Competition of Mechanisms in the Photochemical Cleavage of the C–X Bond of Aryl-Substituted Vinyl Halides

Carlo Galli,*,[†] Patrizia Gentili,[†] Alessandra Guarnieri,[†] Shinjiro Kobayashi,[‡] and Zvi Rappoport[§]

Dipartimento di Chimica, Università "La Sapienza", 00185 Roma, Italy, Institute for Fundamental Research of Organic Chemistry, Kyushu University, Fukuoka 812, Japan, and Department of Organic Chemistry, The Hebrew University, Jerusalem 91904, Israel

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The photolysis of aryl halides causes homolysis of the carbon–halogen bond and formation of aryl radicals. In contrast, photolysis of vinyl halides can induce both heterolysis of the C–X bond, thereby generating vinyl cations, and homolysis, giving vinyl radicals. Examples of this competition among pathways is reported here for three vinylic precursors, namely, 1,2,2-triphenylbromoethene (**1**), 1-phenyl-2,2-bis(*o*-methoxyphenyl)-1-bromoethene (**11**), and *β*-bromostyrene (**19**). Incursion of the photoinduced $S_{RN}1$ process, through the intermediacy of the vinyl radical, is verified in the presence of reducing nucleophiles, such as the enolate ions of ketones, and in part with $(EtO)_2PO^-$. Conversely, incursion of the heterolytic path, and intermediacy of the vinyl cation, occurs in the presence of weak electron-donor anions, such as NO_2^-, N_3^-, and Cl^-. The vinyl cation produced from **19**, which is less stable than those derived from **1** and **11**, gives phenylacetylene via an E1-type elimination. An estimate is provided for the intramolecular rate of interception of the vinyl cation derived from **11** by the *ortho*-methoxy groups of the *β-o*-anisyl substituents. Finally, evidence against a photoinduced electron transfer from RO^- ions to vinyl halide **1** is presented.

The photolysis of aryl halides causes homolysis of the C–X bond.[1] In contrast, for vinyl halides (VyX) the heterolysis of the C–X bond is reported to occur under comparable photochemical conditions (Scheme 1).[1]

Certainly, this scheme delineates two extreme types of behavior, and less clear-cut situations are also documented.[1,2] In any event, it was recently learned that photochemically excited vinyl halides *partition* between homolysis and heterolysis of the C–X bond (Scheme 2),[3] but evidence was also provided that the latter pathway in general prevails for aryl-substituted vinylic structures in solution.[1,3,4]

This significant difference in the photochemical reaction pathways of ArX and VyX species is certainly puzzling, in view of the similarity of their functional group, i.e., the C(sp²)–halogen bond. From a thermochemical point of view, on comparing the gas-phase homolytic[5] and heterolytic[6] bond dissociation energy values of the two typical parent precursors, i.e., Ph–Br and $CH_2=CH–Br$ (Chart 1), or the stability of the
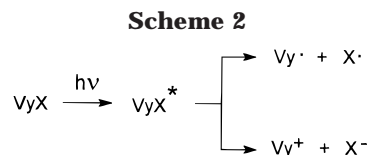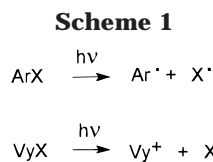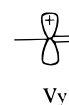
Scheme 1

$$ArX \xrightarrow{h\nu} Ar^{\cdot} + X^{\cdot}$$

$$VyX \xrightarrow{h\nu} Vy^+ + X^-$$

Scheme 2

$$VyX \xrightarrow{h\nu} VyX^* \Big\langle \begin{array}{l} Vy^{\cdot} + X^{\cdot} \\ Vy^+ + X^- \end{array}$$

Chart 1. Relevant Thermochemical Data (in kcal/mol) of Phenyl and Vinyl Bromides and the Derived Radical and Cation Intermediates

$D(R–X)_{homol.}$	Ph-Br 82.6	$CH_2=CH-Br$ 79.5
$D(R–X)_{heter.}$	Ph-Br 197	$CH_2=CH-Br$ 192
$\Delta H_f(R^{\cdot})$	$Ph^{\cdot}$ 81.1	$CH_2=CH^{\cdot}$ 71.7
$\Delta H_f(R^+)$	Ph^+ 273	$CH_2=CH^+$ 262

possibly derived reactive intermediates,[6] only minor differences exist.

The $D(R–X)$ values derive from the heats of formation of the two intermediates resulting from homolytic or heterolytic cleavage of the C–X bond.[6] Unfortunately, the dynamic of the photocleavage of these two chromophores[1,3] has not yet been investigated as thoroughly as in the case of the C–X bond of diphenylmethyl halides, where the

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Chart 2. Relative Carbocation Stabilization Energy to $C_2H_3^+$ (in kcal/mol) from Differences in H^- Affinity

Scheme 3
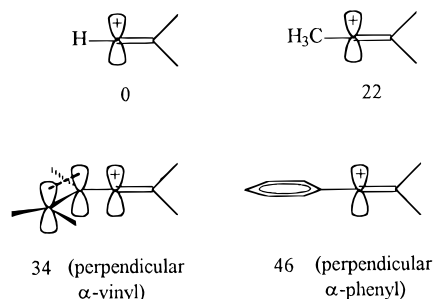
partitioning between radical pair ($R^•X^•$) and contact ion pair (R^+X^-) could be followed kinetically.[12] However, we call the attention upon a structural difference of the phenyl vs vinyl halide: the parent *linear*[13] vinyl cation (Vy^+), in comparison with the necessarily *bent*[14] phenylium ion (Ph^+), is provided with an "extra hand" enabling additional stabilization by substituents (Chart 2). For example, when the α C$-$H bond of $C_2H_3^+$ is substituted with a methyl, a remarkable stabilization of ca. 22 kcal/mol results for $CH_2=C(^+)CH_3$.[15]

A similar gain in stabilization is not possible for the phenylium ion. An even stronger effect results if the α C$-$H of the ethenyl cation is substituted with a group capable of π-conjugation, as for a vinyl substituent being *coplanar* with the empty p orbital and *perpendicular* to the other double bond in $C_4H_5^+$.[15,16] An allylic-type

conjugation becomes then possible, and it is calculated (see Experimental Section) to give an additional stabilization of ca. 12 kcal/mol to the 1,3-butadien-2-yl cation.[15] Analogously, the α-styryl cation is expected and calculated[15] to gain π-p(C^+) stabilization of ca. 24 kcal/mol whenever full conjugation of the positive charge with the aromatic ring is conformationally allowed. It is not unlikely, even though not straightforward, that this structural effect, namely, the absence of conjugative stabilization for the Ph^+ ion, can play a role in the dynamic of the photocleavage process, so to help to explain why photoheterolysis of vinyl halides, bearing appropriate substituents, may take over their photohomolysis (Scheme 1) in solution. An investigation in this direction is desirable and planned.

We became interested in this dichotomy in the behavior of the vinyl halides in connection with our studies on the vinylic $S_{RN}1$ reaction,[17] whose propagation cycle is reported in Scheme 3.

Evidence for the intermediacy of a vinyl radical in this nucleophilic substitution process was provided,[17d] in analogy with the intermediacy of aryl radical in the reaction of aryl halides.[18] In keeping with the aromatic case, the vinylic $S_{RN}1$ process is likely to be initiated by photostimulated electron transfer from a nucleophile[19] to the vinyl halide, forming an intermediate radical anion that then fragments to the vinyl radical. Could the photochemical induction directly provoke also the heterolysis of the C$-$X bond of the substrate, giving the corresponding vinyl cation? The product of the nucleophilic substitution could then (also) arise from a cation-to-anion coupling (eq 1).

To better appreciate this subtle feature of the vinylic $S_{RN}1$, which is not shared by its aromatic counterpart,

(6) The homolytic D(R$-$Br) values given in Chart 1 have already been reported.[5] The heterolytic D(R$-$Br) values are derived from the following thermochemical equations, where IE are the ionization potentials of the radicals: D_{298}(R$-$Br) $= \Delta_fH_{298}$(R$^+$) $+ \Delta_fH_{298}$(Br$^-$) $- \Delta_fH_{298}$(RBr) (eq *a*) and Δ_fH_{298}(R$^•$) $+$ IE $\rightarrow \Delta_fH_{298}$(R$^+$) (eq *b*). The IE of Ph$^•$ is 8.32 eV,[7] while its Δ_fH_{298} is 81.1 kcal/mol;[8] from eq *b* one accordingly obtains 272.8 kcal/mol for Δ_fH_{298}(Ph$^+$). Analogously, the IE of CH$_2$=CH$^•$ is 8.25 eV,[7] and Δ_fH_{298}(CH$_2$=CH$^•$) is 71.7 kcal/mol,[9] from which Δ_fH_{298}(CH$_2$=CH$^+$) = 261.9 kcal/mol. From Δ_fH_{298}(Br$^-$) $= -50.9$ kcal/mol,[10] Δ_fH_{298}(PhBr) = 25.2 kcal/mol,[11] and Δ_fH_{298}(CH$_2$=CHBr) = 18.9 kcal/mol,[11] eq *a* gives the heterolytic D(R$-$Br) values of Ph$-$Br and of CH$_2$=CHBr as 196.7 and 192.1 kcal/mol, respectively (Chart 1).

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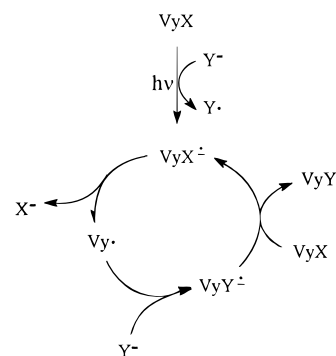
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$$\text{VyX} \xrightarrow[- \text{X}^-]{h\nu} \text{Vy}^+ \xrightarrow{\text{Y}^-} \text{VyY} \qquad (1)$$
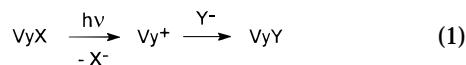
we have carried out an investigation, whose results are herein described.

Results

Competition among Heterolysis, Homolysis, and S$_{RN}$1 with 1,2,2-Triphenylbromoethene (1). The triphenyl-substituted vinyl bromide **1** gives an "S$_N$1" solvolytic reaction in ethanol (eq 2); this occurs either, and
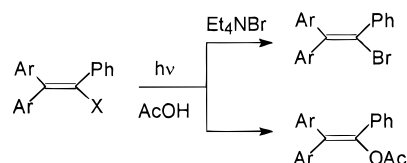
$$\text{(2)}$$
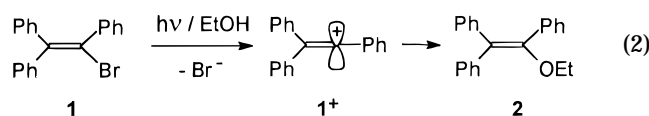
more slowly, upon heating at high temperature[20] or, and more easily, on irradiation with UV lamps.[1,21] Intermediacy of the α-phenyl substituted vinyl cation **1$^+$** was proposed. Structurally similar compounds, where one or more of the phenyl substituents of **1** are replaced by anisyl groups (An), were also investigated (eq 3).[1,3a] On

$$\text{(3)}$$

*via* cationic intermediate

via radical intermediate
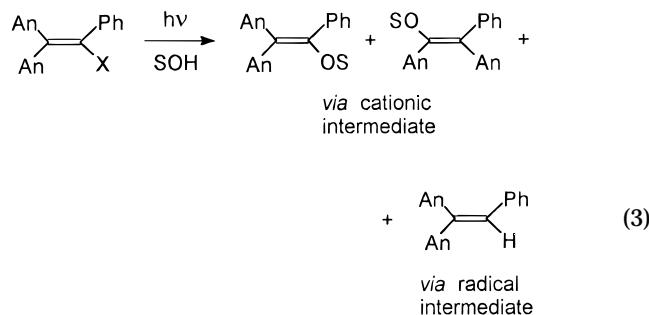
irradiation, solvolysis products were consistently observed, involving also those derived from rearrangements (e.g., 1,2-aryl shift) governed by the tendency to afford the more stabilized vinyl cation,[1,4] accompanied by lower amounts of hydrodehalogenated product(s) deriving from the vinyl radical intermediate (Scheme 2). Whenever the reactivity and selectivity of the photochemically produced vinyl cation was studied, it resembled those of the same species generated by thermal solvolysis, thereby suggesting the intermediacy of a ground-state vinylic ion under photochemical induction.[3a] Capture of this vinylic ion by a nucleophile purposely added in solution was also reported (Scheme 4).[1,3a,4a,22]

In keeping with a photoinduced heterolytic cleavage of the C−Br bond of **1**, we have confirmed (Table 1, expt 1) that a significant yield of the ethoxy-derivative **2** is obtained by irradiation in EtOH at 350 nm and room temperature in our photochemical reactor. This should be compared with the very slow solvolysis reaction of **1** even at a much higher temperature.[20a] However, **1** had also provided an unambiguous example of a photochemi-

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Scheme 4

cally induced S$_{RN}$1 nucleophilic substitution in DMSO solution.[17b] On irradiation at 350 nm in the presence of the enolate ion from pinacolone (Me$_3$CCOCH$_2^-$), which is an electron donor species under photostimulation,[19,23] the nucleophilic substitution product **3** was obtained in a fairly good yield (eq 4; expt 2). It was accompanied by

$$\text{(4)}$$

$$\text{Y}^- = {}^-\text{CH}_2\text{COCMe}_3; \quad {}^-\text{CH}_2\text{COPh}$$
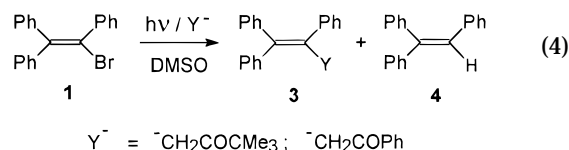
minor amounts of the hydrodehalogenated product **4**, presumably derived from the vinyl radical intermediate by H-atom abstraction from the solvent. An S$_{RN}$1 process was analogously substantiated for a photostimulated reaction of **1** with the enolate ion from acetophenone[17b] and with the conjugate base of nitromethane under entrainment.[24]

Evidence that the substitution product **3** derives from the vinyl radical intermediate within an S$_{RN}$1 cycle was that formation of the substitution product was almost completely suppressed (eq 5; expt 3) when the photo-

$$\text{(5)}$$
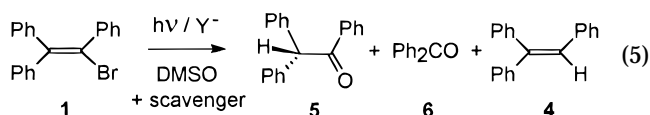
stimulated reaction of **1** with Me$_3$CCOCH$_2^-$ was run in the presence of a 20% molar amount of an electron scavenger, such as *p*-dinitrobenzene. In this case, minor amounts of two previously unobserved products were instead identified (**5** and **6**); **5** is likely to be formed from capture of the intermediate vinyl cation by traces of water present in the reaction environment, while **6** should be a cleavage product from **5**.[3a,20d]

A control experiment indicated that, in the photolysis of **1** in 95% DMSO−5% water (v/v) without added nucleophile, **5** and **6** are indeed produced and that the amount of **5** decreases, while that of **6** increases, for a prolonged irradiation. We conclude that photoejected electrons from a reducing nucleophile convert **1** into the vinyl radical intermediate **1$^•$** through the **1$^{•-}$** fleeting intermediacy (see eq 4 and Scheme 3), and the S$_{RN}$1 substitution product is obtained. In contrast, when purposely added electron scavenger prevents ET events, the S$_{RN}$1 cycle is suppressed so that the direct photoheterolysis of the C−Br takes over (as in eq 5). Under these circumstances, only the formation of the "solvolytic product" **5** (and **6**) is observed, with no traces of the *nucleophilic* substitution product that could conceivably result from coupling of the vinyl cation with the enolate ion (eq 1). The latter process appears therefore unlikely

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**Table 1. Reaction Conditions and Yields of the Photoinduced Reactions**[a]

expt no.	subst RX	conditions	solvent	reagent Y	reactn time (min)	products, yield (%)			recov RX
						RY	RH	others	
1	**1**	$h\nu$, 350 nm	EtOH		20	**2**, 33	**4**, 3		42
2	**1**	$h\nu$, 350 nm	DMSO	$Me_3CCOCH_2^-$	20	**3**, 55	**4**, 4		24
3[b]	**1**	$h\nu$, 350 nm	DMSO	$Me_3CCOCH_2^-$	20	0	**4**, 2	**5**, 4; **6**, 2	80
4	**1**	$h\nu$, 350 nm	DMSO	$(EtO)_2PO^-$	20	**7**, 8	**4**, 38	**5**, 1	35
5[b]	**1**	$h\nu$, 350 nm	DMSO	$(EtO)_2PO^-$	20	0	**4**, 2	**5**, 2	75
6	**1**	$h\nu$, 254 nm	DMSO	$(EtO)_2PO^-$	20	0	**4**, 0.7	**5**, 1.5	20
7	**1**	$h\nu$, 350 nm	DMSO-d_6	$(EtO)_2PO^-$	20	**7**, 8	**4(-d)**, 12	**5**, 0	38
8	**1**	$h\nu$, 350 nm	EtOH	$(EtO)_2PO^-$	60	**2**, 15	**4**, 20		28
9	**1**	$h\nu$, 350 nm	DMSO	NO_2^-	20		**4**, 0.2	**5**, 9; **6**, 0.1	41
10	**1**	$h\nu$, 350 nm	DMSO	N_3^-	20		**4**, 4	**5**, 13; **6**, 0.1	48
11	**1**	$h\nu$, 350 nm	DMSO	$PhCH_2Et_3NCl$	20		**4**, 2	**5**, 12	45
12	**8**	$h\nu$, 350 nm	DMSO	$PhCH_2Et_3NCl$	60	**9**, traces		c, 21	10
13[d]	**1**	$h\nu$, 350 nm	DMSO	NO_2^- and $Me_3CCOCH_2^-$	20	e	**4**, 3		
14	**1**	$h\nu$, 350 nm	DMSO		20		**4**, 1	**6**, 12	62
15	**1**	$h\nu$, 254 nm	DMSO		20		**4**, 0.5	**6**, 35	42
16	**1**	$h\nu$, 419 nm	DMSO		20		**4**, 0.5	**6**, 0	95
17	**1**	$h\nu$, 254 nm	DMSO	$Me_3CCOCH_2^-$	20	**3**, 69	**4**, 3		17
18	**1**	$h\nu$, 419 nm	DMSO	$Me_3CCOCH_2^-$	20	**3**, 29	**4**, 1		51
19	**11**	$h\nu$, 350 nm	DMSO		120	**12**, 33			45
20	**11**	$h\nu$, 254 nm	DMSO		120	**12**, 65			22
21	**11**	$h\nu$, 419 nm	DMSO		120	**12**,6			70
22[f]	E−**13**	$h\nu$, 350 nm	C_6H_6		180	**14**, major	<1	g	
23	Z−**13**	$h\nu$, 350 nm	C_6H_6		180	**14**, major	<1	g	
24	**11**	$h\nu$, 350 nm	DMSO	$Me_3CCOCH_2^-$	60	**17**, 40	**18**, 3		30
25	**11**	80 °C	C_6H_6	$Bu_3SnH/AIBN$	300		**18**, 60		30
26	**11**	$h\nu$, 350 nm	C_6H_6	$Bu_3SnH/AIBN$	360	**12**, 21	**18**, 27		5
27	**11**	$h\nu$, 350 nm	DMSO	$Bu_3SnH/AIBN$	240	**12**, 11	**18,** 19		10
28	**19**	$h\nu$, 254 nm	EtOH		60		**21**, 11	**20**, 5	51
29	**22**	$h\nu$, 254 nm	EtOH		60		**21**, 0	**20**, 35; **23**, 5	37
30	**1**	$h\nu$, 350 nm	EtOH	EtO^-	60	**2**, 12	**4**, 23		35
31	**1**	$h\nu$, 350 nm	t-BuOH		80		**4**, 0.7		42
32	**1**	$h\nu$, 350 nm	t-BuOH	t-BuO$^-$	80		**4**, 0.5		64

[a] Photolyses were run at room temperature under argon. Typical conditions: substrate, 60 μmol; nucleophile, 200 μmol; solvent, 3 mL. [b] In the presence of 15 μmol of *p*-dinitrobenzene. [c] 4,4′-Dimethoxybenzophenone. [d] Entrainment experiment: 84 μmol of Me_3CCOCH_3 and 423 μmol of KNO_2. [e] $Ph_2C=C(Ph)CH_2COCMe_3$ (20%) and traces of $Ph_2C=C(Ph)NO_2$ (by GC-MS). [f] Reported in ref 27. [g] Traces of benzofuranophenanthrene **15** (see ref 27).

under our conditions, at least at the concentration of the anion investigated.

Reactions of Other Nucleophiles with 1. A photo-stimulated $S_{RN}1$ reaction of **1** was analogously attempted with $(EtO)_2PO^-$ as the nucleophile (eq 6). The substitu-

$$\text{(6)}$$
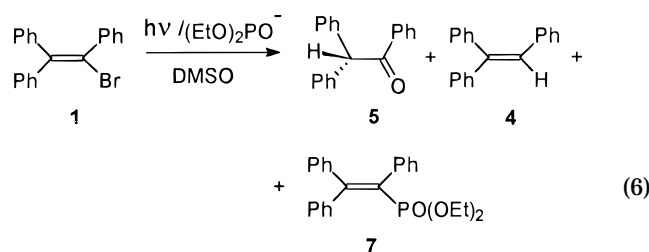
tion product **7** was obtained in low yield, and it was accompanied by major amounts of reduced product **4** (expt 4). In agreement with the occurrence of a $S_{RN}1$ process, the formation of both **7** and **4** was inhibited in the presence of *p*-dinitrobenzene (expt 5). When compared to the case of $Me_3CCOCH_2^-$ as the nucleophile (expt 2), the lower efficiency of $(EtO)_2PO^-$ in the $S_{RN}1$ process (see expt 4) results not only from obtaining a higher amount of **4**, via radical **1•**, but also from the formation of the "solvolytic" product **5** via ion **1⁺**. On irradiation at "254 nm" in a quartz vessel (expt 6), the formation of **7** is completely suppressed, while **5** and **4** are still observed, even though in low yield. This supports a competition between photoejection of electrons from $(EtO)_2PO^-$ ion and direct heterolysis (and homolysis) of the C−Br bond,

with heterolysis contributing more at the shorter irradiation wavelength. This wavelength effect on the efficiency of the photoheterolysis has already been documented.[1,4a]

Reaction of **1** and $(EtO)_2PO^-$ in DMSO-d_6, under otherwise identical conditions, gave a lower amount of deuterated reduction product **4**-d (compare expts 4 and 7). This evidence for a kinetic isotope effect in the H-abstraction event points to the solvent as the source of hydrogen (or, deuterium) in the reduction product. Finally, an $S_{RN}1$ reaction with $(EtO)_2PO^-$ ion in EtOH solution was unsuccessfully attempted (expt 8). Either depression of nucleophilic reactivity of $(EtO)_2PO^-$ by hydrogen bonding, or preferential solvation of the vinyl cation by the solvent, prevented the $S_{RN}1$ process in favor of both the direct heterolysis (with formation of **2**) and homolysis of the C−Br bond (with formation of **4**).

No $S_{RN}1$ process was obtained in photostimulated experiments of **1** with NO_2^-, N_3^-, or Cl^- as nucleophiles, and only the "solvolytic product" **5** (and **6**) was identified (expts 9−11; see eq 5). This is in keeping with photoheterolysis of **1** prevailing over the ET $S_{RN}1$ process for these anions, which are indeed weaker reductants than $(EtO)_2PO^-$ and, even more so, than $Me_3CCOCH_2^-$ (Table 2).[23,25] Only from $An_2C=C(Br)An$ (**8**), which produces a vinyl cation stabilized by an α-anisyl group, photolysis with Cl^- provided a trace of the chloro derivative $An_2C=C(Cl)An$ (**9**; identified by GC-MS); **9** is presumably formed

(25) (a) Eberson, L. In *Electron-Transfer Reactions in Organic Compounds*; Springer-Verlag: Berlin, 1987. (b) *Acta Chem. Scand.* **1984**, *B38*, 439.

Table 2. Oxidation Potentials of Some Relevant Anions Y^- ($E°$ in V vs SCE)[a]

Y^-	$E°$	Y^-	$E°$
$Me_3CCOCH_2^-$	-0.15[b]	MeO^-	0.6
PhS^-	0.1	NO_2^-	0.7
$(EtO)_2PO^-$	0.34[b]	N_3^-	1.3
PhO^-	0.25	Cl^-	1.9

[a] Data in DMSO or MeCN; see refs 23a and 25. [b] E^p values at 500 mV/s on a Pt electrode.

by capture of the intermediate vinyl cation $An_2C=C(^+)$-An by Cl^- (Table 1, expt 12; compare with Scheme 4).

An entrainment experiment of nucleophiles with **1** was attempted between excess NO_2^- and $Me_3CCOCH_2^-$, under irradiation at 350 nm. Only traces of a product that could be **10** were detected by GC-MS (eq 7; expt 13),
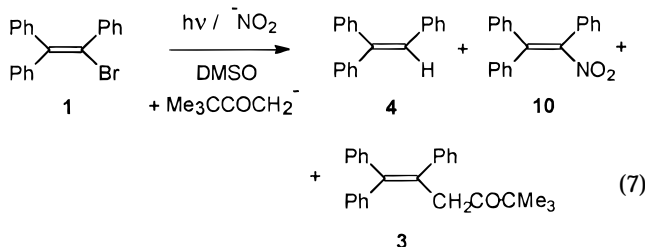
along with the prevailing formation of **3**. This would endorse a slight occurrence of the $S_{RN}1$ propagation cycle with NO_2^-, once the process is initiated by the competing and more efficient reductant $Me_3CCOCH_2^-$ anion, which makes the vinyl radical **1·** available. In the absence of $Me_3CCOCH_2^-$, the poor reducing character of NO_2^- makes inefficient the initiation of the vinylic $S_{RN}1$ process (see expt 9). Examples of entrainment between nucleophiles are well documented both for aromatic and vinylic $S_{RN}1$ processes.[18,24,26] The NO_2^- anion was selected for this entrainment experiment since recent calculations show that in an aromatic $S_{RN}1$ process the coupling of NO_2^- with $Ph·$ is thermodynamically favored.[23a]

Effect of the Irradiation Wavelength. This effect was investigated in the case of **1** in DMSO solution. In the absence of the nucleophile (i.e., $Me_3CCOCH_2^-$), irradiation at 350 nm provides a minor amount of **6** (expt 14); production of **6** is instead substantial (35%) for irradiation at 254 nm in a quartz vessel, while at 419 nm **6** is absent (expts 15 and 16). This confirms that the photoheterolytic cleavage of the C—Br bond is more efficient at a shorter wavelength, since the absorption of **1** is likely to decrease strongly in the visible range.[1,3b] On addition of the enolate ion, the $S_{RN}1$ process takes place and overwhelms the heterolytic route (expt 2), even at 254 nm (expt 17). Even for the $S_{RN}1$ process the efficiency decreases gradually on shifting to a longer wavelength, but formation of the substitution product **3** is still appreciable at 419 nm (expt 18). No measurement of the absorption spectra of the reagents nor of the possible charge-transfer complex (i.e., Y^- plus substrate)[19a] has however been carried out so far.

Competition of Pathways with Substrate 11. Photolysis of **11** in DMSO at 350 nm gave a fairly good conversion to the benzofuran derivative **12** (eq 8; expt 19). Conversion was higher at 254 nm and much less so at 419 nm (expts 20 and 21). Formation of **12** supports the heterolysis of the C—Br bond and the formation of a
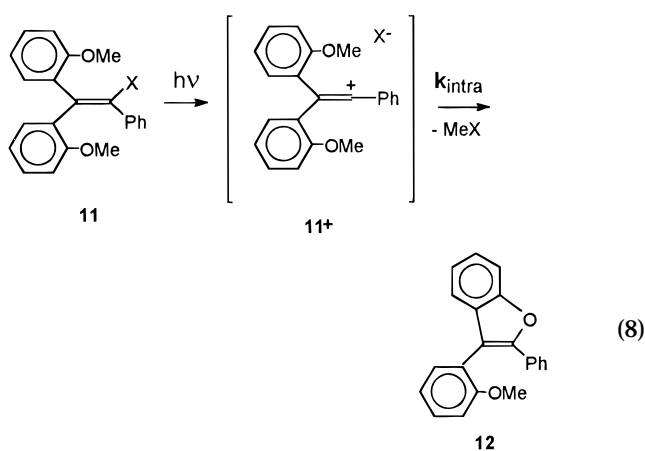
cationic intermediate (**11$^+$**), which is efficiently trapped by the "internal" nucleophile, that is, the methoxy group of the β *ortho*-anisyl moiety. This process had already been documented for **11** in benzene solution.[1,4,20,27]

Photolysis in benzene of the two related isomeric vinyl bromides *E*-**13** and *Z*-**13** consistently afforded **14** (expts 22 and 23). This supports a direct heterolysis of the C—Br bond even in this poorly solvating medium, which is followed by intramolecular capture of the linear vinyl cation intermediate by the *ortho*-anisyl group (eqs 9 and 10). A subsequent photochemical process gave **15**, as we
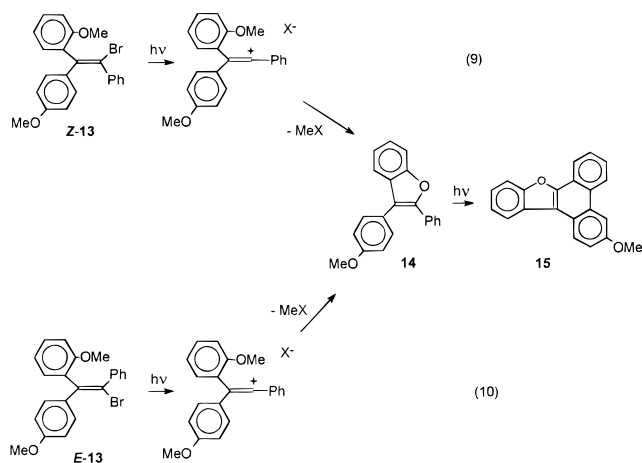
observed a gradual conversion of **14** into **15** when samples of the reaction mixture were withdrawn after 1, 3, and 5 h of photolysis. Such conversion had already been documented.[4b]

Formation of **14** from *Z*-**13** strongly argues against a possible intramolecular assistance of the *ortho*-anisyl group to the departure of the halide concerted with the C—Br bond heterolysis. Such a neighboring group participation could in principle be stereoelectronically possible for the *E*-isomer, in a single-step intramolecular S_N2 fashion but not for the *Z*-isomer. Previous work on structurally similar compounds had ensured that no *E/Z* isomerization of the precursors takes place under this conditions.[17d]

A photochemical reaction of **11** in the better solvating EtOH solvent still does not produce even traces of the intermolecular capture product of the intermediate vinylic cation by the solvent, but only **12** is obtained

(26) Galli, C.; Gentili, P. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1135.

(27) Sonoda, T.; Kobayashi, S.; Taniguchi, H. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2560.

(experiment not shown). This high selectivity underlines the enormous efficiency of the *intra*molecular process of eq 8, which leads to a five-membered cyclic product. The reported *inter*molecular rate constant for capture of the vinylic carbocation by EtOH for the structurally similar compound **16** under flash-photolysis (eq 11)[3b] is $k_{inter} =$

$$\text{(11)}$$
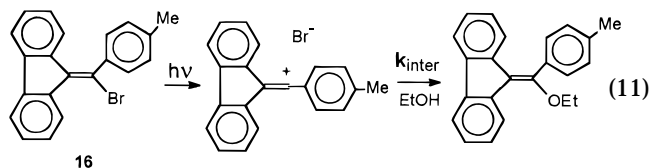
9.7×10^7 M^{-1} s^{-1}. For structurally similar compounds, k_{inter} values in the range of 10^5–10^6 M^{-1} s^{-1} were also reported.[4,28] We tentatively assume that a k_{inter} value of 10^7 M^{-1} s^{-1} also holds for a hypothetical intermolecular capture of the vinyl cation **11**$^+$ by EtOH. However, from the absence of even traces of the *inter*molecular capture product vs that of *intra*molecular capture (i.e., **12**) in the reaction of **11** in EtOH (as in eq 8), we evaluate that the intramolecular process must be ≥100 times more efficient than the intermolecular one. Thus, since the concentration of neat EtOH is 21.7 M, the k_{intra} value in eq 8 would be 10^{10} s^{-1}. Regardless of the approximate nature of this evaluation, we point out that the effective molarity (EM = k_{intra}/k_{inter})[29] for the formation of **12** comes to be 10^3 M, which is a reasonable value among those related to the efficiency of closure of five-membered rings, where typical EM values cluster around 10^4–10^5 M or are even higher.[29b,c] Hence, our evaluation of 10^{10} s^{-1} as the k_{intra} for **11** certainly represents a lower limit, and the value could even be 1 power of 10 higher.

Since **11** is the precursor of **11**$^+$, which is endowed with such a high intramolecular reactivity, we wondered if an $S_{RN}1$ process could efficiently compete with the photoheterolytic route for **11**. Reaction of **11** with $Me_3CCOCH_2^-$ under irradiation at 350 nm in DMSO gave a fairly good conversion into the $S_{RN}1$ substitution product **17**, which was accompanied by minor amounts of the hydrodehalogenation product **18**, without traces of benzofuran **12** (expt 24; eq 12).

$$\text{(12)}$$
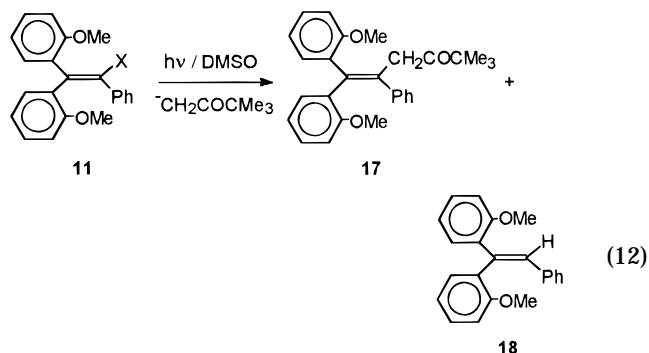
Product **18** was independently obtained as the only product on reacting **11** with the AIBN/Bu$_3$SnH system

(28) (a) Kobayashi, S.; Hori, Y.; Hasako, T.; Koga, K.; Yamataka, H. *J. Org. Chem.* **1996**, *61*, 5274. (b) Kobayashi, S.; Schnabel, W. *Z. Naturforsch.* **1992**, *47b*, 1319.

(29) (a) Jencks, W. P. In *Catalysis in Chemistry and Enzymology*; McGraw-Hill: New York, 1969. (b) Kirby, A. J. *Adv. Phys. Org. Chem.* **1980**, *17*, 183. (c) Mandolini, L. *Adv. Phys. Org. Chem.* **1986**, *22*, 1. (d) Illuminati, G.; Mandolini, L. *Acc. Chem. Res.* **1981**, *14*, 95. (e) Winnik, M. A. *Acc. Chem. Res.* **1977**, *10*, 173.

in boiling benzene (expt 25; eq 13). However, when the

$$\text{(13)}$$
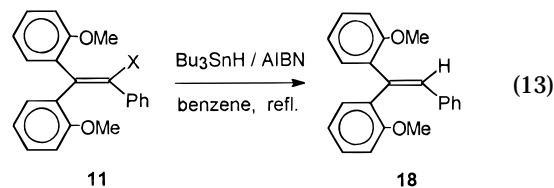
AIBN/Bu$_3$SnH reaction of eq 13 was conducted by *photochemically* inducing the cleavage of AIBN at 350 nm at room temperature, both **18**, derived from **11**·, and **12**, derived from **11**$^+$, were obtained in comparable amounts, both in benzene and in DMSO (expts 26 and 27). Thus, the absence of **12** in expt 24 does suggest that the $S_{RN}1$ route overshadows even a highly efficient photoheterolytic process.

Reactions of β-bromostyrene (19). The lack of an α-aryl substituent in **19** should reduce the stabilization of the intermediate β-phenylethenyl cation, as compared with the corresponding intermediates derived from **1** and **11** (i.e., **1**$^+$ and **11**$^+$), thus making the photoheterolysis less competitive. Indeed, in the photolysis of **19** in EtOH at 350 nm the starting material was quantitatively recovered. Only at 254 nm in a quartz vessel a minor conversion (ca. 5%) into phenylacetylene (**20**) was detected, the latter being the likely product of β-elimination from the intermediate β-phenylethenyl carbocation. No "S_N1" solvolytic product was instead detected, while 11% of styrene (**21**), i.e., the reduction product from the homolytic cleavage of the C–Br bond, was observed (expt 28; eq 14).

$$\text{(14)}$$
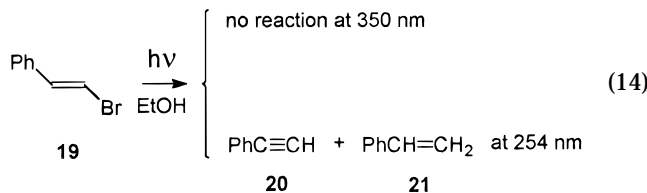
The homolytic cleavage appears to prevail in this system, thereby underlying the importance of having an α-aryl substituent for a successful occurrence of the photoheterolysis. Indeed, photolysis of α-bromostyrene (**22**) at 254 nm in EtOH gave a higher conversion (ca. 35%) to **20**, accompanied by 5% of acetophenone (**23**), the tautomer of the capture product of the α-phenylethenyl cation by adventitious water, but no traces of **21** (expt 29; eq 15).

$$\text{(15)}$$
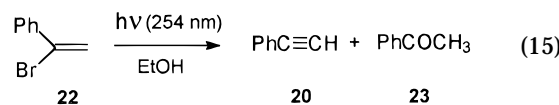
This confirms the prevalence of heterolysis over homolysis for an α-aryl substituted vinyl halide under irradiation.[1,3,4] A search for the possible occurrence of a $S_{RN}1$ process between an enolate ion and **19** indicated that the presence of the neighboring C–H and C–Br bonds allows instead the incursion of an ionic elimination–addition process.[17a,b]

Are the Alkoxide Ions Reductant Species? The reported reaction of the vinyl bromide **24** in MeOH offers further evidence for a competition between photoinduced heterolysis and homolysis of a C–Br bond, since both

solvolytic (**25**) and hydrodehalogenated (**26**) products were obtained at 350 nm (eq 16).[21a]

(16)
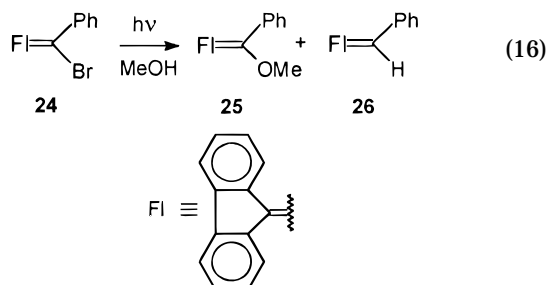
Surprisingly, on addition of MeO⁻ ion, the formation of the *reduction* product **26** was enhanced. This was attributed to MeO⁻ behaving as an electron donor toward **24** (eq 17).[21a] The radical anion **24**•⁻ produced


(17)
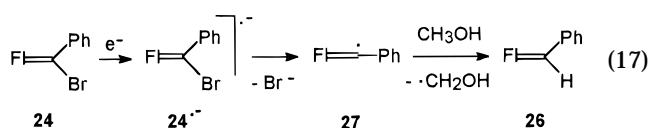
from this ET step will generate the corresponding vinyl radical **27** by loss of bromide ion. Hence, incursion of the photostimulated ejection of electrons from MeO⁻ would spur the production of **27**, from which the reduction product **26** originates, as compared to the formation of **27** by the direct photohomolysis of the C–Br bond (see eq 16) whenever the alkoxide is not present, with that accounting for the experimental finding. In keeping with the evidence delineated in eq 16,[21a] we have found that in the photolysis of **1** in EtOH the formation of reduction product **4** is indeed enhanced when the reaction is conducted in the presence of EtO⁻ (compare expt 30 with 1). However, we believe that the explanation given above[21a] is somewhat unlikely, since the alkoxide ions are *weak* electron donors (Table 2).[23,25] For example, we did not observe any reactivity for PhO⁻ or *t*-BuO⁻ ions in an aromatic $S_{RN}1$ reaction, not even under photostimulation,[23] even though electron transfer from a nucleophile is known to become easier under suitable irradiation.[19c,d] Therefore, it seems more likely to suggest that the vinyl radicals, which are produced from **1** or from **24** by the photohomolysis of the C–Br bond (see Scheme 2), abstract hydrogen atom not only from C_2H_5OH but also from $C_2H_5O^-$, whenever it is present (eq 18). From the

(18)
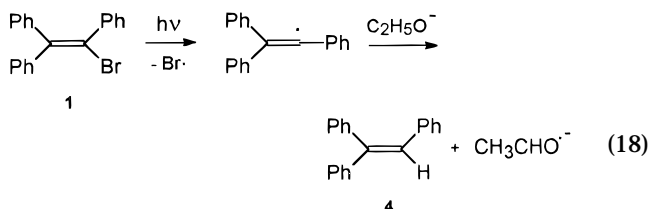
latter a ketyl species would be generated, i.e., the radical anion of acetaldehyde $CH_3CHO^{•-}$, a powerful reductant,[30] which could efficiently transfer an electron to **1** to produce **1**•⁻ (eq 19), and subsequently $Ph_2C=C(Ph)^•$.

In this way the formation of reduced product **4** could indeed be fostered by the presence of the alkoxide ion. There is circumstantial evidence that a ketyl species is

(30) Wardman, P. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1637.

(19)
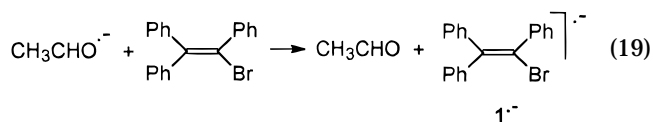
easily produced from an alkoxide ion under radical conditions,[31] and this technique was even recently exploited by us for obtaining an ET-induced hydrodehalogenation from a vinyl halide.[17d]

In contrast to present knowledge,[25] a recent report indicates the *tert*-butoxide ion as a rather strong reductant in solution,[32] on the basis of an extrapolation of its oxidation potential (i.e., $E°$ −0.23 V vs SCE in DMF) from gas-phase data. The suggestion that *t*-BuO⁻ can behave as an electron donor[32] would support the explanation[21a] delineated in eq 17 for a photostimulated process. To clarify this point, we have first irradiated **1** in neat *t*-BuOH and then in *t*-BuO⁻/*t*-BuOH. Only the reduced product **4** was formed, albeit in low yield (expts 31 and 32), with no traces of the solvolytic substitution product; this may be due to the steric bulk of *t*-BuOH compared with EtOH. Although the yields of expts 32 vs 31 are disappointly low, it is however possible to state that there is no evidence for an *enhancement* of the amount of **4** upon the addition of *t*-BuO⁻, in contrast to the increase of **4** in the corresponding expt 30 vs 1. According to our explanation, this negative outcome is due to the lack of α-CH bond in *t*-BuO⁻, which makes impossible the formation of a ketyl species[31a] (as in eq 18). Hence, the latter species would appear to be the likely electron donor (see eq 19), and the hypothesis of a photostimulated ET step from an alkoxide ion, as being responsible for the induction of the hydrodehalogenation reaction (eq 17), seems to lack support, at least for substrates having an electron affinity comparable with that of **1** (E_p −1.86 V vs SCE in THF).[17c]

Experimental Section

Instrumentation. Photochemical reactions were usually conducted in a Rayonet RPR-100 reactor equipped with a set of 16 "350 nm" lamps and occasionally with sets of 16 "419" or "254 nm" lamps. Reactions at 254 nm were conducted in a quartz cuvette, provided with a magnetic ministirrer; otherwise, a small Pyrex flask was used. Characterization of the structure of the reaction products was by conventional NMR techniques (data in CDCl₃), while HRMS determinations were carried out on a Bruker Apex TM47e FTMS.
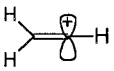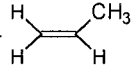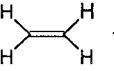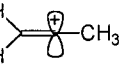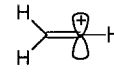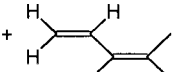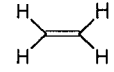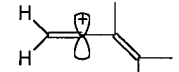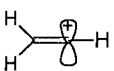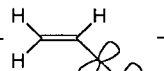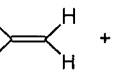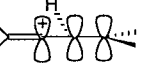
Materials. Reagent grade (Aldrich) α- and β-bromostyrene (**22** and **19**) were distilled prior to use. 1,2,2-Triphenylbromoethene (**1**), 1,2,2-triphenylethoxyethene (**2**), 1,1,2-triphenylethene (**4**), α,α-diphenylacetophenone (**5**), 1,2,2-trianisylbromoethene (**8**), 1-phenyl-2,2-bis(*o*-methoxyphenyl)-1-bromoethene (**11**), 2-phenyl-3-(*o*-methoxyphenyl)benzofuran (**12**), *E*- and *Z*-1-phenyl-2-(*o*-methoxy-phenyl)-2-(*p*-methoxyphenyl)bromoethene (*E*-**13** and *Z*-**13**), 2-phenyl-3-(*p*-methoxyphenyl)-benzofuran (**14**), 2-methoxy-9,10-benzofuranophenanthrene (**15**), and 1-phenyl-2,2-bis(*o*-methoxyphenyl)ethene (**18**) were available from previous investigations.[4b,17,20,27] The solvents were reagent grade commercial samples; benzene was dried over sodium wires, while DMSO (ERBA RPE) was distilled from CaH₂ under vacuum and stored over molecular sieves.

(31) (a) Bunnett, J. F.; Wamser, C. C. *J. Am. Chem. Soc.* **1967**, *89*, 6712. (b) Boyle, W. J.; Bunnett, J. F. *J. Am. Chem. Soc.* **1974**, *96*, 1418. (c) Amatore, C.; Badoz-Lambling, J.; Bonnel-Huyghes, C.; Pinson, J.; Savéant, J.-M.; Thiébault, A. *J. Am. Chem. Soc.* **1982**, *104*, 1979. (d) Bunnett, J. F. *Acc. Chem. Res.* **1992**, *25*, 2.
(32) Workentin, M. S.; Maran, F.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1995**, *117*, 2120.

Table 3. Isodesmic Reactions

	$\Delta H°$ (kcal/mol)

Freshly sublimed *t*-BuOK was employed in the generation of enolate anions.

Photochemical Experiments. With Solvent Only. In a typical experiment, 19 mg of **1** (57 μmol) and the chosen solvent (3 mL), previously purged with argon, were placed in a suitable flask and irradiated at the selected wavelength under argon. Depending on the solvent, either direct injection (for reactions in benzene or EtOH) into GC or GC-MS columns was carried out, after the addition of an internal standard, or a conventional workup (for DMSO) preceded the injection. The GC yield of the products was determined by calibrating the response factors of pure samples of the compounds. In some reactions of **1**, where **5** is obtained (expts 3−7, 9−11), subsequent conversion of **5** to **6** should occur.[33] This would require concurrent formation of benzoic acid.[20d] In one attempt we were able to detect it by MS analysis of the water extracts.

In the Presence of a Nucleophile. The enolate ion Me$_3$CCOCH$_2^-$ was generated in situ by addition of 28 mg of *t*-BuOK (0.25 mmol) to pinacolone (3,3-dimethyl-2-butanone, 25 μL; 0.2 mmol) in 3 mL of DMSO under argon; 20 mg of substrate **1** (60 μmol) was then added and irradiation followed. Similarly, (EtO)$_2$PO$^-$ was generated from (EtO)$_2$PHO (Fluka) with *t*-BuOK. In the attempt to run a reaction of (EtO)$_2$PO$^-$ in EtOH (expt 8), a stoichiometric amount of the base EtONa was produced in situ by the addition of a small piece of sodium of appropriate weight to the solvent, and then (EtO)$_2$PHO was added. Sublimed *t*-BuOK was added to *t*-BuOH in expt 32. Anhydrous commercial salts (KNO$_2$, NaN$_3$, PhCH$_2$Et$_3$NCl) were used as source of the nucleophiles in expts 9−13. In the entrainment expt 13, 423 μmol of KNO$_2$ and 84 μmol of Me$_3$CCOCH$_2^-$ in a photostimulated reaction with 83 μmol of **1** in 4 mL DMSO were employed. Traces of product **10** (*m/e* 301) were detected, alongside the prevailing formation of **3**.

Hydrodehalogenation with Bu$_3$SnH/AIBN. Previously reported conditions of homolytic cleavage of AIBN in boiling benzene were followed,[17d] in order to generate the tributyltin radical in situ. Alternatively, photochemical cleavage of AIBN at 350 nm in either benzene or DMSO was used.

Synthesis of Products. Diethyl (1,2,2-triphenylethenyl)phosphonate (7). Reaction of 90 mg of (EtO)$_2$PHO (0.65 mmol), 80 mg of *t*-BuOK (0.71 mmol), and 61 mg of **1** (0.18 mmol) in 8 mL of DMSO was conducted under photostimulation for 20 min; brine was then added and, following a

conventional workup with CHCl$_3$, a crude oil was obtained. Column chromatography (silica gel) with 6:1 toluene/diethyl ether as the eluent gave 6 mg of **7** (9% yield). ^{1}H NMR (δ, CDCl$_3$): 7.2−6.7 (m, 15H), 3.8 (q, 4H), 1.2 (t, 6H). HRMS: *m/e* 392.4366; C$_{24}$H$_{25}$O$_3$P requires 392.4384.

2,2-Dimethyl-5-phenyl-6,6-bis(2-methoxyphenyl)-5-hexen-3-one (17). Reaction of 0.49 mL of pinacolone (3.9 mmol), 0.56 g of *t*-BuOK (5 mmol), and 0.4 g of **11** (1 mmol) in 24 mL of DMSO was conducted under photostimulation at 419 nm for 3 h. The crude material obtained as above (0.58 g) was chromatographed on silica gel with toluene as eluent. A pure fraction of **17** was collected (130 mg, 43% yield). ^{1}H NMR (δ, CDCl$_3$): 7.3−6.6 (m, 13H), 3.65 (s, 6H), 3.50 (s, 2H), 0.92 (s, 9H). ^{13}C NMR (δ, CDCl$_3$): 213, 157, 143, 135, 132, 131, 128−125, 120, 119, 111, 110, 56, 55, 44, 43, 26. HRMS: 414.5428; C$_{28}$H$_{30}$O$_3$ requires 414.5420.

Calculations. An evaluation of the stabilizing effect from α-substituents in ethenyl cation structures (R$^+$) is presented, to be compared with the literature values quoted in Chart 2,[15] which are derived from H$^-$ affinity data in the reaction: H$^-$ + R$^+$ → RH. We have instead evaluated the α-substituent effect from the isodesmic reactions ($\Delta H°$ reaction in kcal/mol) reported in Table 3. The numbers under the structures are $\Delta_f H_{298}$ values in kcal/mol. For the uncharged species, the parent vinyl cation, and the 2-propenyl cation,[7] these values are taken from the literature.[11] For the other structures, we have calculated the $\Delta_f H_{298}$'s by the Hyperchem program[34] (AM1 level), imposing the desired conformation (single point). We have checked the reliability of these calculations by calculating also the $\Delta_f H_{298}$'s of vinyl (261 kcal/mol) and 2-propenyl (234 kcal/mol) ions: the agreement of these calculated values with those of the literature (261.7[7] and 235.0,[15] respectively), which are reported in Table 3, is remarkable and gives us confidence as to the reliability of our other calculations. From inspection of Table 3, it clearly emerges that α-π-substituents do stabilize the vinyl cation, particularly when they are coplanar with the empty p orbital of the ion and, therefore, able to conjugate with it.

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