Electronic and Conformational Effects in the Photochemistry of α-Alkenyl-Substituted Vinyl Halides

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The photochemical reactions in methanol of the vinylic halides 2-halo-1-phenyl-1,3-butadienes **1−3Z-X** (β-halo-β-alkenylstyrenes) and 1-halo-1,2-diphenylethenes **4Z-X** (α-halostilbenes), with X = Cl or Br, have been studied quantitatively. *E*/*Z* isomerization, dehydrohalogenation, nucleophilic substitution, a [1,3]-halogen shift, a [1,3]-hydrogen shift, and oxidation are observed as the primary reactions. No reductive dehalogenation products are formed. The efficiencies of product formation are dependent on the halogen used, the electron-donating capacity of the α-substituent, the ground state conformation of the starting material, and the wavelength of excitation. Apart from the photoinduced *E*/*Z* isomerization and the oxidation reaction typical for alkenes, product formation occurs exclusively via vinyl−cationic intermediates, which are formed upon photolytic cleavage of the carbon−halogen bond. These ionic species, or part of them, are present as vinyl cation/halide anion-pairs.

Introduction

One of the fascinating features of the photochemistry of vinyl halides is the formation of nucleophilic substitution products in competition with reductive dehalogenation products.[1] It is presumed that the nucleophilic substitution products are formed via photogeneration of a vinyl cation, which is subsequently trapped by the nucleophile present. In the case of triarylvinyl bromides, it has been shown that the nature of the photogenerated vinyl cation is the same as that of the ion involved in thermal nucleophilic substitution reactions. Both the extent of β-aryl rearrangement[2] and the selectivity toward different nucleophiles[3] are the same in photochemically and thermally induced reactions.

Vinyl cations are interesting reactive intermediates,[4] and their photogeneration has been investigated and applied in many studies.[5] At present the amount of information about the effects of substrate structure and reaction conditions on the photoreactivity of vinyl halides as vinyl cation precursors is still limited. Mainly data about the ratio of radical- to ion-derived products as a function of the nature of the halogen as leaving group[6,7] and the α-substituent (hydrogen[6], methyl,[7] and phenyl[2,3]) are available. Scarce examples are also known of the solvent[6b,7,8] and the wavelength of irradiation[9] directing the photoreaction.

Thus far, mainly α-arylvinyl halides have been used as substrates. Vinyl halides in which the α-aryl substituent is replaced by an α-ethenyl group may also yield cationic intermediates. On the basis of the general trend that ground state rules seem to prevail in the photoreactions of vinyl halides,[10] the α-alkenyl substituent is expected to influence the photoreactivity of vinyl halides in a similar manner as an α-phenyl group, in view of the comparable magnitude of their inductive and resonance parameters.[11]

In addition to this electronic substituent effect, a conformational dependence may be present as well. Introduction of the additional double bond makes the vinyl halide a 1,3-diene. Polyenes are known to show a ground-state-conformation dependent photoreactivity, known as the NEER (nonequilibration of excited rotamers) principle.[12] Although the NEER principle is formulated for photocyclization reactions of trienes in which no charged intermediates are involved, it is possible that such a correlation also exists in the photoreactions of 2-halo-1,3-butadienes. The introduction of an α-ethenyl substituent makes the vinyl halide also an allyl halide. The photochemical characteristics of allyl halide chromophores have already been extensively investigated by Cristol and co-workers.[13]

The thermal S_N1 solvolysis reactions of 2-bromo-1,3-butadienes have been investigated by Grob and co-

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[1] For reviews, see: (a) Lodder, G. In *The Chemistry of Halides, Pseudohalides and Azides*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1983; pp 1605−1681. (b) Kropp, P. J. *Acc. Chem. Res.* **1984**, *17*, 131−137.

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

[3] van Ginkel, F. I. M.; Cornelisse, J.; Lodder, G. *J. Am. Chem. Soc.* **1991**, *113*, 4261−4272.

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

[5] (a) For a comprehensive list of references of the photogeneration of vinyl cations from vinyl halides, see: van Ginkel, F. I. M.; Cornelisse, J.; Lodder, G. *J. Am. Chem. Soc.* **1991**, *113*, 4261−4272, refs 1−7. (b) For the photogeneration of vinyl cations via protonation of substituted acetylenes, see: McEwen, J.; Yates, K. *J. Phys. Org. Chem.* **1991**, *4*, 193−206, and references therein.

[6] (a) Kropp, P. J.; McNeely, S. A.; Davis, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 6907−6915. (b) Sket, B.; Zupan, M. *J. Chem. Soc., Perkin Trans. 1* **1979**, 752−756.

[7] Kitamura, T.; Kobayashi, S.; Taniguchi, H. *J. Org. Chem.* **1982**, *47*, 2323−2328.

[8] (a) Sonawane, H. R.; Nanjundiah, B. S.; Udaykumar, M.; Panse, M. D. *Ind. J. Chem.* **1985**, *24B*, 202−203.

[9] Verbeek, J. M.; Cornelisse, J.; Lodder, G. *Tetrahedron* **1986**, *42*, 5679−5684.

[10] Verbeek, J. M.; Stapper, M.; Krijnen, E. S.; van Loon, J.-D.; Lodder, G.; Steenken, S. *J. Phys. Chem.* **1994**, *98*, 9526−9536.

[11] For phenyl: σ_p^+ −0.18, σ_R −0.08, R^+ − 0.30, σ_I 0.10−0.15, and F 0.12. For ethenyl: σ_p^+ −0.16, σ_R −0.01, R^+ −0.29, σ_I 0.07−0.11, and F 0.13. Data from Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−195.

[12] (a) Jacobs, H. J. C.; Havinga, E. *Adv. Photochem.* **1979**, *11*, 305−373. (b) Laarhoven, W. H. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1987; Vol. 9, Chapter 2. (c) Brouwer, A. M.; Cornelisse, J.; Jacobs, H. J. C. *J. Photochem. Photobiol., A: Chem.* **1988**, *42*, 117−126.

[13] (a) Cristol, S. J.; Lee, G. A. *J. Am. Chem. Soc.* **1969**, *91*, 7554−7555. (b) Cristol, S. J.; Lee, G. A.; Noreen, A. L. *Ibid.* **1973**, *95*, 7067−7074. (c) Cristol, S. J.; Micheli, R. P. *J. Org. Chem.* **1975**, *40*, 667−672. (d) Cristol, S. J.; Micheli, R. P. *J. Am. Chem. Soc.* **1978**, *100*, 850−855. (e) Cristol, S. J.; Braun, D.; Schloemer, G. C.; Vanden Plas, B. J. *Can. J. Chem.* **1986**, *64*, 1081−1084.

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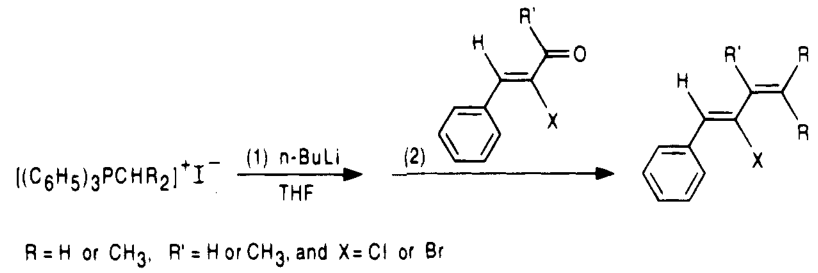
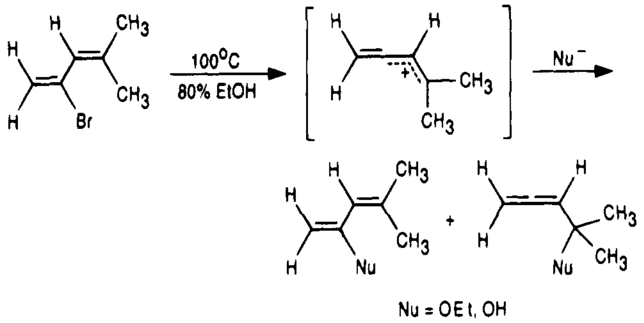
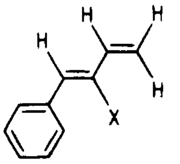
Scheme 1



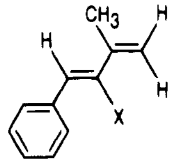
workers.[14] It was found that nucleophilic substitution occurs on both the 1- and 3-position of the mesomeric vinyl cation. Methyl substitution at the terminal carbon atom of the α-alkenyl group in the vinyl halide strongly increases the reactivity of the diene compounds.



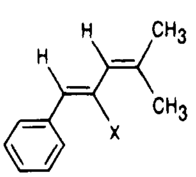
In this paper we report the quantitative study of the photoreactivity in methanol of the series of 1-phenyl-2-halo-1,3-butadienes **1**−**3** (X = Cl, Br) in which the α-alkenyl group is modified by methyl substitution. To compare the effect of the α-alkenyl substituent with that of the α-phenyl group, the α-halostilbenes **4** were investigated under the same reaction conditions. The photochemical reactions of compounds **4** have been studied in solvents of low polarity, such as cyclohexane and diethyl ether.[15]



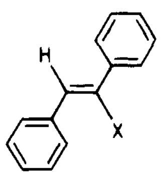
1Z - X



2Z - X



3Z - X



4Z - X

with X = Cl or Br

Results

The 1-phenyl-2-halo-1,3-butadienes **1**−**3** were synthesized via a Wittig reaction of the corresponding α-halogenated aldehyde or ketone (Scheme 1). For compounds **1Z-X** and **3Z-X**, the starting material was the commercially available α-chloro- or α-bromocinnamaldehyde. The α-halo ketone needed to prepare compounds **2Z-X** was synthesized from 1-phenyl-1-buten-3-one via halogenation in tetrachloromethane, followed by dehydrohalogenation using triethylamine as base. In all cases the *Z*-isomer of the 2-halo diene compound was obtained. Attempts to synthesize, via the same route, the diene system with a trimethyl-substituted terminal double bond failed. Compounds **4Z-X** were synthesized according to literature procedures,[16] via halogenation of stilbene with the appropriate halogen in tetrachloromethane and subsequent dehydrohalogenation with sodium hydroxide in ethanol.

Irradiation of the *Z*-isomers of compounds **1**−**4** in methanol with the light of a high-pressure mercury arc leads to the formation of the mixtures of photoproducts depicted in Schemes 2 and 3. A representative example of the product distribution is given in Table 1 for the irradiation of compounds **1Z-Cl** and **1Z-Br** at λ_{exc} = 313 nm. Seven types of photoproducts are formed, six of which are primary. The latter can be rationalized to arise from the excited state of the starting material through reactions 1−6 depicted in the schemes: *E*/*Z* isomerization (reaction 1); dehydrohalogenation, leading to 1-buten-3-yne (reaction 2A) and 1,2,4-pentatriene (reaction 2B) type products; nucleophilic trapping by the solvent leading to *E*- and *Z*-isomers of **10**, **11**, **13**, and **15** and to 1,2-butadiene type products (reactions 3E, 3Z, and 3R, respectively); a [1,3]-halogen shift (reaction 4); a [1,3]-hydrogen shift (reaction 5); and oxidation by oxygen (reaction 6). The oxidation products benzaldehyde and methyl benzoate were not formed when the reaction was carried out under an argon atmosphere. The rate of the photoreaction did not change upon exclusion of oxygen. 9-Chlorophenanthrene (**19-Cl**) is formed as a secondary photoproduct in the irradiation of compound **4Z-Cl**. The product arises through *E*/*Z* isomerization of **4Z-Cl** followed by photochemical ring closure and oxidation of **4E-Cl** (reactions 1 and 7).[17] Both in air- and argon-saturated solutions reductive dehalogenation products are not formed.

The quantum yields of disappearance of starting material and formation of products were determined at λ_{exc} = 313 nm in methanol. In all cases the data for the rates of disappearance of halo diene and formation of products

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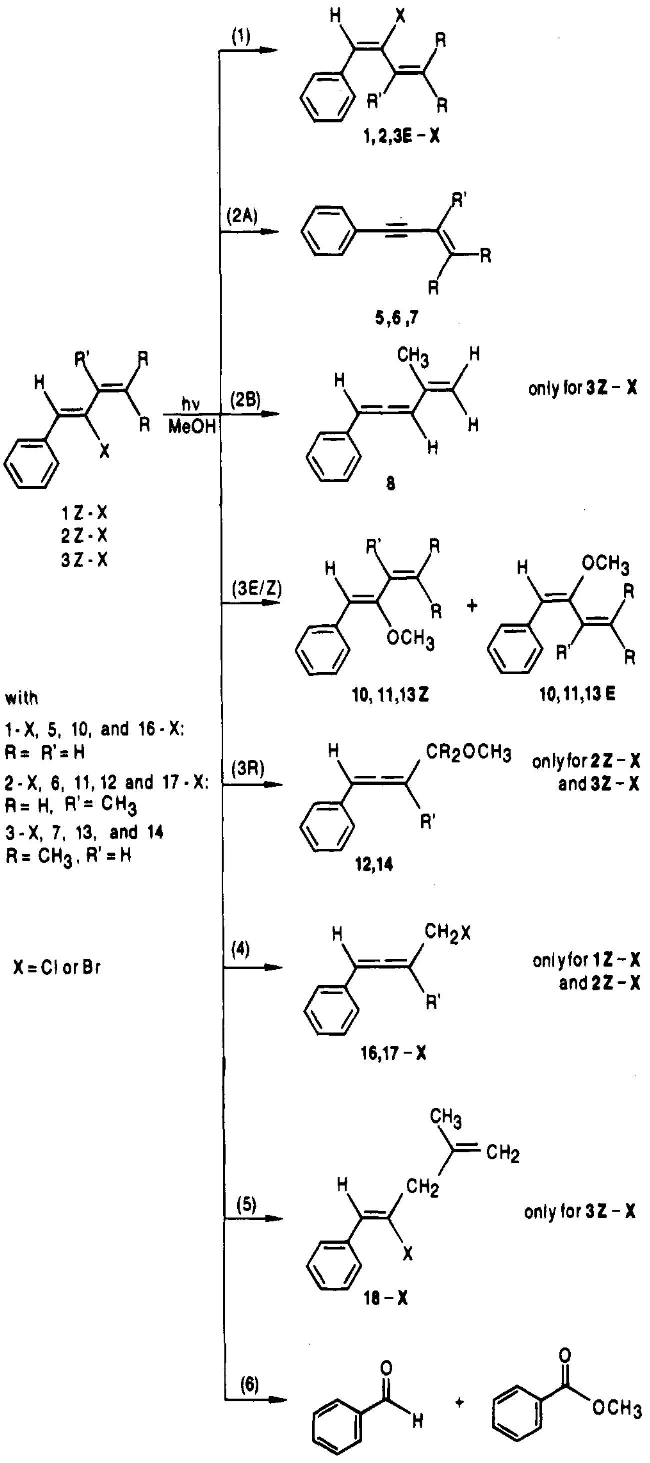
[14] (a) Grob, C. A.; Spaar, R. *Tetrahedron Lett.* **1969**, 1439−1442. (b) Grob, C. A.; Spaar, R. *Helv. Chim. Acta* **1970**, *53*, 2119−2129. (c) Grob, C. A.; Pfaendler, H. R. *Ibid.* **1970**, *53*, 2130−2134.

[15] Sket, B.; Zupan, M. *Collect. Czech. Chem. Commun.* **1978**, *43*, 3396−3403.

[16] (a) Compound **4Z-Cl**: Cristol, S. J.; Bly, R. S. *J. Am. Chem. Soc.* **1960**, *82*, 142−145. (b) Compound **4Z-Br**: Wislicenus, J.; Seeler, F. *Chem. Ber.* **1895**, *28*, 2693−2703.

[17] For reviews of the *cis*-stilbene-type photocyclization, see: (a) Laarhoven, W. H. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 185−204; 241−254. (b) Mallory, F. B.; Mallory, C. W. *Org. React.* **1984**, *30*, 1−456.

Scheme 2



could be fitted according to the previously reported[3,18] kinetic equations (1 and 2). Meeting the conditions of constancy of the quantum yields of all reactions involved, complete absorption of the incident light, and constancy of the absorbance of the reaction mixture,[18] the decrease of starting material RX can be written as

$$\ln [\mathrm{RX}]_t/[\mathrm{RX}]_0 = -k_d t = -\Phi_d t I_0/[\mathrm{RX}]_0 \qquad (1)$$

and the formation of product P as

Scheme 3

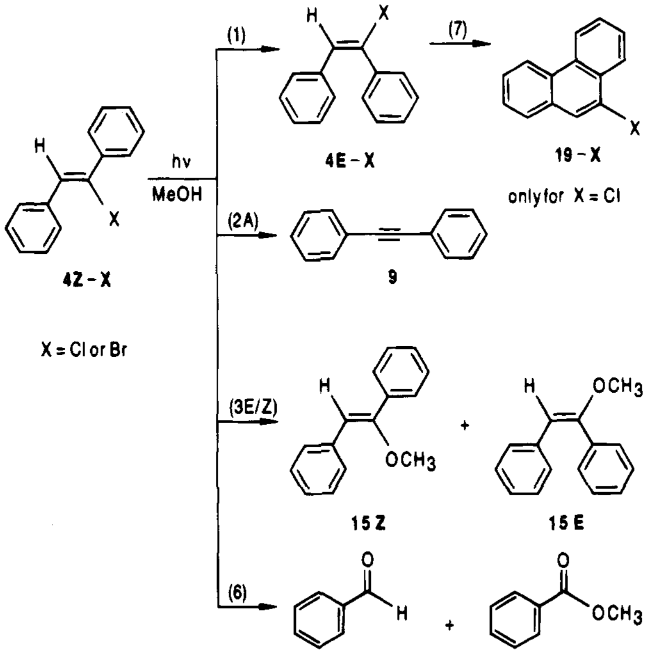


Table 1. Product Distributions (%) in the Irradiation (λ_{exc} = 313 nm) of Compounds 1Z-X in methanol (X = Cl or Br)

RX	1Z	1E	5	10Z	10E	16	oxidation
1Z-Cl	36	16	12	0.8	1	24	1
1Z-Br	9	3	23	0.8	1	48	4

$$[\mathrm{P}]_t = \Phi_x I_0(1 - e^{-k_d t})/k_d \qquad (2)$$

In these equations $[\mathrm{RX}]_t$ represents the concentration of the vinyl halide (RX) in the reaction mixture at time t, k_d is the rate constant of the disappearance of RX, t is the time of irradiation, Φ_d is the quantum yield of the decrease of RX, I_0 is the intensity of the light absorbed by the starting material at time $t = 0$ in einstein L^{-1} s^{-1}, $[\mathrm{P}]_t$ is the concentration of product P in the photolysis mixture at time t, and Φ_p is the quantum yield of formation of product P. The quantum yields of disappearance of starting material and of formation of products are listed in Table 2. In the table and in the text the following will be used: Φ_d, quantum yield of disappearance of starting material; $\Phi_{E/Z}$, quantum yield of *E*/*Z* isomerization; Φ_{-HX}, quantum yield of dehydrohalogenation; Φ_{Nu}, quantum yield of nucleophilic substitution; $\Phi_{[1,3]X}$, quantum yield of [1,3]-halogen shift; $\Phi_{[1,3]H}$, quantum yield of [1,3]-hydrogen shift; and Φ_{Ox}, quantum yield of oxidation.

Reactive Intermediates. To investigate which of the photoproducts are possibly formed through a radical intermediate, vinyl radicals of **1Z-Br**, **3Z-Cl**, and **4Z-Br** were generated using $n\mathrm{Bu_3SnH}$ in refluxing toluene and 2,2'-azobis(2-methyl-propionitrile) (AIBN) as initiator.[19] The reactions were carried out under an argon atmosphere to prevent reaction with oxygen.[20] The main products (over 80%) from the radical intermediates were the *E*-isomers of the reductive dehalogenation products (e.g. Scheme 4). No formation of dehydrohalogenation products **5**, **7**, **8**, or **9** was observed. The products were

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[18] van Ginkel, F. I. M.; Cornelisse, J.; Lodder, G. *J. Photochem. Photobiol. A: Chem.* **1991**, *61*, 301–315.

[19] Neumann, W. P. *Synthesis* **1987**, 665–683.

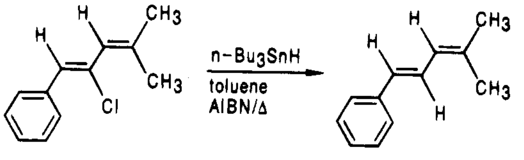
[20] Oxygen had to be removed from the solvent prior to addition of the reagents. This was achieved by refluxing the toluene overnight under an argon atmosphere.

Table 2. Quantum Yields ($10^2\Phi$) of Disappearance of Starting Material and Product Formation of Compounds 1–4 in Methanol at λ_{exc} = 313 nm[a]

			Φ_{-HX}		Φ_{Nu}					
RX	Φ_d	$\Phi_{E/Z}$	A[b]	B[b]	E[b]	Z[b]	R[b]	$\Phi_{[1,3]X}$	$\Phi_{[1,3]H}$	Φ_{Ox}
1Z-Cl	14	9	1		0.08[c]	0.06[c]		2		0.1[c]
1Z-Br	21	5	2		0.1[c]	0.08[c]		6		0.5[c]
2Z-Cl	11	8	1		0.06[c]	0.02[c]	0.1[c]	1		0.1[c]
2Z-Br	59	~12[d]	9		1.0[c]	0.3[c]	~5[d]	25		2
3Z-Cl	33	17	3	5	0.2[c]	0.1[c]	2		6	0.1[c]
3Z-Br	29	9	4	7	0.7	0.5[c]	7		2	0.3[c]
4Z-Cl	34	25	4		0.8	0.2				0.7[c]
4Z-Br	73	24	28		5.4	3.7				2

[a] No other low molecular weight products are found. [b] The product types derive from (A) dehydrohalogenation leading to 1-buten-3-yne-type products; (B) dehydrohalogenation leading to 1,2,4-pentatriene type products; (E and Z) nucleophilic substitution by the solvent forming the *E*- or the *Z*-isomer; (R) nucleophilic substitution by the solvent leading to 1,2-butadiene-type products. [c] Estimated values, calculated from product ratios at longer irradiation times. Product ratios for nucleophilic substitution and oxidation products remain constant in time. [d] Compounds **2E-Br** and **12** are not distinguishable under the GC conditions used. On the basis of GC-MS analyses product ratios could be calculated and quantum yield values estimated.

Scheme 4



3Z-Cl 3E-H

identified by comparison of their GC retention times and mass spectra with those of authentic compounds, independently prepared in the case of **1E-H** and **3E-H**.[21]

The photochemical behavior of compounds **1Z-Cl** and **3Z-Br** was also investigated in tetrahydrofuran. This excellent hydrogen-atom donating solvent was chosen to facilitate the trapping of radicals, in case they were produced in the photolysis of the vinyl halides. The reaction was carried out under an argon atmosphere to prevent scavenging of any radical species by oxygen. The products detected were the *E*-isomers **1E-Cl** and **3E-Br**, the dehydrohalogenation products **5**, **7**, and **8**, and the [1,3]-rearranged products **16-Cl** and **18-Br**. No reductive dehalogenation products were found.

Nanosecond laser flash photolysis experiments[22] with compound **3Z-Br** yielded no evidence for the occurrence of radical or cationic reactive intermediates. Acetonitrile, trifluoroethanol, and hexafluoro-2-propanol were used as solvents. No transients were observed, not even in the highly polar nonnucleophilic solvent hexafluoro-2-propanol.[23]

Reactive Excited State. Triplet sensitization of compounds **1Z-Cl** and **3Z-Br** in methanol using xanthone (E_T = 74 kcal/mol[24]) as sensitizer resulted only in *E*/*Z* isomerization of the starting material and formation of small amounts of benzaldehyde and methyl benzoate. No products from [1,3]X-shifts or rearrangements to cyclopropyl halides, as in the case of triplet sensitization of simple allylic halides,[13] were observed. Attempts to investigate directly the involvement of the singlet excited state were thwarted by the absence of any fluorescence after excitation of compound **1Z-Cl** or **3Z-Br** in methanol and tetrahydrofuran at various wavelengths.

Table 3. Quantum Yields ($10^2\Phi$) of Disappearance of Starting Material and Product Formation of Compounds 1Z-Cl, 3Z-Cl, and 4Z-Br in Methanol at λ_{exc} = 254 nm[a]

			Φ_{-HX}		Φ_{Nu}					
RX	Φ_d	$\Phi_{E/Z}$	A[b]	B[b]	E[b]	Z[b]	R[b]	$\Phi_{[1,3]X}$	$\Phi_{[1,3]H}$	Φ_{Ox}
1Z-Cl	58	39	7		nd[c]	nd		11		nd
3Z-Cl	60	23	8	7	nd	nd	4		10	nd
4Z-Br	99	36	33		5.1	5.5				7

[a] No other low molecular weight products are found. [b] Product types, see Table 2 and text. [c] nd = not detected under the experimental conditions used (confer footnote c in Table 2).

Table 4. Product Distributions (%) in the Thermal (Δ, *T* = 135 °C) and Photochemical (*hν*, λ_{exc} = 313 nm) Solvolysis of 3Z-X in Methanol at Comparable Conversion

	conversion		7		8		14	
RX	Δ	*hν*	Δ	*hν*	Δ	*hν*	Δ	*hν*
3Z-Cl	55	57	3	11		16	1	5
3Z-Br	70	61	30	24	9	17	3	16

Wavelength Dependence. For compounds **1Z-Cl**, **3Z-Cl**, and **4Z-Br**, the quantum yields of disappearance and product formation were also determined upon irradiation at λ_{exc} = 254 nm in methanol (Table 3). Comparison of these results with those presented in Table 2 (λ_{exc} = 313 nm) shows that all products are formed more efficiently at the shorter wavelength but that there is no appreciable difference in product ratios.

Thermal Reactions. Thermal solvolysis reactions of compounds **1Z-Cl**, **3Z-Cl**, and **3Z-Br** were also investigated. No reaction was observed after 6–8 h of reflux in methanol (*T* = 65 °C). At *T* = 135 °C **1Z-Cl** was still unreactive, but **3Z-Cl** and **3Z-Br** solvolyzed in methanol.[25] The time needed for conversion of **3Z-Cl** (3 h) is about nine times as long as for **3Z-Br**. As products the dehydrohalogenation products **7** and **8** and the nucleophilic substitution product **14** (Table 4) were detected. Products **8** and **14** partially decompose under the reaction conditions used.

MO Calculations. The ground state conformations, heats of formation ($\Delta H°_f$), LUMO coefficients, and charge distributions of the starting materials (**1Z-X**, **2Z-X**, **3Z-X**, and **4Z-X**) and the corresponding cationic reactive intermediates were investigated by semiempirical calculations using the PM3 Hamiltonian.[26] The results are presented in the Discussion section.

Discussion

The α-alkenyl substituted compounds **1–3** show six reactions upon photoexcitation in methanol: 1, *E*/*Z* isomerization; 2, dehydrohalogenation; 3, nucleophilic substitution; 4, a [1,3]-halogen shift; 5, a [1,3]-hydrogen shift; and 6, oxidation by oxygen. The α-phenyl substi-

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(21) The synthesis of these reference compounds was performed in the same way as the preparation of compounds **1** and **3**, using the hydrogen analogue of the α-halo aldehyde as starting material.

(22) These experiments were performed at the Max-Planck-Institut für Strahlenchemie, Mülheim a.d. Ruhr, Germany, in cooperation with Prof. Dr. S. Steenken and Dr. J. L. Faria.

(23) McClelland, R. A.; Chan, C.; Cozens, F.; Modro, A.; Steenken, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1337–1339.

(24) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; p 33.

(25) These experiments were performed in sealed vials, submerged in an oil bath of the appropriate temperature.

(26) (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209–220; (b) 221–264.

Table 5. Quantum Yield Ratios[a] (as Percentages) for the Irradiations of Compounds 1–4 in Methanol at λ_{exc} = 313 nm and λ_{exc} = 254 nm

	313 nm		254 nm	
X	$\Phi_{E/Z}/\Phi_d$	Φ_{ion}/Φ_d	$\Phi_{E/Z}/\Phi_d$	Φ_{ion}/Φ_d
1Z-Cl	64	22	67	31
2Z-Cl	73	20		
3Z-Cl	52	49	38	48
4Z-Cl	74	15		
1Z-Br	24	39		
2Z-Br	29	60		
3Z-Br	31	73		
4Z-Br	33	51	36	44

[a] Φ_{ion} is defined as $\Phi_{ion} = \Phi_{-HX} + \Phi_{Nu} + \Phi_{[1,3]X} + \Phi_{[1,3]H}$.

tuted compounds **4** show reactions 1, 2, 3, and 6. Reductive dehalogenation does not occur. The relative importance of the reactions is represented by the quantum yields presented in Tables 2 and 3 and the quantum yield ratios in Table 5.

***E/Z* Isomerization.** Reaction 1 is the photochemical *E/Z* isomerization normal to alkenes.[27,28] Compounds **1–3** contain two C–C double bonds, which can both *E/Z* isomerize; only isomerization around the C(1)–C(2) double bond is detectable. Singlet isomerization in 1,3-dienes is reported to involve only one double bond as in alkenes, whereas the reaction originating from the triplet state involves both double bonds. The latter process is proposed to proceed via a long-lived 1,4-biradical intermediate. The absence of any biradical-derived (e.g. ring-closed) products in our experiments indicates that reaction 1 originates from the S_1 excited state. The quantum yield ratios $\Phi_{E/Z}/\Phi_d$ and Φ_{ion}/Φ_d (defining $\Phi_{ion} = \Phi_{-HX} + \Phi_{Nu} + \Phi_{[1,3]X} + \Phi_{[1,3]H}$) for the compounds **1–4** (Table 5), show that the ratio $\Phi_{E/Z}/\Phi_d$ for the chloro-substituted compounds is close to 0.6, whereas the bromo analogues show a ratio of 0.3. On the other hand Φ_{ion}/Φ_d which represents the fraction of product forming processes from the excited state through the bond breaking reactions 2–5 is lower for the chloro compounds than for the bromo analogues. *E/Z* isomerization and bond breaking processes seem to be in direct competition, indicating that they originate from the same (singlet) excited state.

Formation of Vinyl Cations. 1. General. Reactions 2, 3, 4, and 5 are all best envisioned to proceed via the ionic mechanism depicted in Scheme 5. Heterolytic cleavage of the carbon–halogen bond of the electronically

Scheme 5

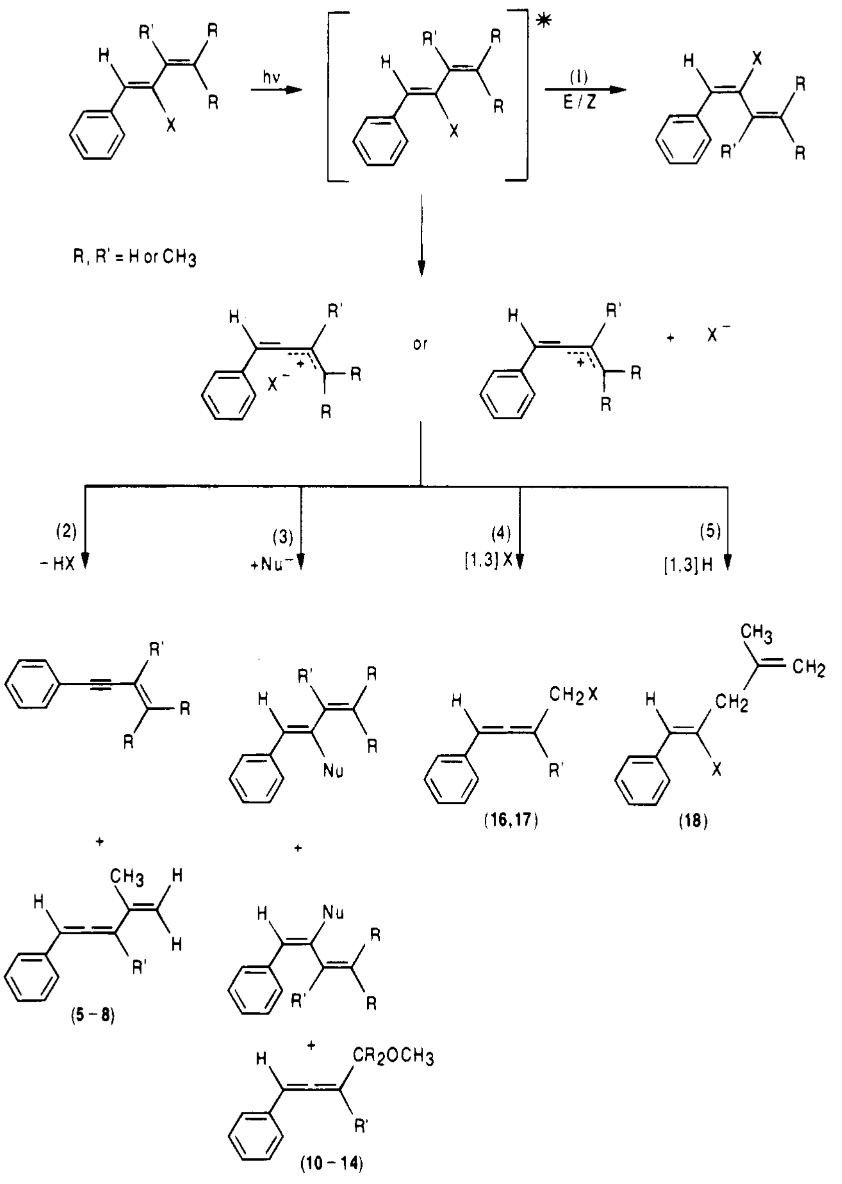

Table 6. PM3-Calculated Heats of Formation (ΔH°_f) of Compounds 1Z-X–4Z-X and of Their Corresponding Cations and Heterolytic Bond Dissociation Energies (BDE)[a] (in kcal/mol)

RX	ΔH°_f(RX)	ΔH°_f(cation)	BDE
1Z-Cl	49.1	276.6	173.3
1Z-Br	63.0	276.6	162.9
2Z-Cl	41.1	266.9	171.6
2Z-Br	54.9	266.9	161.3
3Z-Cl	31.0	243.8	158.6
3Z-Br	45.0	243.8	148.1
4Z-Cl	57.9	275.9	163.8
4Z-Br	72.2	275.9	153.0

[a] BDE = ΔH°_f(cation) + ΔH°_f(X^-) − ΔH°_f(RX).

excited halo diene yields a halide anion and a vinyl cation, which may be present as an ion-pair or as free ions. The vinyl cation intermediates are stabilized by a double bond (compounds **1**–**3**) or a phenyl group at the α-position (compound **4**).

As will be discussed below in greater detail, the cations yield the dehydrohalogenation products **5**–**9** via loss of a proton (reaction 2) and the nucleophilic substitution products **10**–**15** via reaction with a nucleophile (reaction 3). Also recombination of the cations with the halide anion can occur which either produces starting material or the [1,3]-halogen rearranged products **16** and **17** (reaction 4). Still another rearrangement is possible in the vinyl cations derived from compounds **3**. In that case, transfer of a methyl proton, followed by recombination of the resulting vinyl cation and the halide anion, gives the [1,3]-hydrogen shift rearranged product **18** (reaction 5).

2. Leaving Group Effect. In all cases the bromo-substituted compounds react more efficiently via the ionic pathways 2, 3, 4, and 5 (Table 2) than the chloro compounds. The energy required to form the cation from the ground state vinyl bromide or chloride (the heterolytic bond dissociation energy (BDE)) is equal to the difference between the heats of formation of the vinyl halides and their corresponding cations and anions. From the heats of formation of the chlorine and bromine radicals (29.0 and 26.7 kcal/mol,[29] respectively), and their electron affinities (83.2 and 77.4 kcal/mol[30]), one calculates for the heats of formation of the anions $\Delta H^\circ_f(Cl^-) = -54.3$ and $\Delta H^\circ_f(Br^-) = -50.7$ kcal/mol. The data in Table 6 show that gas phase heterolysis is 10–11 kcal/mol more favorable for the vinyl bromides than for the chlorides. Taking into account that the solvation energy of the chloride anion in methanol is about 6–7 kcal/mol[31] larger than that of bromide, heterolytic cleavage of the carbon–bromine bond still is about 4 kcal/mol more favored than that of the carbon–chlorine bond. Clearly the displayed leaving group effect in the photoreactions under study is similar to the effect expected in thermal S_N1 reactions.

3. Substituent Effect. In the series of α-alkenyl-substituted compounds **1**–**3**, the ratio Φ_{ion}/Φ_d decreases in the order **3** > **2** > **1** for both the chloro- and bromo-substituted compounds. This means that a cation is formed more efficiently from vinyl halide **3** than from **2** or from **1**. What factors can be responsible? One suggestion is that as in the case of the leaving group effects, behavior according to ground state rules prevails. The vinyl cation derived from **3** is better stabilized through resonance (involving a tertiary carbon atom) than the cation from **1** (involving a primary carbon atom). This is corroborated by the data in Table 6 which show that the ΔH°_f values of the cations parallel the efficiency of their photochemical formation.

Table 7. Experimental[a] and Calculated[b] UV Absorption Maxima (nm) of 1–3

RX	λ_{max}(exp)	RX	λ_{max}(exp)	λ_{max}(calc)
1Cl	282	**1Br**	282	282
2Cl	273	**2Br**	273	287
3Cl	274	**3Br**	276	292

[a] Experimental values in methanol. [b] Calculated according to the Woodward–Fieser rules using λ_{max} of compound **1** as the base value.[32]

Another factor could be the conformation of the excited state of the dienes. To get maximum stabilization of the cation, the α-alkenyl group has to be rotated out of the plane of the conjugated diene system. The less rotation is needed, the better heterolytic cleavage can compete with other deactivation pathways of the excited state.

Examination of the ultraviolet absorption spectra of the halo dienes **1**–**3** shows a remarkable shift in the position of the absorption maxima (Table 7). This shift is not in the expected direction (the more methyl substituted the π-system, the longer the wavelength), but the other way around. This means that the halo dienes studied already are less than fully conjugated before excitation, i.e. are already somewhat rotated around the C–C single bond of the diene system. If, after a Franck–Condon transition, reaction is faster than rotation (NEER principle[12]) the already rotated α-substituent double bond has to undergo less motion to stabilize the vinyl cation than the α-carbon–carbon double bond in a planar diene. The more overlap between the π-orbital of the α-alkenyl substituent and the incipient empty p orbital prior to excitation, the better the stabilization along the pathway to the resulting vinyl cation. Thus, a kind of anchimeric assistance gives rise to a higher Φ_{ion}/Φ_d ratio. In ground state chemistry the sensitivity of π-conjugative stabilization of allylic carbocations on conformation is a well-known phenomenon.[33]

Semiempirical PM3 calculations support this idea of nonplanar ground state conformations. The optimized ground state structures of compounds **1**–**3** (Table 8) show an increase in the torsion angle between the alkene substituent and the C–C double bond of the vinyl halide (ζ_2) upon increased methyl substitution. This is in agreement with the UV data. The small effect on the torsion angle between the phenyl group and the C–C double bond of the vinyl halide system (ζ_1) is due to the size of the halogen substituent. ^{1}H NMR NOE experiments on **3** show through-space coupling of H-1 and the methyl protons on the α-ethenyl substituent. This is in

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(27) Saltiel, J.; D'Agostino, J.; Megarity, E. D.; Metts, L.; Neuberger, K. R.; Wrighton, M.; Zafiriou, O. C. In *Organic Photochemistry*; Chapman, O. L., Ed.; Marcel Dekker: New York, 1973; Vol. 3, Chapter 1.

(28) Liu, R. S. H.; Butt, Y. *J. Am. Chem. Soc.* **1971**, *93*, 1532–1534.

(29) Egger, K. W.; Cocks, A. T. *Helv. Chim. Acta* **1973**, *56*, 1516–1536.

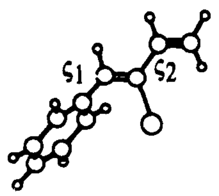
(30) *CRC Handbook of Chemistry and Physics*, 72nd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, 1991; Table 10–180.

(31) (a) Landolt-Börnstein. *Numerical data and functional relationships in science and technology*; Hellwege, K.-H., Ed.; Springer Verlag: Berlin, 1976; Group IV, Vol. 2, Chapter 3.3. (b) Table 5–2 in ref 30.

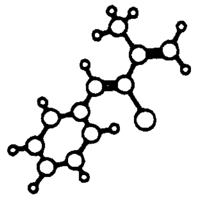
(32) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 5th ed.; John Wiley and Sons: New York, Chichester, Brisbane, Toronto, Singapore, 1991; p 298.

(33) Takeuchi, K.; Kitagawa, T.; Ohga, Y.; Yoshida, M.; Akiyama, F.; Tsugeno, A. *J. Org. Chem.* **1992**, *57*, 280–291, and references therein.

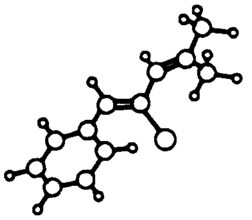
Table 8. PM3-Calculated Torsion Angles ζ_1 and ζ_2 of Compounds 1–4 and Their Cations in the Ground State[a]



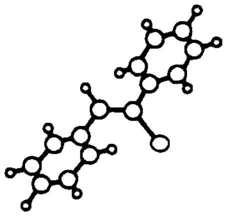
1	ς1	ς2
Cl	45°	3°
Br	52°	3°
cation [b]	5°	90°



2	ς1	ς2
Cl	46°	39°
Br	51°	37°
cation [b]	7°	90°



3	ς1	ς2
Cl	43°	61°
Br	51°	74°
cation [b]	5°	90°



4	ς1	ς2
Cl	44°	42°
Br	51°	40°
cation [b]	4°	90°

[a] The angle ζ_1 is defined as the angle between the plane of the phenyl group and the plane of the central C–C double bond and ζ_2 as the angle between the planes of the two double bonds. [b] The hybridization of C(2) is sp, i.e., the vinyl cation is linear.

line with the PM3-calculated geometry. The distance between the two positions is 4–5 Å. In a planar diene system the protons at the 1 and 5 positions would be too far apart to show any NOE enhancement.[34]

PM3 calculations of the ground state of the resulting cations show all cations to have the same geometry. The α-alkenyl double bond is fully conjugated with the empty p orbital ($\zeta_2 = 90°$) and the β-phenyl group is in better conjugation with the central C–C double bond (ζ_1 ~5°) than in the vinyl halide.

Rates also increase upon increased methyl substitution of the α-alkenyl group in the thermal solvolysis experiments. The halo dienes **3** solvolyse at $T = 135$ °C in methanol; **1** does not. Grob and Spaar found a similar effect with 4,4′-dimethyl-2-bromo-1,3-butadiene, which reacts more than 10^4 times as fast in 80% ethanol as the unsubstituted compound.[14b] The rate increase was partially ascribed to steric hindrance of planarity, which raises the ground state energy of the halo diene. Another factor invoked is the difference in stability of the resulting cations. This is borne out by the calculated $\Delta H°_f$ values of the ions (Table 6).

The vinyl halides **1–3** substituted with an α-alkenyl group are overall less photoreactive than those with an α-phenyl substituent (**4**), as can be seen from the quantum yields of disappearance of starting materials presented in Table 2. In part this might be due to deactivation of the excited states of **1–3** through a nondetectable *E*/*Z* isomerization of the α-alkenyl double bond. On the other hand, the α-alkenyl vinyl halides produce vinyl cations more efficiently in the product-forming reactions 2–5 (i.e. the pathways in which the carbon–halogen bond is broken) than their α-phenyl analogues do, especially when the methyl substitution increases (Φ_{ion}/Φ_d in Table 5).

4. Reactive Excited State. Reactions 2, 3, 4, and 5 solely occur upon direct irradiation. Triplet sensitization gave only *E*/*Z* isomerization (and some oxidation of the starting material, vide infra). Exclusion of oxygen did not change the rate of the direct photoreaction. As already discussed above, *E*/*Z* isomerization in the direct irradiation experiments is ascribed to occur from the singlet excited state. Both the lack of formation of C–X bond cleavage products from the triplet manifold and the oxygen noneffect indicate that all product-forming reactions 1–5 originate from a singlet excited state. The photolysis reactions of 1,1-diaryl-2-halopropenes[7] and α-halostilbenes[15] are also believed to occur via the excited singlet state.

Changing the wavelength of excitation from 313 to 254 nm increased both the quantum yields of disappearance of starting material and of formation of product. There is no appreciable change in the quantum yield ratios $\Phi_{E/Z}/\Phi_d$ and Φ_{ion}/Φ_d. A similar effect has been reported for the photolysis of 9-(α-bromobenzylidene)fluorene.[9] As proposed for that case, the wavelength dependence might be the result of reactions from a higher (h.l. singlet) excited state, fast enough to compete with relaxation to the lowest excited singlet state, which is not or less reactive. However, the electronic configuration of the S_1 states of **1-Br**, **2-Br**, and **3-Br** does not seem to be less suitable than that of the S_2 states for heterolytic bond cleavage. PM3 calculations of these excited states indicate that the S_1 consists of combined $\pi \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ contributions, which lead to the pronounced C–Br bond weakening and development of negative charge on the bromine atom, resulting in a vinylic cation and bromide anion. In all three compounds the S_2 has substantial $n \rightarrow \sigma^*$ contributions, leading to radical-derived products, which are not observed experimentally. We attribute the higher efficiencies of both ion products and *E*/*Z*-isomer formation at 254 than at 313 nm irradiation to selective excitation of different rotamers of the starting materials at the two wavelengths. The rotamers of **1–3** with a large torsion around the C–C single bond of the diene moiety will have UV absorption maxima at shorter λ_{max} and will therefore be excited to a larger proportion upon irradiation at 254 nm than the more planar rotamers. As discussed in the section on substituent effects, conformations of the excited state in which the α-alkenyl group is already rotated are beneficial for the formation of ions. From photochemical studies of hexatrienes, it is known that efficiencies of *E*/*Z* isomerization are enhanced by nonplanarity of the chromophore.[12c]

Reactions of Vinyl Cations. 1. Dehydrohalogenation. Deprotonation of the photochemically generated cations yields the dehydrohalogenation products **5–9** (reaction 2, Scheme 5). The efficiency of this process (Table 2) depends, inter alia, on the number of protons

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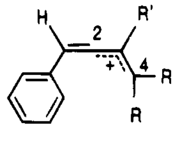
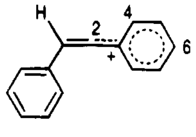
[34] Neuhaus, D.; Williamson, M. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*; VCH: New York, 1989; Chapter 12.

Table 9. PM3-Calculated Charge Densities and LUMO Coefficients in the Cations of 1−3 (C(2) and C(4)) and 4 (C(2), C(4), and C(6))



cations of 1−3



cation of 4

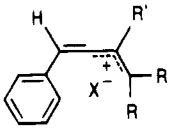
	charge density			LUMO coefficients								
cation from	C2	C4	C6	C2-p_x	C2-p_y	C2-p_z	C4-p_x	C4-p_y	C4-p_z	C6-p_x	C6-p_y	C6-p_z
1	0.135	0.281		0.015	0.463	0.001	0.001	0.432	0.010			
2	0.128	0.262		0.082	0.394	0.010	0.081	0.347	0.008			
3	0.053	0.327		0.008	0.333	0.001	0.009	0.502	0.002			
4	0.093	0.092	0.129	0.070	0.332	0.004	0.032	0.135	0.001	0.038	0.160	0.001

that can be expelled. In the vinyl cation of compound **3** there are seven such Hs, whereas the others have only one. Another factor is the efficiency of competing processes such as nucleophilic trapping (reaction 3) and the [1,3]-shifts (reactions 4 and 5). For all compounds **1**−**4** dehydrohalogenation is more efficient than nucleophilic substitution. A similar preponderance has been observed in the irradiation of α-chloro-2-vinylstilbene in methanol.[35] In principle products **5**−**9** can also be formed via H-atom loss from an intermediate vinyl radical. Treatment of compounds **1Z-Br**, **3Z-Cl**, and **4Z-Br** with tri-*n*-butyltin hydride, however, yielded mainly reductive dehalogenation products and no dehydrohalogenation products.

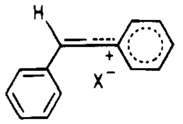
2. Trapping by Nucleophile. The nucleophile can attack at C(2) of the mesomeric cation (reaction 3, Scheme 5), yielding *E*- and *Z*-isomers of the product (reaction 3E/Z), or at C(4), giving rearranged products (reaction 3R). It can be seen from Table 2 that in the series **1**−**3** the percentage of nucleophilic attack at the C(4) position relative to that at C(2) increases in the order **1** < **2** < **3**. This (change in) regioselectivity may be determined by the charge densities at C(2) and C(4) and/or the LUMO coefficients of the C(2) and C(4) p orbitals. The data in Table 9 show that the selectivity is controlled predominantly by the LUMO coefficient whose magnitude parallels the observed change from C(2) attack (compound **1**) to C(4) attack (compound **3**). With the ion of compound **4**, nucleophilic attack by the solvent can occur at C(2), C(4), or C(6). It only takes place at C(2), the position where the LUMO coefficient is larger than at C(4) and C(6). This is in contrast with the case of ipso substitution of α-(*p*-alkoxyphenyl)vinyl cations by alkoxide anions. The use of the hard alkoxide nucleophile makes the reaction charge controlled.[36]

The nucleophilic substitution at C(2) of the vinyl cations of **1**−**4** shows an interesting feature. The quantum yield of formation of nucleophilic substitution product (Φ_{Nu}) is not the same for the *E*- and *Z*-isomers (Table 2). If the reaction involves a free cation, i.e. an sp-hybridized linear vinyl cation, the ratio *E*-isomer/*Z*-isomer is expected to be equal to 1.[3,37,38] The data indicate a more efficient attack of the nucleophile at the side of the cation opposite the leaving halide anion group.

We therefore propose that the product-forming intermediate in the photochemical reactions of compounds **1**−**4** is an ion-pair (**I** for **1**−**3**, **II** for **4**). As in the case of a free cation, the vinyl cation moiety in **I** is linear, but here the approach of the nucleophile to the two lobes of the vacant orbital requires different energies. An ion-pair as intermediate is in contrast with the proposal of a free vinyl cation as intermediate generated in the irradiation of 1-(*p*-methoxyphenyl)-2,2′-diarylvinyl bromides in acetic acid.[3] The difference is probably due to the fact that α-*p*-methoxyphenyl-substituted vinyl cations are inherently more stable than the ions under consideration here.



I



II

Efforts to obtain additional information about the nature of the photochemically generated vinyl cation/halide anion ion-pair by comparing[3] the results obtained with those of corresponding thermal solvolysis (Table 4) were not successful. Due to the severe reaction conditions needed in the thermal solvolysis, a reliable comparison was not possible.

3. [1,3]-Halogen Shift. The concept of an ion-pair as product-forming intermediate not only explains the formation of more *E*-nucleophilic substitution product than *Z*-product starting from the *Z*-isomer but also the occurrence of a [1,3]-halogen shift in the photochemistry of halo dienes **1**−**3** (reaction 4). If this shift were to occur as a nucleophilic substitution reaction on a free cation, the halide anion has to compete with the nucleophilic solvent, namely methanol. From laser flash photolysis experiments of 1-(*p*-methylphenyl)-2,2′-(9-fluorenyl) vinyl bromide in acetonitrile, it is known that the rate constant is 1.3×10^8 M^{-1} s^{-1} for reaction of its vinyl cation with methanol.[10] As this ion is expected to be at least as stable as the cations of **1**−**3**, this rate constant is a minimum value for reaction of the latter species with methanol. The maximum concentration of halide anion is $[X^-]$ = [RX] = 5×10^{-3} M. For this amount of halide to compete with methanol and yield equal amounts of halide- and methoxy-substituted products, the rate constant of reaction with halide has to be at least 5×10^{11} M^{-1} s^{-1}. This value exceeds the rate constant of a diffusion-controlled

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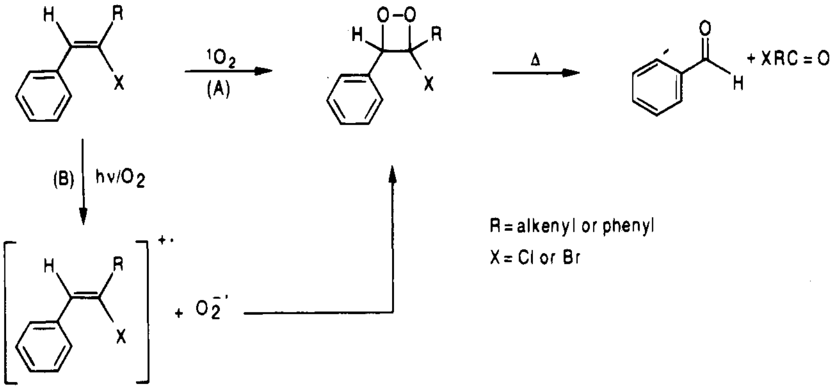
[35] Op den Brouw, P. M.; Laarhoven, W. H. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 58−67.

[36] Kitamura, T.; Kabashima, T.; Nakamura, I.; Fukuda, T.; Taniguchi, H. *J. Am. Chem. Soc.* **1991**, *113*, 7255−7261.

[37] (a) Rappoport, Z. *Acc. Chem. Res.* **1976**, *9*, 265−273. (b) Rappoport, Z. *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum Press: New York, 1983; Vol. 3, pp 427−615. (c) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. In *Vinyl Cations*; Academic Press: New York, 1979; Chapter 6.

[38] van Ginkel, F. I. M.; Hartman, E. R.; Lodder, G.; Greenblatt, J.; Rappoport, Z. *J. Am. Chem. Soc.* **1980**, *102*, 7514−7519.

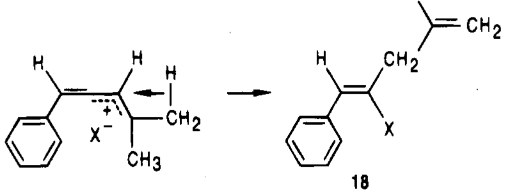
Scheme 6



reaction. However, the methoxy analogue of **16** is not found in the irradiation of **1** in methanol and only small amounts of product **12**, relative to **17**, are produced in the photoreaction of compound **2**. If the [1,3]-halogen shift were to proceed via a free vinyl cation, the yields of these methoxy counterparts of **16** and **17** should have been much higher.

In the case of [1,3]-halogen shifts found in thermal solvolyses[39,40] and photochemical reactions[13] of β-substituted allyl systems, it is also concluded that these shifts are best thought of to proceed via an ion-pair intermediate.[13c] It should be noted though that our results do not exclude the possibility that the [1,3]-halogen shift is a concerted process.

4. [1,3]-Hydrogen Shift. The hydrogen shift (reaction 5) observed upon irradiation of compound **3** can also be explained within the framework of an ion-pair mechanism. Again the rearrangement is not expected to proceed within the free cation; in that case product **18** substituted with a methoxy group instead of a halogen should be observed as well. As with the [1,3]-halogen shift, the halide anion stays in close proximity to the cation. There is a large difference in the quantum yield ratio $\Phi_{[1,3]H}/\Phi_{ion}$ for **3** as a function of the halogen substituent. The cation–chloride pair derived from compound **3Z-Cl** rearranges more efficiently via the [1,3]-hydrogen shift than the cation–bromide pair from **3Z-Br**. The former pair is expected to be tighter than the latter. The large element effect does not completely rule out a concerted mechanism for the [1,3]H-shift in **3** but makes it less likely. No [1,3]-hydrogen migration is observed when the hdyrogen analogue of **3Z-X**, **3E-H**, is irradiated. This suggests that (partial) heterolytic cleavage of the carbon–halogen bond is required to initiate the rearrangement. The PM3-calculated charge distribution in the cation[41] shows that the hydrogens of the methyl groups are slightly positively charged (charge + 0.111) and the central carbon atom of the allylic cation slightly negative (charge −0.185). [1,3]-Hydrogen migration has also been observed as a photoreaction of methyl-substituted arylcyclopropanes.[42] The rearrangement was suggested to have charge-transfer character, with hydrogen migration taking place mainly from a trans methyl group. Ab initio molecular orbital calculations on the [1,3]-hydrogen shift which occurs in propene upon metal complexation show that that reaction is favored by the introduction of charge and radical character.[43]



18

Oxidation. In many investigations of the photochemical reactions of vinyl halides, formation of vinyl radical-derived products has been found to be an important reaction pathway next to the formation of ion-derived products.[1,7,9,15] The vinyl radical intermediates yield either reductive dehalogenation products via H-atom abstraction from the solvent or oxidation products via trapping by oxygen. For some cases it has been reported that exclusion of oxygen increases the yield of reductive dehalogenation products.[9,10] Compounds **1**–**4** do not form reductive dehalogenation products in methanol, not even upon exclusion of oxygen. Changing the solvent from methanol to the better hydrogen donating THF also did not result in the formation of any reductive dehalogenation product, whereas replacement of methanol by THF in the irradiation of 1,1-diaryl-2-halopropenes gave an increased yield of radical-derived product.[7] Upon independent generation of the vinyl radicals via thermal experiments with tri-*n*-butyltin hydride, reductive dehalogenation products were formed. All of this makes the intermediacy of a radical species in the photolyses of **1**–**4** quite unlikely. Therefore, the oxidation reaction 6 has to proceed via a nonvinyl radical route. One possibility is reaction with singlet oxygen,[44] which is generated via triplet sensitization (Scheme 6, pathway A). The triplet states of the styrene or stilbene derivatives **1**–**4** have enough energy (E_T = 50 to 60 kcal/mol[45]) to generate singlet oxygen (E_S = 23 kcal/mol[24]). The reaction of compounds **1**–**4** with singlet oxygen yields a dioxetane, via a concerted or polar [2 + 2] cycloaddition,[46] which undergoes ring cleavage,[47] with benzaldehyde as the only

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[39] DeWolfe, R. H.; Young, W. G. *Chem. Rev.* **1956**, *56*, 753–901.

[40] Kantner, S. S.; Humski, K.; Goering, H. L. *J. Am. Chem. Soc.* **1982**, *104*, 1693–1697.

[41] The charge distribution data are calculated for the free ion, not the ion-pair.

[42] Hixson, S. S.; Gallucci, C. R. *J. Org. Chem.* **1988**, *53*, 2711–2713.

[43] Clark, T. *J. Am. Chem. Soc.* **1989**, *111*, 761–763.

[44] Gilbert, A.; Baggott, J. *Essentials of Molecular Photochemistry*; Blackwell: Oxford, 1991; p 511.

[45] E_T of *cis*-stilbene is <57 kcal/mol, *trans*-stilbene is <50 kcal/mol, styrene 62 kcal/mol (ref 24, p 5 and 20).

[46] Frimer, A. A. *Chem. Rev.* **1979**, *79*, 359–387.

[47] Petersen, B. W.; Pedersen, C. L. *Acta Chem. Scand.* **1980**, *34B*, 523–527.

detectable fragment. This compound is oxidized further to benzoic acid, which is detected (in methanol)[48] as methyl benzoate. Due to the heavy atom effect, vinyl bromides yield more triplets through intersystem crossing than vinyl chlorides and are thus expected to give more oxidation. Another possible mechanism is photooxygenation via electron transfer[50,51] (Scheme 6, pathway B). After excitation of the vinyl halide, an electron is transferred to oxygen, forming a radical-cation and a radical-anion. Combination of the radical-ions results in the formation of a dioxetane, which decomposes as described above. The vinyl bromides are expected to be better electron donors than their chlorine analogues and thus to yield more oxidation. As can be seen from Table 2, the oxidation reaction 6 is indeed more efficient for the bromo compounds. This result is consistent with both mechanisms and no distinction between the two can be made on the basis of our results. It has been reported though that in the case of aryl-substituted olefins the singlet oxygen reaction is slower than the electron transfer route.[50]

Experimental Details

Irradiation Procedure. All irradiations were carried out in a cylindrical Pyrex reaction vessel, in which a quartz tube was immersed. For irradiations at $\lambda = 313$ nm, this quartz tube contained a Hanau TQ-81 high-pressure mercury arc with a quartz 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. This solution only transmits the light of the 313-nm line of the high-pressure mercury arc.[52] For irradiations at $\lambda = 254$ nm, a Hanau TNN-15/32 low-pressure mercury arc was used; the filter solution was replaced with distilled water. For actinometry at $\lambda = 313$ nm and 254 nm, the photolysis of 3-nitroanisole (3.5×10^{-3} M) in a water/methanol (9/1) 0.1 M NaOH solution, which occurs with a quantum yield of 0.22 and 0.21, respectively,[54] was performed in the same reaction vessel under the same conditions as the photochemical experiments under study. The concentrations of the vinyl halides were $2-5 \times 10^{-3}$ M. An equimolar concentration of 1-pentadecanol was used as internal standard. The reaction volume was 250 mL. The temperature was kept at 20 °C.

The disappearance of starting material and the formation of photoproducts were studied as a function of time. This was done by removing aliquots of the reaction mixture (0.5 mL) at appropriate times. These samples were analyzed by means of gas chromatography and monitored using 1-pentadecanol as internal standard. All irradiations were performed in triplicate. The quantum yields were obtained from the kinetic eqs 1 and 2 after least-squares treatment. The values of the quantum yields are average values; the error (i.e., deviation from the mean) is 5–10%.

Generation of Vinyl Radicals. Vinyl radicals were thermally generated with nBu_3SnH in refluxing toluene and 2,2′-azobis(2-methylpropionitrile) (AIBN) as initiator.[19] The reactions were carried out under an argon atmosphere to prevent reaction with oxygen.[20] Typical concentrations used are 1×10^{-3} M vinyl halide, 2×10^{-3} M nBu_3SnH, and a catalytic amount of AIBN.

Equipment. GC analyses were carried out with a Packard model 433 gas chromatograph fitted with a capillary OV-101 column (25 m, i.d. = 0.31 mm). Hydrogen was used as the carrier gas. A temperature program was used starting at 100 °C with a 15°/min rise. Injection and detection temperatures were 250 and 275 °C, respectively. Preparative gas chromatography was performed on a Varian model 920 Aerograph, fitted with a column (6 m, i.d. = 8 mm) filled with 20% SE-30 on Chromosorb WAW, using hydrogen as carrier gas. The column temperature was 130–180 °C; the injection and detection temperatures were 240 and 260 °C. UV spectroscopy (in methanol) was performed using a Varian DMS 200 spectrophotometer. ^1H NMR spectra were recorded on a Bruker WM 300 spectrometer at 300 MHz or a Bruker MSL 400 at 400 MHz (solvent $CDCl_3$, reference TMS (0 ppm)). The ^1H noise-decoupled ^{13}C NMR spectra were recorded on a Jeol JNM FX-200 at 50.3 MHz or a Bruker MSL 400 spectrometer at 100.6 MHz (solvent and reference $CDCl_3$ (77.0 ppm)).

Low-resolution mass spectra were obtained with a GC-MS set-up consisting of a Packard model 438A gas chromatograph, fitted with a CP-SIL 19 CB column (25 m, i.d. = 0.32 mm) using helium as carrier gas, coupled with a Finnigan Mat ITD 700 mass spectrometer using electron-impact ionization. The GC conditions were the same as for the analytical analyses. High-resolution mass spectra were recorded on a V.G. Micromass ZAB-2HF mass spectrometer using electron-impact ionization at 70 and 15 eV. Samples (not pure, contaminated with $CDCl_3$) were introduced via a direct insertion probe into the ion source. The ion source temperature was 150 °C. Fluorescence emission spectra were recorded on a Spex Industries Inc. Fluorolog II spectrofluorimeter. Laser flash photolysis experiments were performed as described in ref 10.

Reagents and Solvents. All vinyl halides were obtained in over 98% purity (GC) and used as such in the photochemical experiments. Methanol, tetrahydrofuran, and toluene (all Baker grade) were distilled before use. All starting materials for synthetic purposes were obtained from Janssen or Aldrich. 1-Pentadecanol (98%), tri-*n*-butyltin hydride (97%), and 2,2′-azobis(2-methylpropionitrile) (AIBN) (98%) were obtained from Janssen, xanthone (>97%) from Fluka, and used without further purification.

Synthesis of Starting Materials. (*Z*)-2-Halo-1-phenyl-1-buten-3-one. To a cooled (0 °C) solution of (*E*)-1-phenyl-1-buten-3-one (0.1 M) in tetrachloromethane chlorine gas or bromine (1.1 molar equiv) was added slowly. After addition of the halogen the reaction mixture was allowed to warm to room temperature. Next triethylamine (1.1 molar equiv) was added dropwise, followed by filtration of the reaction mixture to remove the precipitated salts. The filtrate was washed with a 1 N hydrochloric acid solution, a dilute sodium carbonate solution until pH-neutral, and water. The tetrachloromethane layer was dried over calcium sulfate. Evaporation of the solvent yielded a crude reaction mixture which was separated using column chromatography (silica type 60 (0.063–0.2 mm particle size, hexane/CH_2Cl_2 as eluent). Both (*Z*)-2-halo-1-phenyl-1-buten-3-ones were obtained in a yield of 40% and used to synthesize compounds **2Z-X**.

(*Z*)-2-Chloro-1-phenyl-1-buten-3-one: UV λ_{max} 292 nm (ϵ 18 000), 223 (6000), 203 (6600); ^1H NMR δ 2.48 (s, 3H), 7.37 (m, 3H), 7.68 (s, 1 H), 7.78 (m, 2H); MS *m/z* (relative intensity) 182, 180 (M^+, 20, 56), 181, 179 ($M^+ - H$, 58, 100), 167, 165 ($M^+ - CH_3$, 4, 14), 145 ($M^+ - Cl$, 24), 139, 137 ($M^+ - CH_3 - CO$, 9, 27), 129 ($M^+ - Cl - CH_3 - H$, 22), 115 (13), 102 ($M^+ - Cl - CH_3 - CO$, 76), 77 ($M^+ - Cl - CH_3 - CO - C_2H$, 15), 76 (23), 75 (33).

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[48] The methanol solution becomes acidic as a result of the production of HCl and HBr upon the formation of the solvolysis products and as a result of the photoproduction of formic acid from methanol.[49]

[49] Roussi, G.; Beugelmans, R. *Tetrahedron Lett.* **1972**, *14*, 1333–1336.

[50] Foote, C. S. *Tetrahedron* **1985**, *41*, 2221–2227.

[51] Haugen, C. M.; Bergmark, W. R.; Whitten, D. G. *J. Am. Chem. Soc.* **1992**, *114*, 10293–10297.

[52] (a) The filter solution also transmits a small part of the light of the 334 nm emission line of the high-pressure mercury arc. As this emission is much less intense than the 313 nm one, the transmitted light is essentially monochromatic of the wavelength 313 nm. (b) Although the filter solution is not photostable,[53] no change in its transmission could be detected during irradiation times up to 10 h, which is 20 times the maximum reaction time. Nevertheless, a fresh filter solution was used in each new experiment.

[53] Venigopalam, M.; Pritchard, G. O.; Miller, G. H. *Nature* **1963**, *200*, 568–568.

[54] (a) de Jongh, R. O. Ph.D. Thesis, Leiden University, The Netherlands, 1965. (b) Havinga, E.; de Jongh, R. O. *Bull. Soc. Chim. Belg.* **1962**, *71*, 803–810. (c) de Jongh, R. O.; Havinga, E. *Recl. Trav. Chim. Pays-Bas* **1966**, *85*, 275–283.

(*Z*)-2-Bromo-1-phenyl-1-buten-3-one: UV λ_{max} 294 nm (ϵ 17 500), 223 (6100), 203 (10 200); ^{1}H NMR δ 2.53 (s, 3H), 7.39 (m, 3H), 7.79 (m, 2H), 7.96 (s, 1H); MS *m/z* (relative intensity) 226, 224 (M^+, 33, 33), 225, 223 ($M^+ - H$, 53, 42), 211, 209 ($M^+ - CH_3$, 6, 6), 183, 181 ($M^+ - CH_3 - CO$, 12, 12), 145 ($M^+ - Br$, 67), 129 ($M^+ - Br - CH_3 - H$, 6), 115 (11), 102 ($M^+ - Br - CH_3 - CO$, 100), 77 ($M^+ - Br - CH_3 - CO - C_2H$, 13), 76 (33).

General Procedure for the Synthesis of 1–3. All reactions were carried out under nitrogen and in freshly distilled THF (from $LiAlH_4$). To a cooled (ice bath) 0.3 M solution of Wittig salt in THF was added dropwise an equivalent amount of *n*-butyllithium (1.6 M in hexane). A solution of α-halo aldehyde or ketone (slight excess) in THF was added dropwise to the reaction mixture. For the synthesis of reference compounds **1E-H** and **3E-H**, cinnamaldehyde was used as the starting material. After the reaction was finished, the solution was filtered and the residue washed with diethyl ether. The ethereal solutions were combined and washed with a saturated NaCl solution and dried on $CaSO_4$. Evaporation of the solvent and column chromatography of the residue, using silica type 60 (0.063–0.2 mm particle size) as adsorbant and a mixture of hexane and CH_2Cl_2 as eluent, yielded the halo dienes as oils. The not-optimized yields were 20% (**2Z-X**), 40% (**3Z-X**), and 50% (**1Z-X**).

(*Z*)-2-Chloro-1-phenyl-1,3-butadiene (1Z-Cl): UV λ_{max} 282 nm (ϵ 24 100), 209 (12 900), 204 (11 000); ^{1}H NMR δ 5.32 (d, 1H, J = 10.5 Hz), 5.76 (d, 1H, J = 16.4 Hz), 6.55 (q, 1H), 6.68 (s, 1H), 7.34 (m, 3H), 7.71 (m, 2H); MS *m/z* (relative intensity) 166, 164 (M^+, 12, 38), 129 ($M^+ - Cl$, 100), 102 ($M^+ - Cl - C_2H_3$, 15), 77 ($M^+ - Cl - C_2H_3 - C_2H$, 11); high-resolution MS *m/z* 164.0385 ($C_{10}H_9Cl$ requires 164.0392).

(*Z*)-2-Bromo-1-phenyl-1,3-butadiene (1Z-Br): UV λ_{max} 282 nm (ϵ 22 800), 209 (14 700); ^{1}H NMR δ 5.33 (d, 1H, J = 10.3 Hz), 5.73 (d, 1H, J = 16.2 Hz), 6.50 (q, 1H), 6.97 (s, 1H), 7.38 (m, 3H), 7.70 (m, 2H); MS *m/z* (relative intensity) 210, 208 (M^+, 10, 10), 129 ($M^+ - Br$, 100), 102 ($M^+ - Br - C_2H_3$, 7), 77 ($M^+ - Br - C_2H_3 - C_2H$, 4); high-resolution MS *m/z* 207.9905 ($C_{10}H_9Br$ requires 207.9888).

(*E*)-1-Phenyl-1,3-butadiene (1E-H): ^{1}H NMR δ 5.10 (dd, 1H, J = 9.4 Hz), 5.25 (dd, 1H, J = 17 Hz), 6.41 (q, 1H, J = 11 Hz), 6.46 (d, 1H, J = 16 Hz), 6.71 (q, 1H), 7.1–7.3 (m, 5H); MS *m/z* (relative intensity) 130 (M^+, 78), 129 ($M^+ - H$, 100), 115 (60), 102 (11), 77 (20).

(*Z*)-2-Chloro-3-methyl-1-phenyl-1,3-butadiene (2Z-Cl): UV λ_{max} 273 nm (ϵ 13 700), 208 (6100); ^{1}H NMR δ 2.11 (m, 3H), 5.22 (d, 1H), 5.70 (dd, 1H), 6.80 (s, 1H), 7.30 (m, 3H), 7.67 (m, 2H); MS *m/z* (relative intensity) 180, 178 (M^+, 3, 10), 143 ($M^+ - Cl$, 100), 128 ($M^+ - Cl - CH_3$, 90), 102 ($M^+ - Cl - CH_3 - C_2H_2$, 10), 77 ($M^+ - Cl - CH_3 - C_2H_2 - C_2H$, 20); high-resolution MS *m/z* 178.0551 ($C_{11}H_{11}Cl$ requires 178.0549).

(*Z*)-2-Bromo-3-methyl-1-phenyl-1,3-butadiene (2Z-Br): UV λ_{max} 273 nm (ϵ 15 800), 209 (13 100); ^{1}H NMR δ 2.13 (m, 3H), 5.25 (s, 1H), 5.66 (d, 1H), 7.05 (s, 1H), 7.31 (m, 3H), 7.61 (m, 2H); MS *m/z* (relative intensity) 224, 222 (M^+, 2, 2), 143 ($M^+ - Br$, 95), 128 ($M^+ - Br - CH_3$, 100), 102 ($M^+ - Br - CH_3 - C_2H_2$, 15), 77 ($M^+ - Br - CH_3 - C_2H_2 - C_2H$, 12); high-resolution MS *m/z* 222.0039 ($C_{11}H_{11}Br$ requires 222.0044).

(*Z*)-2-Chloro-4-methyl-1-phenyl-1,3-pentadiene (3Z-Cl): UV λ_{max} 274 nm (ϵ 17 600), 209 (11 900); ^{1}H NMR δ 1.86 (d, 3H, J = 1.3 Hz), δ 1.92 (d, 3H, J = 1.2 Hz), 5.84 (m, 1H), 6.47 (s, 1H), 7.3 (m, 3H), 7.65 (m, 2H); MS *m/z* (relative intensity) 194, 192 (M^+, 14, 52), 179, 177 ($M^+ - CH_3$, 20, 56), 157 ($M^+ - Cl$, 100), 142 ($M^+ - Cl - CH_3$, 67), 141 (58), 129 (31), 115 ($M^+ - Cl - C(CH_3)_2$, 73), 102 (11), 77 ($M^+ - Cl - C(CH_3)_2 - C_2H$, 20); high-resolution MS *m/z* 192.0710 ($C_{12}H_{13}Cl$ requires 192.0706).

(*Z*)-2-Bromo-4-methyl-1-phenyl-1,3-pentadiene (3Z-Br): UV λ_{max} 276 (ϵ 16 100), 205 (17 000); ^{1}H NMR δ 1.86 (d, 3H, J = 1.3 Hz), 1.90 (d, 3H, J = 1.3 Hz), 5.95 (m, 1H), 6.69 (s, 1H), 7.33 (m, 3H), 7.63 (m, 2H); MS *m/z* (relative intensity) 238, 236 (M^+, 18, 18), 223, 221 ($M^+ - CH_3$, 18, 18), 157 ($M^+ - Br$, 100), 142 ($M^+ - Br - CH_3$, 87), 141 (53), 129 (88), 115 ($M^+ - Br - C(CH_3)_2$, 80), 102 (11), 91 (36), 77 (31); high-resolution MS *m/z* 236.0194 ($C_{12}H_{13}Br$ requires 236.0201).

(*E*)-4-Methyl-1-phenyl-1,3-pentadiene (3E-H): ^{1}H NMR δ 1.80 (s, 6H), 5.95 (m, 1H), 6.38 (d, 1H, J = 17 Hz), 6.90 (m, 1H), 7.3 (m, 5H); MS *m/z* (relative intensity) 158 (M^+, 78), 143 ($M^+ - CH_3$, 100), 128 ($M^+ - CH_3 - CH_3$, 51), 115 (38), 102 (7), 91 (11), 77 (11).

Synthesis of 4. Compounds **4Z-X** were synthesized according to literature procedures.[16]

(*Z*)-1-Chloro-1,2-diphenylethene (4Z-Cl): UV λ_{max} 271 nm (ϵ 11 000), 223 (20 000); ^{1}H NMR δ 6.9–7.4 (m); MS *m/z* (relative intensity) 216, 214 (M^+, 24, 69), 179 ($M^+ - Cl$, 100), 178 (87), 152 (16), 102 ($M^+ - Cl - C_6H_5$, 8); oil.

(*Z*)-1-Bromo-1,2-diphenylethene (4Z-Br): UV λ_{max} 260 nm (ϵ 11 000), 226 (19 300); ^{1}H NMR δ 6.9–7.4 (m); MS *m/z* (relative intensity) 260, 258 (M^+, 47, 47), 179 ($M^+ - Br$, 100), 178 (82), 152 (13), 102 ($M^+ - Br - C_6H_5$, 7); mp 31 °C.

Identification of Products. After addition of $NaHCO_3$ to the reaction mixture, most of the methanol was evaporated and the residue was dissolved in diethyl ether. The ether solution was washed with a saturated NaCl solution and dried over $CaSO_4$. Evaporation of the solvent yielded a product mixture which was separated using preparative gas chromatography. Products were identified on the basis of their ^{1}H NMR spectra, using homodecoupling or 2-D experiments, mass spectra, and GC retention times. For some products it was necessary to obtain additional information from ^{13}C NMR. The spectral data are listed below. For reference purposes compounds **13Z**, **13E**, **15Z**, and **15E** were synthesized independently by treatment of 2-oxo-4-methyl-1-phenylpent-3-ene[55] or deoxybenzoin with trimethyl orthoformiate in methanol in the presence of *p*-toluenesulfonic acid,[35] followed by photochemical *E/Z* isomerization in *n*-hexane.

(*E*)-2-Chloro-1-phenyl-1,3-butadiene (1E-Cl): ^{1}H NMR δ 5.39 (dd, 1H, J = 10.8 Hz, J = 1.4 Hz), 5.83 (dd, 1H, J = 16.3 Hz), 6.85 (dd, 1H), 6.90 (s, 1H), 7.3 (m, 5H); MS *m/z* (relative intensity) 166, 164 (M^+, 2, 6), 129 ($M^+ - Cl$, 100), 102 ($M^+ - Cl - C_2H_3$, 11), 77 ($M^+ - Cl - C_2H_3 - C_2H$); high-resolution MS *m/z* 164.0389 ($C_{10}H_9Cl$ requires 164.0392).

(*E*)-2-Bromo-1-phenyl-1,3-butadiene (1E-Br): ^{1}H NMR δ 5.42 (dd, 1H, J = 11.5 Hz), 5.71 (dd, 1H, J = 17.2 Hz), 5.99 (dd, 1H), 6.93 (s, 1H), 7.3 (m, 5H); MS *m/z* (relative intensity) 210, 208 (M^+, 5, 5), 129 ($M^+ - Br$, 100), 102 ($M^+ - Br - C_2H_3$, 15), 77 ($M^+ - Br - C_2H_3 - C_2H$, 12); high-resolution MS *m/z* 207.9895 ($C_{10}H_9Br$ requires 207.9888).

(*E*)-2-Chloro-3-methyl-1-phenyl-1,3-butadiene (2E-Cl): ^{1}H NMR δ 1.97 (t, 3H), 5.12 (m, 1H), 5.16 (m, 1H), 6.67 (s, 1H), 7.25 (m, 5H); MS *m/z* (relative intensity) 180, 178 (M^+, 5, 5), 143 ($M^+ - Cl$, 100), 128 ($M^+ - Cl - CH_3$, 85), 102 ($M^+ - Cl - CH_3 - C_2H_2$, 5), 77 ($M - Cl - CH_3 - C_2H_2 - C_2H$, 20); high-resolution MS *m/z* 178.0551 ($C_{11}H_{11}Cl$ requires 178.0549).

(*E*)-2-Bromo-3-methyl-1-phenyl-1,3-butadiene (2E-Br): ^{1}H NMR δ 2.00 (s, 3H), 5.08 (s, 1H), 5.17 (s, 1H), 6.87 (s, 1H), 7.3 (m, 5H); MS *m/z* (relative intensity) 224, 222 (M^+, 2, 2), 143 ($M^+ - Br$, 85), 128 ($M^+ - Br - CH_3$, 100), 102 ($M^+ - Br - CH_3 - C_2H_2$, 13), 77 ($M^+ - Br - CH_3 - C_2H_2 - C_2H$, 15); high-resolution MS *m/z* 222.0051 ($C_{11}H_{11}Br$ requires 222.0044).

(*E*)-2-Chloro-4-methyl-1-phenyl-1,3-pentadiene (3E-Cl): ^{1}H NMR δ 1.58 (d, 3H, J = 1.2 Hz), 1.80 (d, 3H, J = 1.4 Hz), 5.90 (m, 1H), 6.69 (s, 1H), 7.3 (m, 5H); MS *m/z* (relative intensity) 194, 192 (M^+, 5, 20), 179, 177 ($M^+ - CH_3$, 14, 33), 157 ($M^+ - Cl$, 100), 142 ($M^+ - Cl - CH_3$, 73), 141 (56), 129 (42), 115 ($M^+ - Cl - C(CH_3)_2$, 62), 102 (5), 91 (31), 77 (20); high-resolution MS *m/z* 192.0691 ($C_{12}H_{13}Cl$ requires 192.0706).

(*E*)-2-Bromo-4-methyl-1-phenyl-1,3-pentadiene (3E-Br): ^{1}H NMR δ 1.53 (d, 3H, J = 1.5 Hz), 1.80 (d, 3H, J = 1.4 Hz), 5.98 (m, 1H), 6.94 (s, 1H), 7.3 (m, 5H); MS *m/z* (relative intensity) 238, 236 (M^+, 4, 4), 223, 221 ($M^+ - CH_3$, 11, 11), 157 ($M^+ - Br$, 100), 142 ($M^+ - Br - CH_3$, 90), 141 (72), 129 (78), 115 ($M^+ - Br - C(CH_3)_2$, 77), 102 (16), 91 (40), 77 (27); high-resolution MS *m/z* 236.0196 ($C_{12}H_{13}Br$ requires 236.0201).

4-Phenyl-1-buten-3-yne (5): ^{1}H NMR δ 5.54 (q, 1H, J = 11.1, 2.1 Hz), 5.74 (q, 1H, J = 17.6, 2.1 Hz), 6.02 (q, 1H), 7.31 (m, 3H), 7.45 (m, 2H); MS *m/z* (relative intensity) 128 (M^+,

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[55] Smissman, E. E.; Johnsen, R. H.; Carlson, A. W.; Aycock, B. F. *J. Am. Chem. Soc.* **1956**, *78*, 3395–3400.

100), 102 ($M^+ - C_2H_2$, 45); high-resolution MS *m/z* 128.0638 ($C_{10}H_8$ requires 128.0626).

2-Methyl-4-phenyl-1-buten-3-yne (6): ^{1}H NMR δ 1.99 (s, 3H), 5.30 (s, 1H), 5.40 (s, 1H), 7.31 (m, 3H), 7.44 (m, 2H); ^{13}C NMR δ 88, 91; MS *m/z* (relative intensity) 142 (M^+, 98), 141 ($M^+ - H$, 100), 127 ($M^+ - CH_3$, 30); high-resolution MS *m/z* 142.0800 ($C_{11}H_{10}$ requires 142.0783).

5-Phenyl-2-methyl-2-penten-4-yne (7): ^{1}H NMR δ 1.87 (s, 3H), 1.98 (s, 3H), 5.48 (s, 1H), 7.29 (m, 3H), 7.41 (m, 2H); MS *m/z* (relative intensity) 156 (M^+, 100), 141 ($M^+ - CH_3$, 47), 128 (22), 115 ($M^+ - C(CH_3)_2 + H$, 82); high-resolution MS *m/z* 156.0946 ($C_{12}H_{12}$ requires 156.0938).

4-Methyl-1-phenyl-1,2,4-pentatriene (8): ^{1}H NMR δ 1.82 (d, 3H), 4.93 (q, 1H), 5.05 (d, 1H), 6.34 (d, 1H, $J = 6.4$ Hz), 6.42 (d, 1H), 7.3 (m, 5H); MS *m/z* (relative intensity) 156 (M^+, 78), 141 ($M^+ - CH_3$, 75), 115 ($M^+ - C(CH_3)_2 + H$); high-resolution MS *m/z* 156.0940 ($C_{12}H_{12}$ requires 156.0938).

(*Z*)-2-Methoxy-1-phenyl-1,3-butadiene (10Z): MS *m/z* (relative intensity) 160 (M^+, 40), 129 ($M^+ - OCH_3$, 100), 102 ($M^+ - OCH_3 - C_2H_3$, 40).

(*E*)-2-Methoxy-1-phenyl-1,3-butadiene (10E): MS *m/z* (relative intensity) 160 (M^+, 50), 129 ($M^+ - OCH_3$, 100), 102 ($M^+ - OCH_3 - C_2H_3$, 5).

(*Z*)-2-Methoxy-3-methyl-1-phenyl-1,3-butadiene (11Z): MS *m/z* (relative intensity) 174 (M^+, 25), 159 ($M^+ - CH_3$, 30), 144 ($M^+ - CH_3 - CH_3$, 70), 128 ($M^+ - OCH_3 - CH_3$, 100), 77 (C_6H_5, 65).

(*E*)-2-Methoxy-3-methyl-1-phenyl-1,3-butadiene (11E): MS *m/z* (relative intensity) 174 (M^+, 55), 159 ($M^+ - CH_3$, 90), 144 ($M^+ - CH_3 - CH_3$, 100), 128 ($M^+ - OCH_3 - CH_3$, 55), 77 (C_6H_5, 30).

4-Methoxy-3-methyl-1-phenyl-1,2-butadiene (12): ^{1}H NMR δ 1.84 (d, 3H, $J = 2.9$ Hz), 3.36 (s, 3H), 4.01 (d, 2H), 6.14 (m, 1H), 7.3 (m, 5H); MS *m/z* (relative intensity) 174 (M^+, 2), 129 ($M^+ - OCH_3 - C_2H_2$, 100); high-resolution MS *m/z* 174.1068 ($C_{12}H_{14}O$ requires 174.1045).

(*Z*)-2-Methoxy-4-methyl-1-phenyl-1,3-pentadiene (13Z): ^{1}H NMR δ 1.75 (s, 3H), 1.79 (s, 3H), 3.67 (s, 3H), 5.66 (s, 1H), 5.86 (s, 1H), 7.0–7.6 (m, 5H); MS *m/z* (relative intensity) 188 (M^+, 62), 173 ($M^+ - CH_3$, 60), 158 ($M^+ - CH_3 - CH_3$, 64), 157 ($M^+ - OCH_3$, 56), 141 ($M^+ - OCH_3 - CH_3 - H$, 60), 128 (67), 115 ($M^+ - OCH_3 - C(CH_3)_2$, 69), 102 (24), 91 (100), 77 (20); high-resolution MS *m/z* 188.1224 ($C_{13}H_{16}O$ requires 188.1200).

(*E*)-2-Methoxy-4-methyl-1-phenyl-1,3-pentadiene (13E): ^{1}H NMR δ 1.85 (s, 3H), 1.91 (s, 3H), 3.62 (s, 3H), 5.43 (s, 1H), 5.74 (s, 1H), 7.1–7.7 (m, 5H); Ms *m/z* (relative intensity) 188 (M^+, 51), 173 ($M^+ - CH_3$, 56), 158 ($M^+ - CH_3 - CH_3$, 38), 157 ($M^+ - OCH_3$, 42), 141 ($M^+ - OCH_3 - CH_3 - H$, 45), 128 (33), 115 ($M^+ - OCH_3 - C(CH_3)_2$, 56), 102 (11), 91 (100), 77 (18); high-resolution MS *m/z* 188.1233 ($C_{13}H_{16}O$ requires 188.1200).

4-Methoxy-4-methyl-1-phenyl-1,2-pentadiene (14): ^{1}H NMR δ 1.34 (s, 3H), 1.37 (s, 3H), 3.29 (s, 3H), 5.56 (d, 1H, $J = 6.4$ Hz), 6.27 (d, 1H, $J = 6.4$ Hz), 7.25 (m, 5H); ^{13}C NMR δ 26.3, 26.5, 50.7, 75.0, 96.6, 101.4, 126–134, 204.1; MS *m/z* (relative intensity) 188 (M^+, 4), 173 ($M^+ - CH_3$, 4), 157 ($M^+ - OCH_3$, 4), 141 ($M^+ - OCH_3 - CH_3 - H$, 7), 115 ($M - OCH_3 - C(CH_3)_2$, 23), 102 (2), 73 (100); high-resolution MS *m/z* 188.1213 ($C_{13}H_{16}O$ requires 188.1200).

(*Z*)-1-Methoxy-1,2-diphenylethene (15Z): ^{1}H NMR δ 3.57 (s, 3H), 6.07 (s, 1H), 7.15–7.71 (m, 10H); MS *m/z* (relative intensity) 210 (M^+, 100), 195 ($M^+ - CH_3$, 6), 179 ($M^+ - OCH_3$, 13), 167 (62), 165 (93), 152 (56), 105 (67), 91 (67), 77 (36); high-resolution MS *m/z* 210.1064 ($C_{15}H_{14}O$ requires 210.1045).

(*E*)-1-Methoxy-1,2-diphenylethene (15E): ^{1}H NMR δ 3.79 (s, 3H), 5.82 (s, 1H), 7.2 (m, 10H); MS *m/z* (relative intensity) 210 (M^+, 100), 195 ($M^+ - CH_3$, 4), 179 ($M^+ - OCH_3$, 18), 167 (62), 165 (89), 152 (60) 105 (73), 91 (60), 77 (36); high-resolution MS *m/z* 210.1060 ($C_{15}H_{14}O$ requires 210.1045).

4-Chloro-1-phenyl-1,2-butadiene (16-Cl): ^{1}H NMR δ 4.16 (dd, 2H, $J = 7.6, 2.0$ Hz), 5.80 (dt, 1H, $J = 7.2$ Hz), 6.34 (dt, 1H, $J = 7.2$ Hz), 7.3 (m, 5H); ^{13}C NMR δ 66, 206; MS *m/z* (relative intensity) 166, 164 (M^+, 4, 13), 129 ($M^+ - Cl$, 100), 115 ($M^+ - Cl - CH_2$, 25), 102 ($M^+ - Cl - CH_2 - CH$, 15), 77 ($M^+ - Cl - CH_2 - CH - C_2H$, 18); high-resolution MS *m/z* 164.0394 ($C_{10}H_9Cl$ requires 164.0392).

4-Bromo-1-phenyl-1,2-butadiene (16-Br): ^{1}H NMR δ 4.05 (dd, 2H, $J = 7.3$ Hz), 5.92 (dt, 1H, $J = 7.3$ Hz), 6.30 (dt, 1H, $J = 7.3$ Hz), 7.3 (m, 5H); MS *m/z* (relative intensity) 210, 208 (M^+, 5, 5), 129 ($M^+ - Br$, 100), 115 ($M^+ - Br - CH_2$, 10), 102 ($M^+ - Br - CH_2 - CH$, 15), 77 ($M^+ - Br - CH_2 - CH - C_2H$, 15); high-resolution MS *m/z* 207.9890 ($C_{10}H_9Br$ requires 207.9888).

4-Chloro-3-methyl-1-phenyl-1,2-butadiene (17-Cl): ^{1}H NMR δ 1.94 (d, 3H, $J = 2.9$ Hz), 4.17 (q, 2H), 6.20 (m, 1H), 7.3 (m, 5H); ^{13}C NMR δ 16.4, 47.7, 95.2, 101.2, 127–134, 204.3; MS *m/z* (relative intensity) 180, 178 (M^+, 5, 17), 143 ($M^+ - Cl$, 85), 128 ($M^+ - Cl - CH_3$, 100), 102 ($M^+ - Cl - CH_3 - C_2H_2$, 15), 77 ($M^+ - Cl - CH_3 - C_2H_2 - C_2H$, 15); high-resolution MS *m/z* 178.0553 ($C_{11}H_{11}Cl$ requires 178.0549).

4-Bromo-3-methyl-1-phenyl-1,2-butadiene (17-Br): ^{1}H NMR δ 1.90 (d, 3H, $J = 3.0$ Hz), 4.09 (q, 2H), 6.17 (m, 1H), 7.3 (m, 5H); MS *m/z* (relative intensity) 224, 222 (M^+, 2, 2), 143 ($M^+ - Br$, 85), 128 ($M^+ - Br - CH_3$, 100), 102 ($M^+ - Br - CH_3 - C_2H_2$, 12), 77 ($M^+ - Br - CH_3 - C_2H_2 - C_2H$, 12); high-resolution MS *m/z* 222.0041 ($C_{11}H_{11}Br$ requires 222.0044).

(*Z*)-2-Chloro-4-methyl-1-phenyl-1,4-pentadiene (18-Cl): ^{1}H NMR δ 1.90 (d, 3H), 3.90 (s, 2H), 4.94 (s, 1H), 5.02 (q, 1H), 6.31 (s, 1H), 7.3 (m, 5H); ^{13}C NMR δ 20, 41; MS *m/z* (relative intensity) 194, 192 (M^+, 4, 12), 179, 177 ($M^+ - CH_3$, 13, 38), 157 ($M^+ - Cl$, 87), 142 ($M - Cl - CH_3$, 100), 141 (69), 115 ($M - Cl - C(CH_3)_2$, 78), 102 (9), 91 (33), 77 (36); high-resolution MS *m/z* 192.0715 ($C_{12}H_{13}Cl$ requires 192.0706).

(*Z*)-2-Bromo-4-methyl-1-phenyl-1,4-pentadiene (18-Br): ^{1}H NMR δ 1.91 (d, 3H, $J = 1.0$ Hz), 4.03 (s, 2H), 4.96 (s, 1H), 5.02 (q, 1H), 6.59 (s, 1H), 7.3 (m, 5H); MS *m/z* (relative intensity) 238, 236 (M^+, 4, 4), 223, 221 ($M^+ - CH_3$, 12, 12), 157 ($M^+ - Br$, 98), 142 ($M^+ - Br - CH_3$, 100), 141 (60), 115 ($M^+ - Br - C(CH_3)_2$, 78), 102 (15), 91 (40), 77 (36); high-resolution MS *m/z* 236.0208 ($C_{12}H_{13}Br$ requires 236.0201).

Supplementary Material Available: Copies of the ^{1}H NMR spectra of **1–4ZX** (**X** = Cl, Br), **1E-H**, **3E-H**, **1–3EX**, **5–8**, **12**, **13Z**, **13E**, **14**, **15Z**, **15E**, **16Cl**, **17Cl**, **18X**, and the synthetic intermediates (*Z*)-2X-1-phenyl-1-buten-3-ones (32 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.