/dissimilarities in the nature of the photochemically and thermally generated intermediate.

The thermal solvolysis reactions of α-arylvinyl halides have been extensively investigated.[16] In most cases, the reactions occur via the S_N1 mechanism and the product-forming intermediate is a free sp-hybridized α-arylvinyl cation.[16] Previously we have reported reactivity and nucleophile selectivity data for the simultaneous thermal (radioactive) bromide exchange and acetolysis reactions of the α-anisylvinyl bromides **1a–1d** and **2** in acetic acid/sodium acetate/tetraethylammonium bromide.[17] In this paper, we report[18] similar data for the photochemical reactions of these compounds in the same medium as well as data for the photochemical reactions of the α-phenylvinyl bromides **1e–1g**, for which thermal reactivity data are also available.[19]



1



2

a: $R_1 = OCH_3$, $R_2 = OCH_3$, $R_3 = OCH_3$
b: $R_1 = OCH_3$, $R_2 = OCH_3$, $R_3 = H$
c: $R_1 = OCH_3$, $R_2 = H$, $R_3 = OCH_3$
d: $R_1 = OCH_3$, $R_2 = H$, $R_3 = H$
e: $R_1 = H$, $R_2 = OCH_3$, $R_3 = OCH_3$
f: $R_1 = H$, $R_2 = OCH_3$, $R_3 = H$
g: $R_1 = H$, $R_2 = H$, $R_3 = OCH_3$

The reactivity data will usefully extend the at present scarce quantitative knowledge of the relationship between the structure

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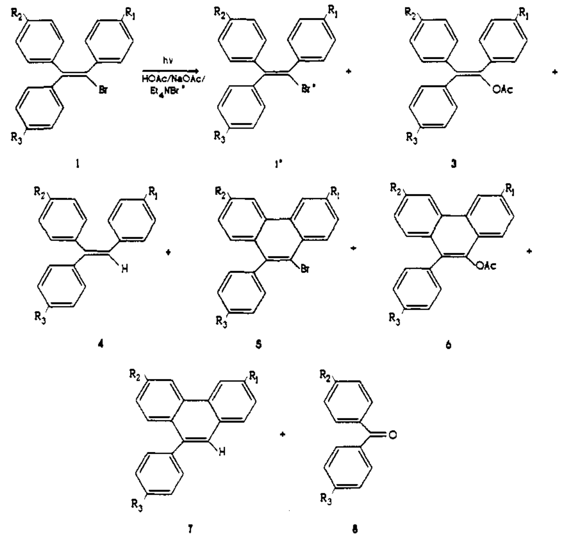
of vinyl halides and their photoreactivity. The selectivity data, in combination with the rearrangement and *E*/*Z* isomerization data, will probe for the intermediacy of a vinyl cation and allow comparison of the nature of this reactive intermediate with that of its thermally generated counterpart.

Results

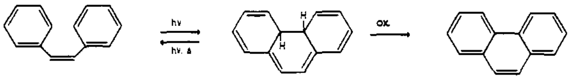
1-*p*-Anisyl-2,2-diarylvinyl Bromides 1a–1d. Product Studies. Irradiation of any of the compounds **1** in acetic acid in the presence of sodium acetate and tetraethylammonium bromide produces fairly complex product mixtures. The composition of these mixtures varies with the substituents R_1, R_2, and R_3 as well as with the presence or absence of oxygen. Furthermore (radioactive) bromide exchange can be observed. The mixtures resulting from the irradiations of **1a** and **1d** are most easily analyzed. They contain the nucleophilic substitution products **3**, the reduction products **4**, and the oxidation products **8**, although the latter two only in minor quantities. Also the phenanthrene derivatives **5**, **6**, and **7** are present, all as depicted in eq 1.



(1)

The compounds **5** are obviously products of a *cis*-stilbene-type photocyclization[20] of starting material **1**. The apparently secondary photoproducts **6** and **7** are either the photocyclization products of the primary products **3** and **4** or are formed by nucleophilic photosubstitution or photoreduction of the primary cyclization product **5**. Possibly both routes are operative.

It was attempted to simplify the composition of the reaction mixtures by suppressing the photocyclization (and oxidation) reactions. This was done by removing oxygen from the reaction mixture with argon, since the *cis*-stilbene-type photocyclization is known[20] to proceed through the intermediacy of a *trans*-4a,4b-dihydrophenanthrene, which is subsequently oxidized (in this case, by dissolved oxygen) to the phenanthrene (eq 2).



(2)

Indeed, in the absence of oxygen, the formation of benzophenone derivatives is completely suppressed, but not the cyclization reaction, although the yield of products **5** was diminished considerably. However, several new unidentified products, which did not appear in the reaction mixtures from irradiations in the presence of oxygen, were now found. Instead of simplifying the composition of the reaction mixtures, the exclusion of oxygen actually complicates it.

Clearly, reliable kinetic data for the primary photoreactions of compounds **1** can only be obtained if the origin of the secondary phenanthrene photoproducts is established. Figure 1 shows the concentration versus time profile of the vinyl acetate **3a** and the phenanthrenyl acetate **6a** during the photolysis of vinyl bromide **1a**. At longer reaction times, there exists a steady-state concentration of **3a**. Some compounds **3** were also irradiated separately. Upon irradiation (λ = 313 nm), **3a** and a 1:1 mixture of **3b** and **3c** in $AcOH/NaOAc/Et_4NBr$ rapidly produce the corresponding phenanthrenyl acetates. Quantum yields of these reactions are presented in Table I. Comparison of the quantum yields of disappearance of **3** with the quantum yields of appearance of **6** shows a quantitative conversion of **3** into **6** in air-saturated solutions. In an argon-saturated medium, however, the formation of **6** is diminished and other products are formed, while the disappearance of the vinyl acetates is only slightly slower than the analogous photoreaction in an oxygen-containing solution. The products formed next to the cyclized vinyl acetates were not identified, but their HPLC retention times indicate that they are the same as the unidentified products formed in the irradiations of compounds **1** in argon-saturated solutions.

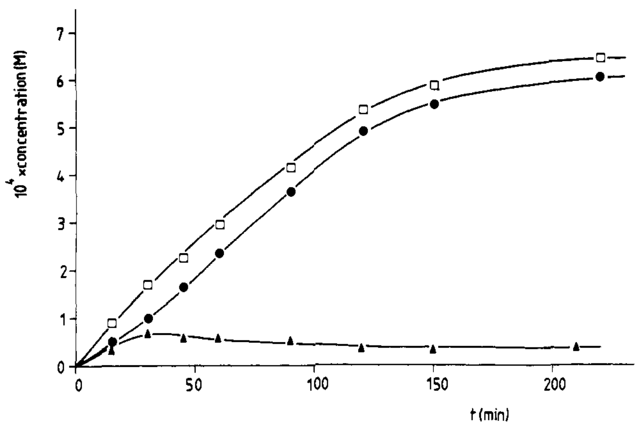


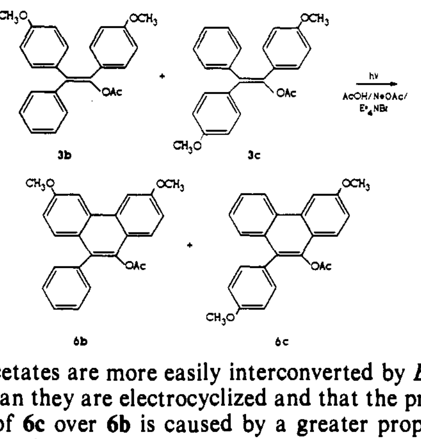
Figure 1. Concentrations (M) of acetate **3a** (▲), cyclized acetate **6a** (●) and **3a** + **6a** (□) during irradiation (λ = 313 nm) of 4.7×10^{-3} M **1a** in $AcOH/NaOAc/Et_4NBr$ as a function of time.

Table I. Quantum Yields (λ = 313 nm) of Disappearance (ϕ_d) and Cyclization (ϕ_c) of Compounds **3a–c** in $AcOH/NaOAc/Et_4NBr$

ROAc	atmosphere	$10^2\phi_d$	$10^2\phi_c$
3a	air	13	12
3b, **3c**[a]	air	15	14
3b, **3c**[a]	argon	12	4.2

[a] 1:1 mixture.

It is rather interesting to observe that, in the case of the 1:1 mixture of **3b** and **3c**, the two phenanthrenyl acetates **6b** and **6c** are formed in a ratio of 1:3 (eq 3). That ratio is found already at very low conversion of **3b** and **3c**, while the ratio of **3b** to **3c** stays approximately 1:1 during the reaction. This shows that



(3)

the vinyl acetates are more easily interconverted by *E*/*Z* isomerization than they are electrocyclized and that the preferential formation of **6c** over **6b** is caused by a greater propensity for phenanthrene formation of the *Z* isomer **3c** than that of the *E* isomer **3b**. A similar predominance of phenyl-*p*-methoxyphenyl cyclization product over *p*-methoxyphenyl-*p*-methoxyphenyl cyclization product has been observed in a study of the photochemistry of a series of para-substituted tetraphenylethylenes.[21]

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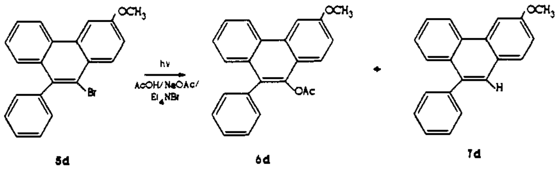
[20] For reviews, see: (a) Laarhoven, W. H. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 185, 241. (b) Mallory, F. B.; Mallory, C. W. *Org. React. (N.Y.)* **1984**, *30*, 1.

The regioselectivity can be ascribed to either preferential formation[21] or differential trapping by the not very efficient oxidant atmospheric air[22,23] of one of the isomeric intermediate dihydrophenanthrenes.

The photoreactivity of the cyclized bromide **5d** was also investigated. Irradiation (λ = 313 nm) of **5d** in AcOH/NaOAc/$\mathrm{Et_4NBr}$ shows the following relatively inefficient but interesting reaction (eq 4). While there is ample precedent for the formation of reductive debromination products such as **7d** from polycyclic aromatic bromides,[24,25] examples of nucleophilic aromatic photosubstitution reactions of such compounds with oxygen nucleophiles leading to products such as **6d** are scarce.[25,26] The quantum yield of disappearance of compound **5d** is 1.0×10^{-3}, which remains unaltered when $\mathrm{Et_4NBr}$ is not included in the reaction mixture. The ratio of the products **6d** and **7d** does, however, depend on the presence of $\mathrm{Et_4NBr}$. It is 3:2 in the presence of $\mathrm{Et_4NBr}$, 3:1 in its absence. In the presence of $\mathrm{Et_4NBr}$, substitution by NaOAc is relatively less important. When a mixture of products from exhaustive photolysis of **1d** in AcOH/NaOAc/$\mathrm{Et_4NBr}$ is further irradiated after addition of $[^{82}\mathrm{Br}]\mathrm{Et_4NBr}$, exchange of radioactivity is observed. In this mixture, the compounds **5d**, **6d**, **7d**, and **8d** are present. If **5d** is held responsible for the observed exchange reaction, the quantum yield of the reaction can be estimated to be ca. 1.0×10^{-2}.



5d **6d** **7d** (4)

The cyclized acetates are also photoreactive. Compound **6a** has, e.g., a quantum yield of disappearance of 3.0×10^{-3} under the standard reaction conditions. Product formation was not investigated.

Irradiation of compounds **1b** and **1c** produces the same types of products as does the irradiation of **1a** and **1d**. However, the reaction scheme turns out to be more complicated due to the occurrence of *E*/*Z* isomerization of both starting materials and products **3b** and **3c** (and **4b** and **4c**). Already at very low conversion of **1b** (containing less than 1% **1c**), the ratio of the *E* and *Z* isomers of the vinyl acetates formed is almost 1:1. These vinyl acetates are in turn transformed into their cyclized products **6b** and **6c**. The two triarylethenes **4b** and **4c** are formed in trace amounts only. The amounts are too small to allow determination of the *E*:*Z* ratio of these isomers.

Kinetics. The disappearance of the vinyl bromides and the appearance of the products were studied as a function of the time of irradiation. Aliquots taken from the solution at appropriate times were analyzed by means of HPLC and monitored for radioactivity. Reliable kinetic data for the exchange and acetolysis reactions of compounds **1** in air-saturated solutions can be obtained by monitoring the incorporation of radioactivity in the organic fraction and the formation of compounds **3** plus **6**, respectively. These data represent the formation of product **1***, which has incorporated radioactivity, and the initial formation of the nucleophilic substitution product **3**. This is the case, by summarizing and generalizing the information detailed in the preceding section, because (a) the vinyl acetates **3**, upon excitation in air-saturated solutions, are within experimental error completely converted into the corresponding phenanthrenyl acetates **6**, (b) the phenanthrenyl acetates **6** are essentially photostable as their quantum yields of disappearance are negligible compared to their quantum yields of formation from **3**, and (c) the quantum yields of exchange of compounds **5** are negligible compared to those of compounds **1** and so are the quantum yields of formation of **6** from **5** compared to those for the formation of **6** from **3**.

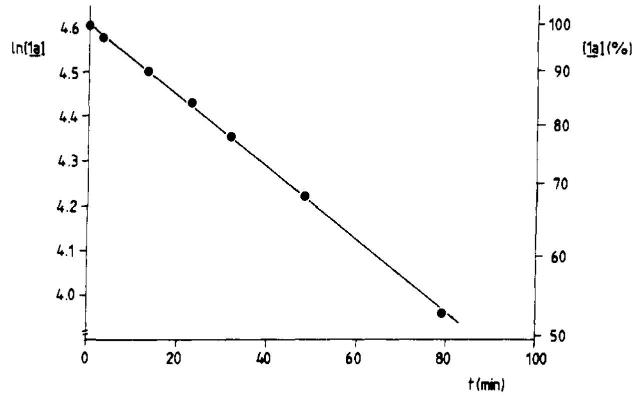


Figure 2. (Semilogarithmic) plot of the concentration (%) of vinyl bromide **1a** during irradiation (λ = 313 nm) in AcOH/NaOAc/$\mathrm{Et_4NBr}$ as a function of time.

In a detailed analysis reported elsewhere,[27] kinetic expressions have been derived specifically for systems such as those studied here, in which in the course of the photoreaction an increasing part of the incident light is absorbed by reaction products but the optical density of the reaction mixture does not change significantly and remains higher than 2. According to these expressions, the decrease of starting material, the formation of product, and the radioactive bromide exchange should adhere to eqs 5, 6, and 7, respectively.

$$\ln \frac{[\mathrm{RBr}]_t}{[\mathrm{RBr}]_0} = -k_d t = -\phi_d t \frac{I_0}{[\mathrm{RBr}]_0} \tag{5}$$

$$[\mathrm{X}]_t = \phi_x \frac{I_0}{k_d}(1 - e^{-k_d t}) \tag{6}$$

$$\ln \frac{n_\infty(n_\infty - n_t)^{-1}}{e^{tk_d} - n_\infty(n_\infty - n_t)^{-1}(e^{tk_d} - 1)} = \phi_{ex} I_0 t \frac{[\mathrm{RBr}]_0 + [\mathrm{Et_4NBr}]_0}{[\mathrm{RBr}]_0[\mathrm{Et_4NBr}]_0} \tag{7}$$

In these equations, $[\mathrm{RBr}]_t$ and $[\mathrm{RBr}]_0$ represent the concentration of vinyl bromide RBr in the photolysis mixture at times t and 0, k_d stands for the rate constant of disappearance of RBr, t is the time of irradiation, ϕ_d is the quantum yield of decrease of RBr, I_0 is the intensity of the light absorbed by RBr at time $t = 0$, $[\mathrm{X}]_t$ is the concentration of product X at time t, ϕ_x is the quantum yield of formation of product X, and n_t and n_∞ are the specific radioactivities of RBr at time t and at equilibrium. n_∞ can be calculated from the specific radioactivity of the labeled $\mathrm{Et_4NBr}$ at $t = 0$. In eq 7, the term presented in eq 8 represents a correction factor for the decrease of starting material RBr concurrent with the exchange process.[27]

$$\left\{e^{tk_d} - \frac{n_\infty}{n_\infty - n_t}(e^{tk_d} - 1)\right\}^{-1} \tag{8}$$

In all cases, excellent adherence to the theoretical eqs 5–7 was found. Representative examples are shown in Figures 2–5, where the disappearance of vinyl bromide **1a**, the formation of acetate **3a** and of cyclization product **5a**, and the bromide exchange in **1a** are graphically represented. From the slopes of the graphs, the quantum yields of the various reactions were obtained. From the quantum yields of exchange (ϕ_{ex}) and acetate formation (ϕ_{OAc}), the selectivity parameter (α) for capture with bromide versus capture with acetate can be calculated according to eq 9.

$$\alpha = \frac{k_{ex}}{k_{OAc}} = \frac{\phi_{ex}}{\phi_{OAc}} \frac{[\mathrm{NaOAc}]_0}{[\mathrm{Et_4NBr}]_0} \tag{9}$$

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Table II. Quantum Yields (ϕ) and Selectivity Parameters (α) in the Photochemical Reactions of Various 1-Arylvinyl Bromides in AcOH/NaOAc/Et$_4$NBr (λ = 313 nm, [RBr] = 4.7 × 10^{-3} M, [NaOAc] = 87 × 10^{-3} M, [Et$_4$NBr] = 71 × 10^{-3} M)[a,b]

RBr	atmosphere	$10^2\phi_d$	$10^2\phi_{OAc}$	$10^2\phi_{ex}$	$10^2\phi_{red}$	$10^2\phi_c$	$10^2\phi_{rearr}$	$\alpha_{h\nu}$
1a	air	2.9	0.97	20	0.15	0.6		26
1a	argon	2.1	>0.7	19	0.5	0.15		n.d.
1b, 1c	air	4.1	1.1	23	~0	1.1		25
1d	air	5.6	1.5	28	~0	2.0		23
1d	argon	3.9	>0.9	30	~0.1	0.2		n.d.
1e	air	20	0.8[c]	15[d]	0	n.d.	19	23
1f, 1g	air	6.0	3.9	6.2	0	n.d.	<0.06	2
2	air	1.8	<0.01	<0.5	0	1.7		68[e]
2	argon	1.3	<0.01	n.d.	0	0.4		n.d.

[a] n.d. means not determined. [b] In this and the other tables, ϕ_d is the quantum yield of disappearance of starting material (not corrected for the degenerate exchange process), ϕ_{ex} the quantum yield of the exchange reaction, ϕ_{OAc} the quantum yield of acetate formation, ϕ_c the quantum yield of the cyclization reaction, ϕ_{red} the quantum yield of formation of reduction products, ϕ_{rearr} the quantum yield of rearrangement, and α the selectivity parameter (eq 9). [c] Only rearranged acetates formed. [d] Measured at a very early stage of the reaction and not corrected for product formation. [e] Estimated value (see text).

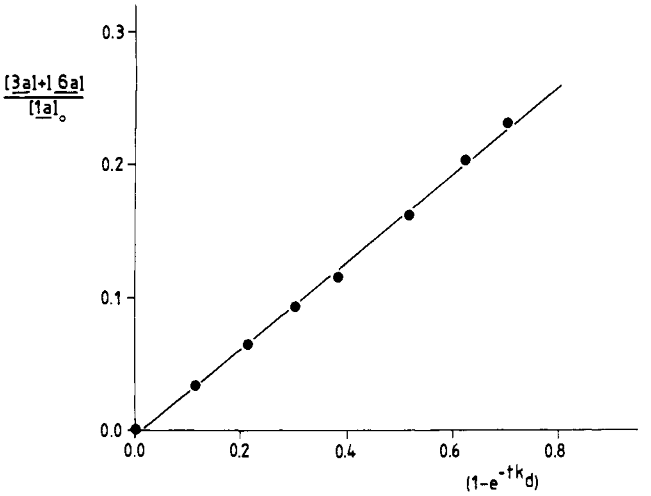


Figure 3. Concentration of the acetates **3a** + **6a** relative to [**1a**]$_0$ during the irradiation (λ = 313 nm) of **1a** in AcOH/NaOAc/Et$_4$NBr as a function of ($1 - e^{-tk_d}$) with k_d = 8.1 × 10^{-3} min^{-1}.

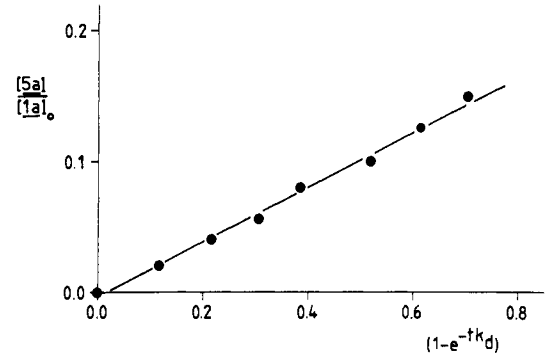


Figure 4. Concentration of cyclization product **5a** relative to [**1a**]$_0$ during the irradiation (λ = 313 nm) of **1a** in AcOH/NaOAc/Et$_4$NBr as a function of ($1 - e^{-tk_d}$) with k_d = 8.1 × 10^{-3} min^{-1}.

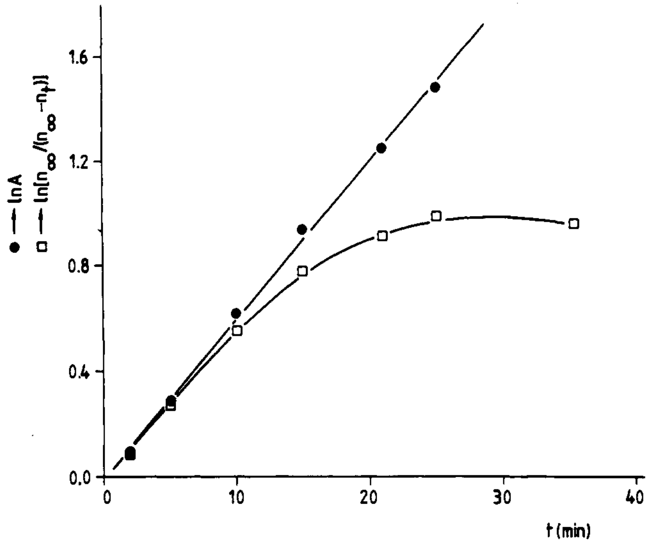


Figure 5. Photochemical (λ = 313 nm) bromide exchange of **1a** in AcOH/NaOAc/Et$_4$NBr: ln $n_\infty/(n_\infty - n_t)$ (no correction for product formation) (□) and ln A (values corrected for product formation) (●) as a function of time (see eq 7).

$$\ln A = \frac{n_\infty(n_\infty - n_t)^{-1}}{e^{tk_d} - n_\infty(n_\infty - n_t)^{-1}(e^{tk_d} - 1)}$$

Table III. Quantum Yields of the Photolysis (λ = 313 nm) of **1d** in Nitrogen-Saturated Acetic Acid at Various Concentrations of NaOAc and Et$_4$NBr

10^3[NaOAc]	10^3-[Et$_4$NBr]	$10^2\phi_d$	$10^2\phi_{ex}$	ϕ_{ex}/ϕ_d	$10^2\phi_{OAc}$[a]
		1.9			0.4
87		10.4			6.8
	71	2.9	28	9.7	0.3
87	71	3.9	30	7.7	1.2

[a] Minimum values (vinyl acetates not photostable; degradation partly leading to unidentifiable products).

Table IV. Quantum Yield and Selectivity Factors of the Photochemical Reaction (λ = 313 nm) of Compound **1a** in AcOH/NaOAc/Et$_4$NBr at 23 and 60 °C

T (°C)	$10^2\phi_d$	$10^2\phi_{OAc}$	$10^2\phi_{ex}$	$\alpha_{h\nu}$
23	2.9	0.97	20	25.5
60	5.1	1.58	31	23.7

The quantum yields and selectivity constants obtained in irradiations of compounds **1a**–**1d** are given in Table II (entries 1–5). The effects of changing the concentration of NaOAc and Et$_4$NBr are illustrated in Table III. The data in this table are obtained from experiments with **1d** in acetic acid solutions saturated with nitrogen. This means that, like in an argon-saturated medium, the quantum yields of formation of the acetates **3d** + **6d** are minimum values.

The effects of changing the temperature at which irradiations are carried out are shown in Table IV. The effects shed light on the possibility of a temperature effect on the selectivity parameters α, which one has to consider in comparing the α values found in the photoreactions at 23 °C with the α values measured in the thermal reactions performed at 120 °C (see ref 17). The temperature effect was probed by irradiating compound **1a** at 23 and 60 °C under otherwise identical standard conditions. A temperature of 60 °C turned out to be high enough to detect an effect and low enough for thermal reactions to still be negligible. Neither radioactive exchange nor acetate formation were found when a control experiment was carried out at 60 °C in the dark. The results listed in Table IV show that while at both temperatures the same products are formed, the photoreactions are much more

Table V. Selectivity Parameters (α) for the Photochemical and Thermal Reactions of Compounds **1a–1d** in $AcOH/NaOAc/Et_4NBr$

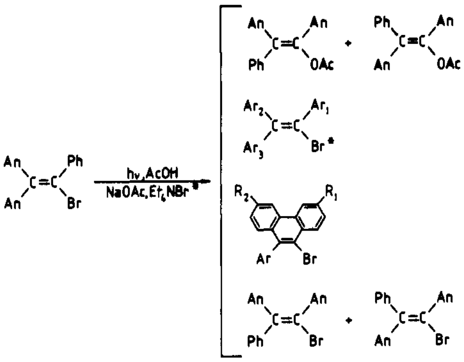
RBr	$\alpha_{h\nu}{}^{23}$	$\alpha_{h\nu}{}^{120\,a}$	$\alpha_{\Delta}{}^{120\,b}$
1a	26	22	22
1b, **1c**	25	21	19
1d	23	19	19

[a] Extrapolated value. [b] Reference 17.

efficient at 60 °C than at room temperature. Since the effect is larger for acetate formation than for exchange, the value of α at 60 °C is lower. Usually[28,29] the relation between the selectivity parameter α and the (absolute) temperature (T) can be described as shown in eq 10, where $\Delta H^{\ddagger}{}_{OAc}$ and $\Delta H^{\ddagger}{}_{Br}$ represent the enthalpies of activation of the reaction with ^{-}OAc and Br^{-}, respectively and $\Delta S^{\ddagger}{}_{OAc}$ and $\Delta S^{\ddagger}{}_{Br}$ stand for the corresponding entropies of activation. On the basis of this relation and the values of the enthalpies of activation obtained from Eyring treatment of the data in Table IV ($\Delta H^{\ddagger}{}_{OAc}$ = 2.0 kcal/mol, $\Delta H^{\ddagger}{}_{Br}$ = 1.7 kcal/mol), the selectivity factor α for the photoreaction of **1a** at 120 °C is 22. Assuming the differences in the enthalpies of activation for **1b–1d** to be the same as those for compound **1a**, one can calculate the selectivity parameters at 120 °C for these vinyl bromides. The results are listed in Table V together with measured values of α at 120 °C in thermal experiments. The values are in excellent agreement.

$$\log \alpha = \frac{\Delta H^{\ddagger}{}_{OAc} - \Delta H^{\ddagger}{}_{Br}}{2.303RT} - \frac{\Delta S^{\ddagger}{}_{OAc} - \Delta S^{\ddagger}{}_{Br}}{2.303R} \qquad (10)$$

1-Phenyl-2,2-diarylvinyl Bromides 1e–1g. Product Studies and Kinetics. The primary products of the photochemical reaction of vinyl bromide **1e** in $AcOH/NaOAc/Et_4NBr$ are shown in eq 11. Apart from the occurrence of products from β-aryl rearrangement, the products are similar to those found in the photochemical reactions of compounds **1a–1d**. In addition to the rearranged vinyl bromides **1b** and **1c**, as acetates only the rearranged acetates **3b** and **3c** were detected. Measured at the earliest possible stage of the reaction, the ratio of **3b** to **3c** is approximately 1:1. Of course, **3b** and **3c** as well as **1b** and **1c** produce their own cyclized phenanthrene derivatives. The quantum yields of disappearance of **1e** and appearance of primary products are listed in Table II (entry 6). The data show that the rearrangement of **1e** to **1b** and **1c** is very efficient and, with $\phi_{rearr} \approx 0.94\phi_d$, by far the major pathway of disappearance. Including the formation of rearranged acetates **3b** and **3c** in our considerations, rearrangement forms the (almost) exclusive pathway of disappearance ($\phi_{rearr} + \phi_{OAc} \approx 0.99\phi_d$).



(11)

The value of ϕ_{OAc} was measured at the earliest possible reaction time at which the amounts of **3b** and **3c** could be determined with sufficient accuracy because, as the data in Table VI show, the rate of acetate formation increases with increasing conversion, in marked contrast with all other irradiations. The explanation for this different behavior is simple: (a) the rearranged vinyl bromides **1b** and **1c** are formed in increasing amounts and start to produce the acetates **3b** and **3c** themselves and (b) the quantum yield of acetate formation from **1b** (ϕ_{OAc} = 0.011) is higher than that of the acetate formation from **1e** ($\phi_{OAc} \leq 0.008$).

Table VI. Relative Concentrations of Vinyl Bromide **1e** and Quantum Yields of Formation of Acetates **3b** and **3c** in the Photoreaction (λ = 313 nm) of **1e** in $AcOH/NaOAc/Et_4NBr$ at Various Times of Irradiation

time of irradiation (min)	[**1e**] (%)	$10^2\phi_{OAc}$
10	56	0.8
15	40	1.1
55	10	2.9

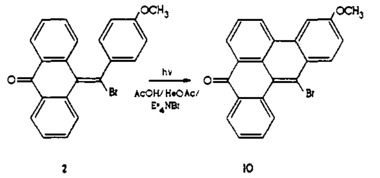
When the radioactivity of the vinyl bromides is monitored during the photoreaction of **1e**, it is possible to calculate a rate constant for exchange. The exchange reaction is somewhat different from the previously described bromide exchange reactions. Due to the extensive rearrangement of **1e**, one does not measure the bromide exchange reaction of **1e** but the formation of the radioactive rearranged vinyl bromides **1b*** and **1c***. As the exchange reaction is not a degenerate process in this case, the correction factor for product formation on the quantum yield ϕ_{ex} (eq 8) cannot be applied. The parameter ϕ_{ex}, which thus concerns the formation of **1b** and **1c** rather than the exchange of **1e**, was therefore determined with use of the noncorrected eq 12 at lowest possible conversion.

$$\ln \frac{n_\infty}{n_\infty - n_t} = k_{ex}t = \phi_{ex}tI_0\frac{[RBr]_0 + [Et_4NBr]_0}{[RBr]_0[Et_4NBr]_0} \qquad (12)$$

Irradiation of a 42:58 mixture of the 1-phenylvinyl bromides **1f** and **1g** gives only reactions similar to those found with compounds **1b** and **1c**, i.e., acetate formation, cyclization, extensive E/Z isomerization of both starting materials and products, but little, if any, nondegenerate β-aryl rearrangement (Table II, entry 7). Bromide exchange occurs with low efficiency: ϕ_{ex} = 0.062. No indications were found for the formation of rearranged vinyl bromides. The contribution of rearranged acetate to the mixture of acetates constitutes at most a few percent. Even that figure is dubious as it is solely based on the equivocal assignment of an HPLC peak to compound **6d**, the cyclized product of rearranged acetate **3d**.

9-(α-Bromo-p-methoxybenzylidene)anthrone (2). Of all α-anisylvinyl bromides described in the present paper, compound **2** has the largest selectivity factor α in thermal reactions toward bromide and acetate ions, as measured by the solvolysis–exchange method (α_Δ = 75).[17] It was therefore looked upon as the most promising, sensitive probe for comparing selectivity constants of photochemically and thermally induced reactions.

Regrettably, for our purpose, compound **2** is extremely insensitive toward photoreactions of the carbon–bromine bond. Irradiation of **2** in air-saturated $AcOH/NaOAc/Et_4NBr$ results in the formation of only one major product (**10**) in a chemical yield >94% (eq 13).



2 10 (13)

During the reaction, the *cis*-stilbene-type photocyclization product **10** precipitates and can easily be filtered off. No formation of acetates or reduction products could be detected. Some bromide exchange is found (Table II, entry 8). The value of ϕ_{ex} = 0.005–0.01 is based on the reasonable assumption that—in view of the much larger quantum yield of exchange of compound **1d** compared to that of compound **5d**—compound **2** and not compound **10** is responsible for the exchange and is rather inaccurate due to the fact that since ϕ_d is large relative to ϕ_{ex}, a large correction factor (eq 8) has to be used.

An estimation of the detection limit for acetate formation gives an upper limit for $\phi_{OAc} < (0.005\text{–}0.01)\phi_d$. On this admittedly

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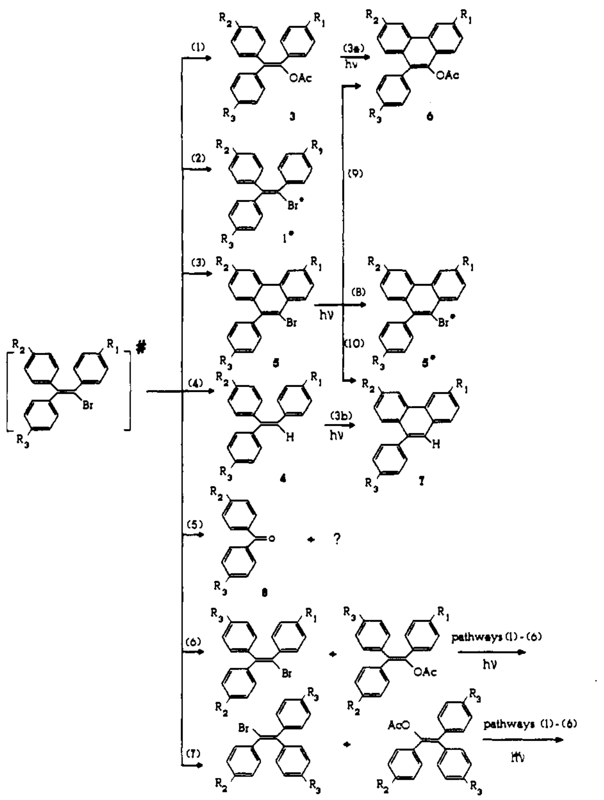
(28) Giese, B. *Angew. Chem.* **1977**, *89*, 162.
(29) Giese, B.; Keller, K. *Chem. Ber.* **1979**, *112*, 1743.

Scheme II



rickety basis, a rough estimate of the selectivity constant α for **2** can be made, yielding $\alpha_{h\nu} \approx 68 \pm 32$, a value of the same order of magnitude as that found for its thermal reaction.

In order to suppress the cyclization reaction, compound **2** was also irradiated in argon-saturated solution. ϕ_d is somewhat lower than and ϕ_c is only one quarter of the value measured in air atmosphere. Still no acetate formation is observed (Table II, entry 9).

Discussion

The data presented in the preceding section show that vinyl bromides **1** upon irradiation in acetic acid with or without added nucleophiles such as NaOAc and (labeled) Et_4NBr, disappear via seven different pathways as summarized in Scheme II.

In addition to the products from these primary pathways, several secondary photoproducts are found in the irradiated solutions. Although it appeared impossible to suppress the secondary reactions, also summarized in Scheme II, it turned out still to be possible to obtain reliable kinetic data for the primary photoreactions. Quantitative assessment of the secondary pathways learned that the phenanthrene acetates **6** are essentially photostable and are formed, quantitatively within experimental error, from the vinyl acetates **3**. In other words, formation of **6** via pathway 3 + 9 in Scheme II is negligible compared to formation via pathway 1 + 3a. This allows the quantum yield for the formation of acetates **3** to be calculated by monitoring the formation of both **3** and **6** as a function of time. Also (radioactive) bromide exchange of the bromophenanthrenes **5** (pathway 8 in Scheme II) is negligible compared to that of the vinyl bromides **1** (pathway 2 in Scheme II). This allows the calculation of ϕ_{ex} of compounds **1** by measuring the incorporation of radioactivity in the organic fraction of the irradiation mixture.

The relative importance of the primary pathways is represented by the quantum yields reported in Tables II (irradiations at room temperature in the presence of both NaOAc and Et_4NBr), III (effects of changes in the concentrations of the added nucleophiles), and IV (temperature effects).

Nucleophilic Substitution. Nucleophile Selectivity. The data in Table II show that nucleophilic substitution reactions are by far the most important pathways of disappearance of compounds **1**. Both for the α-anisyl- and α-phenyl-substituted compounds, substitution is quite efficient: 10–30% of electronically excited **1** is converted to vinyl acetates and labeled vinyl bromides. The vinyl acetates **3** can in principle be formed with either HOAc or NaOAc acting as the nucleophile. The data in Table III show that even in the absence of added NaOAc, some vinyl acetate is formed from compound **1d** ($\phi_{OAc} = 0.004$). Addition of NaOAc, however, strongly increases ϕ_{OAc} (0.068 at [NaOAc] = 87 × 10^{-3} M), and the vinyl acetate **3d** is the main primary product. This indicates that, in the presence of NaOAc, acetates are created from **1d** predominantly via reaction with NaOAc and not with HOAc. Thus, NaOAc and not HOAc is the capturing nucleophilic species. This is also the case in the thermal nucleophilic substitution reactions of α-anisylvinyl bromides.[17,30] An alternative explanation[31] of the effects of NaOAc presented in Table III could be that NaOAc acts as a "special" salt.[32a,b] In that case, solvent-separated ion pairs $R^+\|Br^-$ and $R^+\|OAc^-$ and not the free ion R^+ (see below) would be the intermediates with which NaOAc reacts and for which NaOAc and Et_4NBr compete. The small change in the quantum yield of exchange when NaOAc is added to a solution of **1d** and Et_4NBr in acetic acid seems to argue against this alternative. From the data in Table III and eq 14,

$$\phi = \phi_0(1 + b[\text{salt}]) \qquad (14)$$

the parameter of the salt effect of NaOAc is calculated to be 0.8 ± 0.3. Its magnitude is that of a "normal" salt effect.[32a,c] For NaOAc as a special salt, much larger effects would be expected.[32,33] Moreover, the value is—within experimental error—equal to b(NaOAc) = 1.4 ± 0.3 measured for the corresponding thermal reaction of **1a** under the same reaction conditions.[17] In the thermally induced reaction in $HOAc/NaOAc/Et_4NBr$, ≥94% of the substitution products have been shown to be formed from the free ion. This situation may not pertain, however, to the photoreaction in acetic acid in the absence of salts. Upon flash photolysis of compound **1d** in HOAc in the absence and in the presence of salts, formation of ions was only observed in the latter case.[6a]

When labeled Et_4NBr is present in the photoreaction mixture of **1a**–**1d**, an exchange of the radioactive label is observed, which is more efficient than acetate formation, leading to values of the selectivity parameters α of 26, 25, and 23 for **1a**, **1b**/**1c**, and **1d**, respectively. The quite similar values of α for the compounds **1a**–**1d**, all of which have an anisyl group as the α-substituent, show that the selectivity is mainly determined by the α-substituent and only to a small extent influenced by variation of the β-substituent, again as it is in the thermal reactions of the same compounds.[16,17]

The data in Table IV show that the quantum yields ϕ_d, ϕ_{ex}, and ϕ_{OAc} of compound **1a** increase with an increase in temperature. This indicates the presence of (an) energy barrier(s) on the pathways between the excited state and the products. As the measured enthalpy of activation is higher for acetate formation than for exchange, the former process becomes more important relative to the latter at higher temperatures and consequently the selectivity defined as k_{ex}/k_{OAc} decreases when the reaction temperature is increased. Presumably the temperature effect also exists in the case of the other α-arylvinyl bromides. As a point of general interest, it should be mentioned that although it seems quite logical that the selectivity factor decreases with increasing temperature, this is not in fact generally true. As eq 10 clearly shows, it is actually the relative magnitude of the enthalpies of activation for the two processes concerned that determines the dependence of the selectivity on the temperature. Several examples of selectivities increasing with temperature have been reported.[34,35]

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[30] (a) Rappoport, Z.; Apeloig, Y. *J. Am. Chem. Soc.* **1975**, *97*, 821. (b) Rappoport, Z.; Apeloig, Y.; Greenblatt, J. *J. Am. Chem. Soc.* **1980**, *102*, 3837.

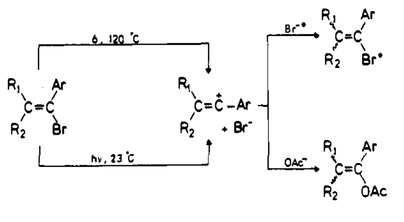
[31] We thank one of the reviewers for bringing this point to our attention.

[32] (a) Winstein, S.; Appel, B.; Baker, R.; Diaz, A. *Chem. Soc., Spec. Publ.* **1965**, *19*, 109. (b) Winstein, S.; Klinedinst, P. E.; Robinson, G. C. *J. Am. Chem. Soc.* **1961**, *83*, 885. (c) Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1956**, *78*, 2763.

[33] Cristol, S. J.; Noreen, A. L.; Nachtigall, G. W. *J. Am. Chem. Soc.* **1972**, *94*, 2187.

[34] Giese, B. *Acc. Chem. Res.* **1984**, *17*, 438.

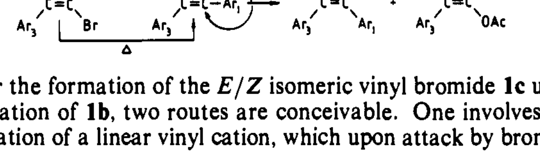
The selectivity values α of **1a**–**1d** calculated from ϕ_{OAc} and ϕ_{ex} are very close to the ones obtained in the corresponding thermal experiments. If the (small) temperature effect is taken into account via the use of eq 10, the extrapolated values for α in the photoreaction at 120 °C are in excellent agreement with the actually measured ones in the thermal experiments at 120 °C (Table V). This strongly suggests that, in the photochemical substitution reaction of α-arylvinyl bromides, an intermediate is involved that is identical with or very similar to the intermediate in the thermal experiments, i.e., a vinyl cation with all the properties of a thermally generated ion: free, "nonhot" (thermally relaxed), and linear[16] as depicted in eq 15. The same conclusion has been reached by Kitamura et al. on the basis of a study of degenerate β-aryl rearrangements of triphenyl-, tri-*p*-tolyl-, and tri-*p*-anisylvinyl bromides.[4k] The photochemically and thermally induced solvolytic rearrangements of these compounds occur in comparable extent.



(15)

An interesting point to note—already alluded to in the Introduction section—is that similarity of selectivities toward different nucleophiles in photochemically and thermally induced reactions is by no means a common feature. On the one hand, Cristol and Greenwald found similar selectivities toward methanol and 2-propanol for both the sensitized photosolvolysis and the silver-promoted thermal solvolysis of benzyl chloride.[12] McKenna and co-workers reported a comparable result for the nucleophilic capture ratio of methanol and water in the direct photolysis of the same compound.[13] On the other hand, Morrison and co-workers measured a selectivity factor for methanol vs water capture of 1.36 in the photosolvolysis of (the homobenzylic) *exo*-chlorobenzonorbornene, while in the ground-state reaction a ratio of 0.66 was found.[14] Cristol and co-workers note a difference in the selectivities toward water and methanol in the photoinduced and thermally induced solvolysis of methanesulfonate esters of (the homobenzylic) 3-(3,5-dimethoxyphenyl)-2-butanol.[15] Also quite recently Anderson and Yates reported a clear disparity in the selectivities for thermally and photochemically induced acid catalyzed nucleophilic additions to a range of substituted styrenes.[36]

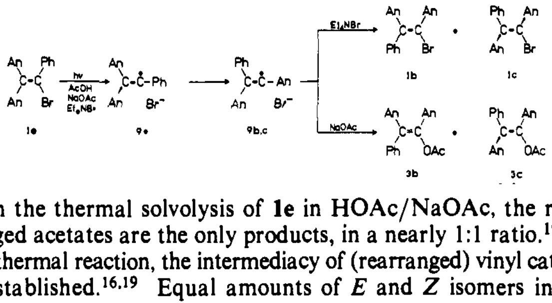
***E*/*Z* Isomerization.** Another feature of the photochemistry of triarylvinyl bromides is the occurrence of *E*/*Z* isomerization. Irradiation of, e.g., **1b** (*E* isomer), not only leads to the formation of **1c** (*Z* isomer) but also to two sets of products. However, already at very low conversion of **1b**, the ratio of the *E* and *Z* isomers in the vinyl acetates **3b** and **3c** is almost 1:1. This is in line with the vinyl acetates being formed via a linear intermediate, which shows no preference in the reaction with the attacking nucleophile NaOAc for producing either (*E*)- or (*Z*)-vinyl acetate (eq 16). Thermal experiments with **1b** under otherwise identical reaction conditions show a ratio of **3b**:**3c** = 52:48 for the vinyl acetates formed.[17] In these experiments, the occurrence of a linear vinyl cation is highly probable.



(16)

For the formation of the *E*/*Z* isomeric vinyl bromide **1c** upon irradiation of **1b**, two routes are conceivable. One involves the generation of a linear vinyl cation, which upon attack by bromide ion yields (*E*)- and (*Z*)-vinyl bromide; the other one implies direct photoisomerization around the carbon–carbon double bond without C–Br bond cleavage.

Rearrangement. Many aspects of the behavior of the α-phenyl-substituted compound **1e** upon irradiation in HOAc/NaOAc/Et$_4$NBr are similar to those of the α-anisyl-substituted compounds **1a**–**d**. Acetates, cyclization products, and (radioactive) bromide exchange products are formed. There is one large difference through. In the case of **1e**, β-anisyl rearrangement to the vinyl bromides **1b** and **1c** is the major pathway of disappearance. The quantum yield of this rearrangement process almost equals ϕ_d (Table II). As acetates, only rearranged acetates are detected. The ratio of the acetates **3b**:**3c** is approximately 1:1, even at low conversion of **1c**, at which stage the *E*/*Z* photoisomerization of **3b** and **3c** can still be neglected. The amounts of **3b** and **3c** as well as their ratio are determined at a stage in which the extent of the rearrangement of **1e** to **1b** and **1c** is still quite small. Therefore, it is assumed that the acetates **3b** and **3c** are not formed via a photoreaction of **1b** and **1c**. The observation of an anisyl 1,2-shift strongly supports the idea that vinyl cations are intermediates in the photochemical reaction of α-arylvinyl bromides in acetic acid. Such a shift is a well-known phenomenon in thermal vinyl cation chemistry.[16] Aryl 1,2-shifts across the double bond do not occur in vinyl radicals.[37] Since no nonrearranged products are found in the reaction mixture of **1e**, the 1,2-shift of the initially formed vinyl cation **9e** must be a much faster process than capture of **9e** by nucleophiles. The nucleophile capture products are formed from the rearranged vinyl cation **9b,c** as illustrated in eq 17.



(17)

In the thermal solvolysis of **1e** in HOAc/NaOAc, the rearranged acetates are the only products, in a nearly 1:1 ratio.[19] In the thermal reaction, the intermediacy of (rearranged) vinyl cations is established.[16,19] Equal amounts of *E* and *Z* isomers in the products derived from a vinyl cation imply not only the presence of free ions but also a linear geometry of the ions. Attack by the incoming nucleophile is then equally probable on either side of the ion.

Next to product formation, exchange is found during the irradiation of **1e** in acetic acid solutions. It is clear that the exchange reaction really measures the rate of formation of radioactive rearranged vinyl bromides (eq 17). ϕ_{ex} should therefore equal ϕ_{rearr}. However, a small difference between the values of ϕ_{ex} and ϕ_{rearr} is found (Table II). If this difference is significant, this means that some rearrangement occurs via vinyl cations that are not free ions.

The selectivity factor α determined for **1e** shows only a small difference in magnitude with the same parameter obtained for vinyl bromides **1b** and **1c** (Table II). This observation is easily explained on the basis of the reaction scheme depicted in eq 17. Irradiation of **1e** yields a rearranged vinyl cation, which is identical with the cation formed in the photoreaction of **1b**. Therefore, the selectivities in both photochemical reactions should be the same. The small difference found is either due to experimental error or to a small contribution of reaction via the nonrearranged cation. The latter explanation is less likely, as no nonrearranged acetates are found. The selectivity of an α-phenylvinyl cation such as **9e** is expected to be small in analogy with our data for the α-phenyl-substituted systems **1f** and **1g** (see below). The presumed nonoccurrence of an aryl 1,2-shift in vinyl radicals[37] cannot be checked in this system, as no reduction products are found.

The α-phenyl-substituted compounds **1f** and **1g** differ from **1e** in having a phenyl and an anisyl group instead of two anisyl groups

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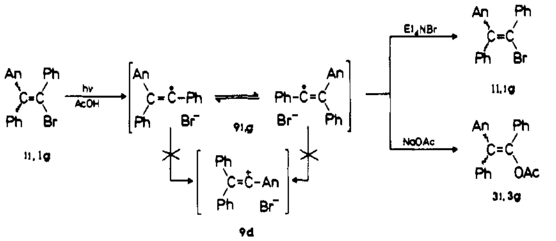
(35) (a) Mayr, H.; Schneider, R.; Grabis, U. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1017. (b) Mayr, H.; Schneider, R.; Grabis, U. *J. Am. Chem. Soc.* **1990**, *112*, 4460.

(36) Anderson, S. W.; Yates, K. *Can. J. Chem.* **1988**, *66*, 2412.

(37) Haynes, J. K.; Kampmeier, J. A. *J. Org. Chem.* **1972**, *37*, 4167.

at the β-position. This means that only a phenyl 1,2-shift will give rise to a nondegenerate rearrangement product. As Table II shows, irradiation of a 42:58 mixture of **1f** and **1g** in AcOH/NaOAc/Et_4NBr produces acetates much more efficiently than does **1e**, whereas the exchange reaction shows an opposite effect, yielding a much smaller value for the selectivity parameter ($\alpha = 2$) than for any of the other compounds reported upon here. The acetates formed are the nonrearranged acetates **3f** and **3g**. If any of the rearranged acetate **3d** is present in the reaction mixture, it is so in less than 3%. No rearranged vinyl bromide **1d** is detected. Combined with the low value ($\alpha = 2$) of the selectivity constant, which is not consistent with the intermediacy of α-anisylvinyl cation **9d** (for which a selectivity constant $\alpha = 23$ was determined), these data show that formation of the nucleophilic substitution products occurs through capture of the α-phenyl-substituted ion **9f,g** and that a phenyl 1,2-shift to the more stable ion **9d** does not occur under the conditions used (eq 18).



(18)

Thermal solvolysis of **1f** and **1g** in AcOH/AgOAc yields a mixture of the acetates **3f** and **3g** in a ratio of 45:55. No **3d** is found.[19] The ratio of **3f** to **3g** closely resembles the value found in the photochemical reaction of **1f** and **1g** at the lowest possible measurable conversion, i.e., 42:58. Once more the exact same chemical behavior is found in the thermally and photochemically induced reactions.

Capture of the primarily formed vinyl cation **9f,g** is apparently faster than the phenyl 1,2-shift yielding vinyl cation **9d**. In a laser flash photolysis study of compounds **1f** and **1g**,[4j] it was shown that β-phenyl rearrangement of **9f,g** to its more stable isomer **9d** does occur in acetonitrile and 2,2,2-trifluoroethanol, but that, in the more nucleophilic solvent ethanol, nucleophilic capture of the cation **9f,g** is faster than rearrangement to **9d**. In a study of degenerate β-aryl rearrangements in photochemically generated vinyl cations, the incidence of migration was also found to be dependent on the nucleophilicity of the solvent.[4k] Under the reaction conditions used here, the presence of the added potent nucleophiles NaOAc and Et_4NBr readily explains the nonoccurrence of the β-phenyl rearrangement of **9f,g** to **9d**. The much faster β-anisyl rearrangement of vinyl cation **9e** to **9b,c** (the An/Ph migration ratio is estimated to be 63)[19c,38] is not prevented by their presence. The present measurements do not permit conclusions with respect to the occurrence of a degenerate anisyl 1,2-shift. Rappoport and co-workers[19c]—through labeling of the β-phenyl group with deuterium—have shown that the anisyl 1,2-shift is an important process in the thermal solvolysis of **1f** and **1g** in solvent systems such as AcOH/AgOAc and 60% EtOH. Kobayashi[39] —through labeling of the β-carbon atom of the double bond with ^{13}C—found that, upon irradiation of a mixture of **1f** and **1g** in methanol, anisyl group migration occurs.

The similarity in the amount of rearrangement in the photochemically and thermally induced reactions of the vinyl halides studied is not found for alkyl halides.[2,11,14,15,40] Kropp and co-workers reported quite different amounts of rearrangement in the photoinduced and ground-state silver ion assisted methanolysis of 1-(iodomethyl)norbornane.[2b,40] Morrison and co-workers found that, upon irradiation of *exo*-2-benzonorbornenyl chloride in methanol, a rearranged substitution product is formed, which is not at all observed in the corresponding ground-state reaction.[14] Cristol and co-workers found complete retention of diastereomeric identity in the thermal solvolysis of the methanesulfonate esters of 3-(3,5-dimethoxyphenyl)-2-butanol but considerable diastereomixing in their photosolvolysis.[15]

Cyclization. The occurrence of *cis*-stilbene-type photocyclization reactions of both starting material and primary products has already been discussed in some detail in the Results section, and further discussion can be succinct. From the data in Table II, it is clear that these reactions are the most important pathway of disappearance competing with nucleophilic substitution. In fact, it is the only reliable observable photoreaction of vinyl bromide **2**, but for all compounds **1** even this most important side reaction plays only a minor role compared with the nucleophilic substitution reactions.

Reduction and Oxidation. Minor amounts of two further types of photoproducts have been detected, i.e., the reduction products **4** (with their cyclization products **7**) and the oxidation products **8**. With the exception of compound **1a**, where some reduction product was formed in the presence of oxygen, formation of the reduction and oxidation products is mutually exclusive. In the presence of oxygen, oxidation products are formed, and if oxygen is removed reduction products are detected. This strongly suggests that both types of products are formed from the same intermediate, believed to be a vinyl radical. The formation of the reduction products **4** from a vinyl radical would appear to be a quite straightforward process involving hydrogen abstraction, most probably from the solvent. Abstraction of hydrogen by a vinyl radical from an sp^3 carbon atom is 10–15 kcal mol^{-1} exothermic.[41] The fact that the reduction products are only formed in minor amounts is therefore not due to the thermodynamical infeasibility of the formation of such products from the vinyl radicals. The formation of (substituted) benzophenones from triarylvinyl radicals is clearly a more complicated process, which has been reported upon in detail in a previous paper from our laboratories.[6b] There the study of a vinyl bromide (9-(α-bromobenzylidene)fluorene) is reported for which the formation of radical products is a much more important pathway of disappearance than for all systems investigated here.

Substituent Effects. Comparison of the quantum yields listed in Table II for the vinyl bromides **1b,c** and **1f,g**, which differ only in their α-substituent (*p*-anisyl versus phenyl), shows that the nature of the α-substituent has a pronounced effect on the selectivity of the photogenerated vinyl cations ($\alpha = 25$ versus $\alpha = 2$). The better stabilized cation **9b,c** is more selective than the cation **9f,g**. Clearly these photogenerated vinyl cations do not behave according to Ritchie's rule of constant selectivity[42] but rather according to the reactivity–selectivity principle.[43] It has been proposed that such behavior means that the reaction of the cation with the more reactive nucleophile (in this case, Br^-) is diffusion-controlled, whereas the reaction with the less reactive nucleophile (in this case, ^-OAc) is activation-controlled.[43a,44] Only in the latter case the rate of the reaction depends on the substrate. Results of our flash photolysis study of **9d**[6a] show that it is quenched by Et_4NBr in acetic acid/3% H_2O[45] with a rate constant $k_q = 6 \times 10^9$ M^{-1} s^{-1}, which is indeed very close to the rate of a diffusion-controlled reaction in acetic acid ($k_{diff} \approx 6 \times 10^9$ M^{-1} s^{-1}).[46] An accurate value of k_q for quenching of **9d** with NaOAc in acetic acid/3% H_2O cannot be obtained, as the Stern–Volmer plot does not show a linear dependence on the quencher concen-

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[38] Lee, C. C.; Ko, E. C. F.; Rappoport, Z. *Can. J. Chem.* **1980**, *58*, 884.

[39] Kobayashi, S. Private communication.

[40] Kropp, P. J.; Poindexter, G. S.; Pienta, N. J.; Hamilton, D. C. *J. Am. Chem. Soc.* **1976**, *98*, 8135.

[41] Weast, R. C., Ed. *Handbook of Chemistry and Physics*, 66th ed.; CRC Press, Inc.: Boca Raton, FL, 1985; p F-185.

[42] (a) Ritchie, C. D. *Acc. Chem. Res.* **1972**, *5*, 348. (b) Ritchie, C. D. *Can. J. Chem.* **1986**, *64*, 2239.

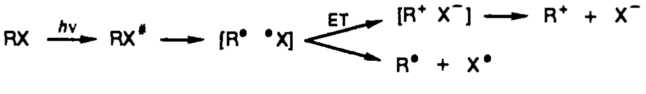
[43] (a) Ta-Shma, R.; Rappoport, Z. *J. Am. Chem. Soc.* **1983**, *105*, 6082. (b) Buncel, E.; Wilson, H. *J. Chem. Educ.* **1987**, *64*, 475. (c) Johnson, C. D. *Tetrahedron* **1980**, *36*, 3461.

[44] (a) Richards, J. P.; Rothenberg, M. E.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1361. (b) Richards, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1373.

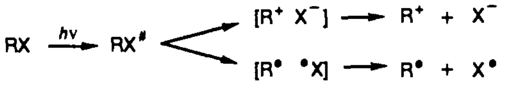
[45] Without the addition of water to acetic acid, no ionic transients are observed.[6a]

[46] Ridd, J. H. *Adv. Phys. Org. Chem.* **1978**, *16*, 1.

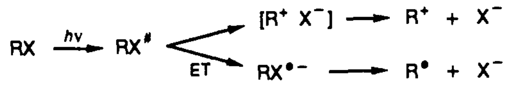
Scheme III



Scheme IV



Scheme V



tration. From the slope of the tangent of the curve at low concentrations of NaOAc though, a value of k_q on the order of 2×10^7 M^{-1} s^{-1} can be estimated.

A profound effect of the β-substituent on the ease of photoformation of vinyl cations is revealed by the differences between the quantum yields of compound **2** and those of compounds **1a–1d** (Table II). Upon replacement of the β-anisyl or β-phenyl groups by an anthronylidene group, ions virtually cease to be formed. The origin of the effect is not clear. It is not so that the replacement makes **2** overall photoinreactive. Its photocyclization still occurs with about the same efficiency as those of compounds **1a–1d**.

The nature of the α-substituent also has an effect on the ease of formation of vinyl cations; e.g., $\phi_{OAc} + \phi_{ex} = 24 \times 10^{-2}$ in the case of the α-anisyl-β,β′-(anisyl,phenyl)vinyl bromides **1b** and **1c** and 10×10^{-2} in the case of the α-phenyl-β,β′-(anisyl,phenyl)vinyl bromides **1f** and **1g**. The better stabilized cation **9b,c** is apparently formed more efficiently than cation **9f,g**. However, no complementarity in the yields of ionic products and radical products of compounds **1** can be detected. The decrease in the amount of ionic products on changing the α-substituent from *p*-anisyl to phenyl is not accompanied by an increase in the yield of radical products. This point brings us briefly to the question of the mechanism of formation of the vinyl radical and the vinyl cation. Most researchers[3,4,5,7] favor the mechanism depicted in Scheme III, in analogy with the mechanism proposed for simple alkyl halides.[2b] Initial homolysis of the carbon–halogen bond of the excited vinyl halide is followed either by electron transfer within a primarily formed radical pair, resulting in the formation of an ion pair that then may dissociate, producing a vinyl cation, or by direct diffusion apart of the components of the radical pair, producing a vinyl radical.

The validity of such a mechanism has, however, been questioned for benzyl halides,[47] in which not the carbon–halogen bond but rather an aromatic system serves as the chromophore. For such systems, the question has been raised whether or not a direct heterolytic cleavage of the carbon–halogen bond of the excited (benzyl) halide occurs, thus bypassing the radical pair stage that, in this proposal, would only lead to radical products (Scheme IV).

So far this question has not been answered satisfactorily,[11a] but it has been shown that the reaction pattern of benzyl[11] and naphthylmethyl halides[48] is much more complex than that of simple alkyl halides. As an alternative route for the formation of radicals in competition with cations, electron transfer to the excited RX has been proposed.[6b] The resulting radical anion rapidly yields a radical by expulsion of X$^-$ (Scheme V).

Evidence for the occurrence of such a mechanism has been obtained in a study of the photochemical behavior of α-phenyl-β,β-fluorenylidenevinyl bromide in methanol in the presence of sodium methoxide.[6b] An increase in the concentration of methoxide brings about an increase in the quantum yield of formation of the reduction product. Sodium methoxide acts as an electron donor.

The increased yield of ionic product in the photoreaction of compounds **1** upon changing the α-substituent in **1** from phenyl to *p*-anisyl, i.e., upon the possibility of formation of a more stabilized vinyl cation, is compatible with all schemes. The above noncomplementarity of yields of products derived from the vinyl cation and the vinyl radical, however, argues against a mechanism for vinyl halides—which also possess an extended chromophore—in which the ions and radicals are formed from a common radical pair precursor (Scheme III) but is in line with a mechanism in which ions and radicals are formed directly from an electronically excited state of **1** (Scheme IV) and with a mechanism in which cations and radical anions are formed directly from excited **1** (Scheme V). Further research on this subject is in progress in our laboratories.

Conclusion

In this study, we have been concerned with the quantitative photochemical behavior of a series of α-aryl-substituted vinyl bromides and have probed the nature of the reactive intermediates involved in their nucleophilic photosubstitution reactions. The compounds **1** exhibit the same behavior in both photochemically and thermally induced nucleophilic photosubstitution reactions, both with respect to selectivity toward different nucleophiles and with respect to their propensity for rearrangement and *E*/*Z* isomerization. We therefore conclude that the photochemically and thermally induced reactions proceed via exactly the same intermediate, a thermally relaxed linear free vinyl cation.

Experimental Section

Procedure. All irradiations were carried out in a cylindrical Pyrex reaction vessel, in which a quartz tube was immersed. This quartz tube contained a Hanau TQ81 high-pressure mercury arc with a Pyrex cover glass, surrounded by a glass spiral tube through which cooling water was pumped, and a filter solution consisting of 0.025 M potassium biphthalate, 1.0 M $NiSO_4$, and 0.25 M $CoSO_4$ in water, which only transmits the light of the 313-nm line of the high-pressure mercury arc.[49] The optical path length in the filter solution was 6.7 mm; in the reaction vessel, it was 0.65 mm.

The concentrations of the vinyl bromides were invariably 4.7×10^{-3} M. If NaOAc and $[^{82}Br]Et_4NBr$ were present in the reaction mixtures, they were so in concentrations of 87×10^{-3} M and 71×10^{-3} M, respectively. The volume of the reaction solution was 55 mL.

In the cases when irradiations were carried out in an atmosphere other than air, the solutions were presaturated with argon or nitrogen (ca. 45 min) and the gas was bubbled through continuously during the experiment.

The cylindrical reaction vessel was placed in a water bath, which made it possible to perform the irradiations at different temperatures.

The progress of the reactions was followed by removing 0.5-mL samples from the reaction solution at appropriate intervals. These samples were added to 10.0 mL of hexane, which contained a known amount of anisole as internal standard for the HPLC analysis. After it was carefully washed with 10 mL of a saturated $NaHCO_3$ solution and with 10 mL of water to remove the inorganic bromide, 4.0 mL of the hexane solution was analyzed for radioactivity incorporation and 20 μL of the hexane solution was injected into an HPLC column for analysis of product formation and disappearance of starting material. The total amount of radioactivity added was determined by measuring unwashed samples.

For all compounds studied, control experiments at room temperature in the dark showed that neither product formation nor radioactive bromide exchange occurs thermally under the standard reaction conditions, not even in periods 10–20 times longer than the usual irradiation times.

Kinetics. The quantum yields were obtained from the kinetic eqs 5, 6, and 7 after least-squares treatment. The quantum yields for acetate

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(47) (a) Cristol, S. J.; Stull, D. P.; Daussin, R. D. *J. Am. Chem. Soc.* **1978**, *100*, 6674. (b) Cristol, S. J.; Daussin, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 2866.

(48) (a) Slocum. G. H.; Schuster, G. B. *J. Org. Chem.* **1984**, *49*, 2177. (b) Arnold, B.; Donald, L.; Jurgens, A.; Pincock, J. A. *Can. J. Chem.* **1985**, *63*, 3140.

(49) (a) The filter solution also transmits a small part of the 334-nm emission line of the high-pressure mercury arc. As this emission is much less intense then the 313-nm line, the transmitted light is essentially monochromatic of the wavelength 313 nm. (b) Although the filter solution is not photostable,[50] no change in its transmission of light could be detected during irradiation times of up to 10 h, which is 5 times the maximum reaction time, when a Pyrex cover glass of the lamp was used. Nevertheless, fresh filter solutions were used in each new experiment.

(50) Venigopalam, M.; Pritchard, G. O.; Miller, G. H. *Nature* **1963**, *200*, 568.

formation were obtained from eq 6 by monitoring both the concentrations of the vinyl acetates **3** and their secondary photoproducts, the phenanthrene acetates **6**. The values of n_t and n_∞, which represent the specific activity of compound **1*** at time *t* and at equilibrium, if no process next to exchange would have occurred, were corrected for radioactive decay in the conventional fashion. Please note that the quantum yields of disappearance ϕ_d are not corrected for the degenerate process of bromide exchange.

In the case of vinyl bromide **1e**, the incorporation of radioactive bromide does not represent the usual degenerate exchange process but rather the formation of the rearranged compounds **1b** and **1c**. ϕ_{ex} was therefore calculated via eq 12 from data obtained at lowest possible conversion.

For actinometry, the photolysis of 3-nitroanisole in an aqueous 0.1 M NaOH solution, which occurs with a quantum yield of 0.22 (corrected for both internal and external filter effects) at 313 nm,[51] was performed in the same reaction vessel under the same conditions as the photochemical experiments under study.[52] The 3-nitroanisole concentration was 3.5×10^{-3} M, and the reaction was carried out in water/methanol (90:10). The values of the light flux I_0 so determined were introduced in eqs 6, 7, 8, and 12.

All irradiations were performed in triplicate. The values of the quantum yields and selectivity constants reported are average values; the error (i.e., deviation from the mean) is 5–10%.

Equipment. HPLC analyses were carried out with a system consisting of a (Kipp 9208) pump, an (Kipp 9202) UV detector (254 nm), and a column packed with (Partisil 5) silica, either 15 cm/4.6 mm or 20 cm/9.6 mm. The pump was equipped with a (Rheodyne 7120) sample valve (20-μL loop), and the output of the UV monitor was integrated with an (Becker 7021) analogue integrator. The eluents used were 1.5–20% THF in hexane. The response of the system was calibrated with use of standard solutions of the starting material and the products.

Radioactivity measurements of the 0.77 MeV γ-emission of ^{82}Br were conducted with a Philips scintillation counter with a 3 × 3 in. well-type thallium-activated sodium iodide crystal.

UV spectroscopy was performed in *n*-hexane/2% $CHCl_3$ on a (Perkin-Elmer 124) spectrophotometer, and NMR spectra were recorded in $CDCl_3$ or CCl_4 with a (Jeol JNM-PS 100) spectrometer. Low-resolution electron impact (EI) mass spectrometry was carried out with a (Kratos MS-9/50) mass spectrometer and high-resolution EI mass spectrometry with a V.G. Micromass ZAB-HFqQ mass spectrometer, an instrument with reverse geometry, fitted with a high-field magnet and coupled to a V.G. 11/250 data system. During the high resolution EIMS measurements, a resolving power of 15 000 (10% valley definition) was used.

Purification of Reagents and Solvents. Sodium acetate (Baker) and tetraethylammonium bromide (Fluka) were analytical grade and used as such. Acetic acid (from 1% acetic anhydride[53]), THF (from $LiAlH_4$), and hexane were distilled before use.

Synthesis of Starting Materials. The vinyl bromides **1a**–**1d** and **2** were available from a previous study.[17] The syntheses and spectral data of these compounds have been reported: 1-bromo-1,2,2-tris(*p*-methoxyphenyl)ethene (**1a**),[54,55] (*E*/*Z*)-1-bromo-1,2-bis(*p*-methoxyphenyl)-2-phenylethene (**1b,c**),[53] 1-bromo-1-(*p*-methoxyphenyl)-2,2-diphenylethene (**1d**),[55] and 9-(α-bromo-*p*-methoxybenzylidene)anthrone (**2**).[56] The vinyl bromides **1e**–**1g** were synthesized according to literature procedures via bromination and dehydrobromination of the corresponding ethylene compounds: 1-bromo-2,2-bis(*p*-methoxyphenyl)-1-phenylethene (**1e**)[19b,57] and (*E*/*Z*)-1-bromo-2-(*p*-methoxyphenyl)-1,2-diphenylethene (**1f,g**).[19b,58] The preparation of [^{82}Br]Et_4NBr by neutron irradiation of Et_4NBr has already been reported.[17] The irradiations were performed at the Interfaculty Reactor Institute in Delft, The Netherlands.

Identification of Products. The reaction products of the irradiations of the vinyl bromides were isolated by adding hexane or chloroform to the reaction mixtures, washing with a saturated $NaHCO_3$ solution and water, drying ($MgSO_4$), filtering, and evaporating the solvent. The residues were separated into their components by column chromatography with silica type 60 (0.063–0.2-mm particle size) as adsorbant and mixtures of hexane and $CHCl_3$ as eluent. In some cases, semipreparative HPLC or TLC was used. The products were identified on the basis of their NMR, mass, and UV spectra and their HPLC retention times. In many cases, the reaction products could be compared with authentic samples. Of these, 4,4′-dimethoxybenzophenone (**8a**), 4-methoxybenzophenone (**8b**), and benzophenone (**8d**) were commercially available and 1,2,2-tris(*p*-methoxyphenyl)ethene (**4a**), (*E*/*Z*)-1,2-bis(*p*-methoxyphenyl)-1-phenylethene (**4b,c**), 2-(*p*-methoxyphenyl)-1,1-diphenylethene (**4d**), 1,1-bis(*p*-methoxyphenyl)-2-phenylethene (**4e**), and (*E*/*Z*)-1-(*p*-methoxyphenyl)-1,2-diphenylethene (**4f,g**) were intermediate products in the syntheses of the corresponding compounds **1** (see above). Compounds **3** were prepared by refluxing a solution of the corresponding vinyl bromides **1** in acetic acid in the presence of an excess of silver acetate.[19a,53,54] Their spectral data are in agreement with those reported in the literature: 1-acetoxy-1,2,2-tris(*p*-methoxyphenyl)ethene (**3a**),[54] (*E*/*Z*)-1-acetoxy-1,2-bis(*p*-methoxyphenyl)-2-phenylethene (**3b,c**),[19a,53] 1-acetoxy-1-(*p*-methoxyphenyl)-2,2-diphenylethene (**3d**),[19a] and (*E*/*Z*)-1-acetoxy-2-(*p*-methoxyphenyl)-1,2-diphenylethene (**3f,g**).[19a] Compounds **6** and **7** were prepared by independent photocyclization of the compounds **3** and **4**, respectively. The spectral data are listed below.

9-Bromo-3,6-dimethoxy-10-(*p*-methoxyphenyl)phenanthrene (5a): UV λ_{max} 253 nm (ϵ 48 500), 261 (49 100), 288 (23 800), 304 (14 200), 313 (15 000), 352 (3200), 370 (2800); ^{1}H NMR δ 3.92 (s, 3 H, OCH_3), 4.00 (s, 3 H, OCH_3), 4.05 (s, 3 H, OCH_3), 7.01–7.43 (m, 3 H, ArH, AA′BB′, 4 H, AnH), 7.96–8.01 (2 d, 2 H, H-4, H-5), 8.42 (d, 1 H, H-8); MS *m*/*z* (relative intensity) 424, 422 (M^+, 100, 100), 409, 407 ($M^+ - CH_3$, 12, 12); high-resolution MS *m*/*z* 422.0521 ($C_{23}H_{19}O_3Br$ requires 422.0518).

9-Bromo-3,6-dimethoxy-10-phenylphenanthrene (5b): UV λ_{max} 255 nm (ϵ 45 700), 262 (49 300), 288 (17 400), 302 (11 600), 315 (13 200), 335 (3300), 353 (1700), 370 (2000); ^{1}H NMR δ 4.00 (s, 3 H, OCH_3), 4.06 (s, 3 H, OCH_3), 7.10–7.50 (m, 8 H, ArH), 7.96–8.02 (2 d, 2 H, H-4, H-5), 8.42 (d, 1 H, H-8); MS *m*/*z* (relative intensity) 394, 392 (M^+, 100, 100), 379, 377 ($M^+ - CH_3$, 23, 23), 270 (26), 255 (18), 227 (26), 226 (30); high-resolution MS *m*/*z* 392.0408 ($C_{22}H_{17}O_2Br$ requires 392.0412).

10-Bromo-3-methoxy-9-(*p*-methoxyphenyl)phenanthrene (5c): UV λ_{max} 253 nm (ϵ 45 800), 260 (48 400), 300 (12 500), 312 (14 700), 344 (1600), 362 (1600); ^{1}H NMR δ 3.92 (s, 3 H, OCH_3), 4.06 (s, 3 H, OCH_3), 7.02–7.54 (m, 8 H, ArH, in which centered at 7.17 ppm, AA′BB′, 4 H, AnH), 8.10 (d, 1 H, H-4), 8.45 (d, 1 H, H-1), 8.63 (br d, 1 H, H-5); MS *m*/*z* (relative intensity) 394, 392 (M^+, 100, 100), 379, 377 ($M^+ - CH_3$, 15, 15), 270 (14), 255 (27), 227 (27), 226 (39); high-resolution MS *m*/*z* 392.0413 ($C_{22}H_{17}O_2Br$ requires 392.0412).

10-Bromo-3-methoxy-9-phenylphenanthrene (5d): UV λ_{max} 260 nm (ϵ 51 500), 278 (27 600), 298 (18 400), 310 (14 300), 342 (1700), 359 (1700); ^{1}H NMR δ 4.04 (s, 3 H, OCH_3), 7.24–7.70 (m, 9 H, ArH), 8.06 (d, 1 H, H-4), 8.40 (d, 1 H, H-1), 8.58 (br d, 1 H, H-5); MS *m*/*z* (relative intensity) 364, 362 (M^+, 100, 100), 349, 347 ($M^+ - CH_3$, 14, 14), 283 ($M^+ - Br$, 9), 268 (16), 240 (77), 239 (85); high-resolution MS *m*/*z* 362.0310 ($C_{21}H_{15}OBr$ requires 362.0306).

9-Acetoxy-3,6-dimethoxy-10-(*p*-methoxyphenyl)phenanthrene (6a): UV λ_{max} 251 nm (ϵ 44 100), 258 (45 200), 288 (21 800), 298 (11 100), 308 (11 200), 352 (1400), 371 (1500); ^{1}H NMR δ 2.09 (s, 3 H, CH_3), 3.90 (s, 3 H, OCH_3), 4.01 (s, 3 H, OCH_3), 4.03 (s, 3 H, OCH_3), 6.97–8.01 (m, 10 H, ArH, in which centered at 7.16 ppm, AA′BB′, 4 H, AnH); MS *m*/*z* (relative intensity) 402 (M^+, 33), 361 (30), 360 (M^+ − ketene, 100), 345 (M^+ − ketene − CH_3, 30), 331 (13), 243 (15); high-resolution MS *m*/*z* 402.1460 ($C_{25}H_{22}O_5$ requires 402.1467).

9-Acetoxy-3,6-dimethoxy-10-phenylphenanthrene (**6b**) was identified by comparing its HPLC retention time with that of the photocyclization product of vinyl acetate **3b**.

10-Acetoxy-3-methoxy-9-(*p*-methoxyphenyl)phenanthrene (6c): UV λ_{max} 256 nm (ϵ 43 200), 275 (18 000), 294 (10 700), 306 (11 000), 342 (1200), 359 (1200); ^{1}H NMR δ 2.09 (s, 3 H, CH_3), 3.90 (s, 3 H, OCH_3), 4.04 (s, 3 H, OCH_3), 7.16 (AA′BB′, 4 H, AnH), 7.21–7.69 (m, 4 H, ArH), 7.80 (d, 1 H, H-1), 8.10 (d, 1 H, H-4), 8.40 (br d, 1 H, H-5); MS *m*/*z* (relative intensity) 372 (M^+, 20), 331 (23). 330 (M^+ − ketene, 100), 316 (18), 315 (M^+ − ketene − CH_3, 15), 288 (13); high-resolution MS *m*/*z* 372.1350 ($C_{24}H_{20}O_4$ requires 372.1362).

10-Acetoxy-3-methoxy-9-phenylphenanthrene (6d): UV λ_{max} 256 nm (ϵ 45 800), 277 (14 200), 294 (9300), 306 (10 700), 342 (1300), 358 (1300); ^{1}H NMR δ 2.08 (s, 3 H, CH_3), 4.02 (s, 3 H, OCH_3), 7.20–7.64 (m, 9 H, ArH), 7.74 (d, 1 H, H-1), 8.03 (d, 1 H, H-4), 8.56 (br d, 1 H, H-5); MS *m*/*z* (relative intensity) 342 (M^+, 12), 301 (21), 300 (M^+ − ketene, 100), 285 (M^+ − ketene − CH_3, 6), 271 (15), 255 (10), 239 (21), 228 (23), 226 (31); high-resolution MS *m*/*z* 342.1250 ($C_{23}H_{18}O_3$ requires 342.1256).

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9-Acetoxy-3-methoxy-10-phenylphenanthrene (6f) and 9-Acetoxy-10-(*p*-methoxyphenyl)phenanthrene (6g) were identified on the basis of their HPLC retention times in comparison with those of the products from the separately performed photocyclization of the vinyl acetates **3f** and **3g**.

3,6-Dimethoxy-9-(*p*-methoxyphenyl)phenanthrene (7a): UV λ_{max} 246 nm (ϵ 20 600), 275 (11 900), 300 (8500), 350 (4300), 368 (4000); ^{1}H NMR δ 3.90 (s, 3 H, OCH_3), 4.03 (s, 6 H, 2 OCH_3), 6.98–8.03 (m, 11 H, ArH); MS *m/z* (relative intensity) 344 (M^+, 100), 329 ($M^+ - CH_3$, 42), 301 ($M^+ - CH_3 - CO$, 13); high-resolution MS *m/z* 344.1421 ($C_{23}H_{20}O_3$ requires 344.1412).

3-Methoxy-9-phenylphenanthrene (7d): UV λ_{max} 253 nm (ϵ 36 300), 277 (14 200), 308 (10 500), 342 (1700), 358 (1600); ^{1}H NMR δ 3.85 (s, 3 H, OCH_3), 6.65–7.81 (m, 11 H, ArH), 7.93 (s, 1 H, H-4), 8.54 (d, 1 H, H-5); MS *m/z* (relative intensity) 284 (M^+, 100), 269 ($M^+ - CH_3$, 21), 241 ($M^+ - CH_3 - CO$, 16), 240 (24), 239 (58), 226 (16); high-resolution MS *m/z* 284.1213 ($C_{21}H_{16}O$ requires 284.1201).

13-Bromo-3-methoxy-8-oxonaphtho[2,3,4-*de*]anthracene (10): UV λ_{max} 229 (ϵ 40 200), 265 (39 400), 291 (18 700), 304 (17 500), 376 (12 400), 393 (13 300), 413 (15 000); ^{1}H NMR δ 4.08 (s, 3 H, OCH_3), 7.26–8.04 (m, 5 H, ArH), 8.41–9.08 (m, 5 H, ArH); MS *m/z* (relative intensity) 390, 388 (M^+, 100, 100), 375, 373 ($M^+ - CH_3$, 4, 4), 347, 345 ($M^+ - CH_3 - CO$, 11, 11); high-resolution MS *m/z* 388.0099 ($C_{22}H_{13}O_2Br$ requires 388.0089).

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Stable 2-Vinylsiliranes

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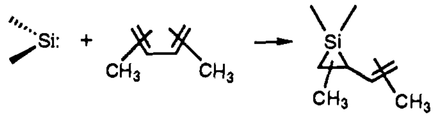
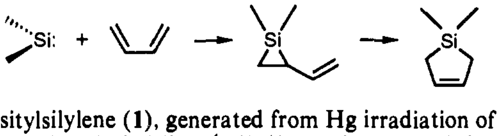
Contribution from the Center for Organometallic Research and Education, Department of Chemistry, University of North Texas, Denton, Texas 76203. *Received June 4, 1990. Revised Manuscript Received February 1, 1991*

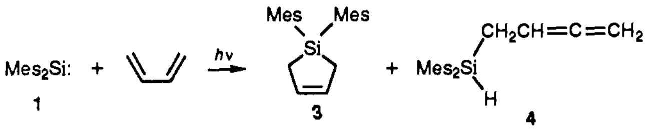
Abstract: Seven 2-vinyl-1,1-dimesitylsiliranes, stable at room temperature over months, have been synthesized from the addition of dimesitylsilylene to 2,3-dimethylbutadiene, 2-methylbutadiene, *trans,trans*-2,4-hexadiene, *cis,cis*-2,4-hexadiene, and *cis,-trans*-2,4-hexadiene. Addition of dimesitylsilylene to the π bond of the diene was stereospecific as indicated by ^{29}Si NMR. Secondary photodecomposition of 2-vinylsiliranes containing a vinylic hydrogen α to the silirane ring led to 2,3-dienylsilanes. Formation of *cis*-2,5-dimethyl-1,1-dimesitylsilacyclopent-3-ene from photolysis of solutions containing *trans,trans*-2,4-hexadiene, 2,2-dimesitylhexamethyltrisilane, and *trans*-2-methyl-3-(1-*trans*-propenyl)-1,1-dimesitylsilirane was stereospecific.



Dienes have long been the reagents of choice for detecting the presence the silylenes from a wide variety of thermal, photochemical, and bimolecular sources in both solution- and gas-phase experiments.[1] In most earlier studies the products have been silacyclopentenes although it has been suggested that these five-membered silacycles likely originate from secondary isomerization of the initial 1,2-adduct, a transient 2-vinyl-1-silirane.[2,3] Herein, we report preparation of seven vinylsiliranes from the addition of dimesitylsilylene to various 1,3-dienes as well as the stereoselectivity and stereospecificity of these reaction paths.



Dimesitylsilylene (**1**), generated from Hg irradiation of hexamethyl-2,2-dimesityltrisilane[4] (**2**) (0.1 M in pentane) for 3 h in a solution saturated with butadiene, afforded dimesitylsilacyclopent-3-ene (**3**) and 2,3-butadienyldimesitylsilane (**4**) in ~1:1 ratio.



At shorter photolysis times the same two products, **3** and **4** were again formed in a similar distribution. The isolation of **4**, a product observed once previously[3a] in earlier studies of thermal and photochemical silylene/diene reactions,[5] suggested that the initial adduct, a 2-vinylsilirane, might be sufficiently long-lived to undergo secondary photolysis to the allenylsilane.

Exploring this suggestion, we have investigated the possibility that other dienes bearing methyl substituents on the π bond might lead to less ephemeral 2-vinylsiliranes. When 2,3-dimethylbutadiene was the trapping agent for the silylene and the photolysis was monitored by ^{1}H NMR (Chart I) two new sets of signals attributable to **5a** appeared in the olefinic region as a doublet at δ 4.47 and a multiplet centered at δ 4.55 after 2-h photolysis.

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