Reactivity of Aryl and Vinyl Radicals: Abstraction of Hydrogen Atom or Reaction with a Nucleophile

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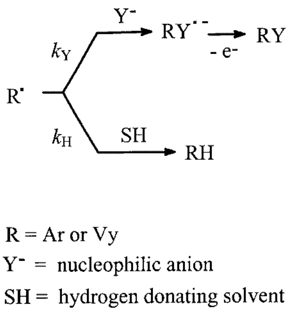
The reactivities of aryl and vinyl radicals, two fundamental transient intermediates, have been investigated with respect to two elementary processes: H-atom abstraction and reaction with a nucleophile (Y^-, in the $S_{RN}1$ reaction). The radicals of interest were generated from haloarene or haloethene precursors, either by use of the Bu_3SnH/AIBN system or by photostimulated electron transfer from a nucleophile, and the partition of the intermediate radical between competing pathways was investigated. Use both of indirect methods (such as the study of the reaction products in competition experiments; use of a radical-clock probe) and of direct ones (such as the detection of the radicals by flash photolysis experiments) enabled the following rate constants to be obtained (all values in $M^{-1}\cdot s^{-1}$ at 25 °C). For phenyl-type radicals, the rate constants for H abstraction (k_H) from the solvents Me_2SO ($2.8\cdot10^6$) and CH_3CN ($6.7\cdot10^6$) and the rate constant for combination with a nucleophile (k_Y) such as $Me_3CCOCH_2^-$ ion ($3.3\cdot10^9$) were determined. For vinyl radical $Ph_2C{=}C(^\cdot)Ph$ (**7**$^\cdot$), the k_H values from Me_2SO ($1.1\cdot10^5$), CH_3CN ($1.2\cdot10^5$), Bu_3SnH ($7.5\cdot10^8$), and $(Me_3Si)_3SiH$ ($1.6\cdot10^9$) and the k_Y values with $Me_3CCOCH_2^-$ ($3.9\cdot10^7$), $(EtO)_2PO^-$ ($2.8\cdot10^6$), and PhS^- ($1.9\cdot10^7$) ions were determined. Semiempirical calculations confirmed a stabilization of radical **7**$^\cdot$ by the α-Ph substituent (ca. 8 kcal/mol), and provided the BDE of the C–Y bond for the vinylic substitution products of **7**$^\cdot$.

Introduction

In the past 30 years the determination of rate constants of radical reactions in solution has provided a major contribution to understanding of the course of radical processes,[1−3] as well as to the achievement of valuable synthetic results.[4−7] Aryl radicals are important reactive intermediates, involved in many reactions of synthetic relevance.[8,9] The theoretical and practical relevance of the other sp^2-like structure − the vinyl radical − is comparable.[8b] Nevertheless, surprisingly, not many kinetic data are available for the fundamental steps in which these particular radicals are involved.[10,11] We have investigated both aryl and vinyl radical intermediates in the past few years, and met with difficulty in locating these kinetic data in an investigation intended to provide rate constant values (k_Y) for reactions between phenyl radical and a series of nucleophiles (Y^-) (the $S_{RN}1$ reaction).[12] To ascertain these k_Y values, we needed to know the rate constant of a competing reaction (Scheme 1). Strangely enough, not many kinetic data could be found for a reaction as simple as H-atom abstraction (k_H) by phenyl radical from common H-donor solvents.[11]



Scheme 1

In particular, no precise k_H data for the solvent Me_2SO were available. This investigation was therefore aimed towards the determination of k_H from Me_2SO by phenyl radical. This k_H value, in turn, enabled the k_Y value for the reaction between a phenyl-type radical and the enolate ion of a ketone to be obtained in a competition experiment. Because of our interest in the vinylic counterpart of the aromatic $S_{RN}1$ reaction, the determination of the corresponding k_H and k_Y rate constants for vinyl radical $Ph_2C{=}C(^\cdot)Ph$, which bears an α-Ph substituent, was also undertaken. Because these vinylic rate constants proved to be lower in value than their aromatic counterparts, a stereoelectronic stabilization effect of the $Ph_2C{=}C(^\cdot)Ph$ radical by the α-Ph substituent was inferred. Semiempirical calculations were performed in order to provide support for this inference, and the results are reported here.

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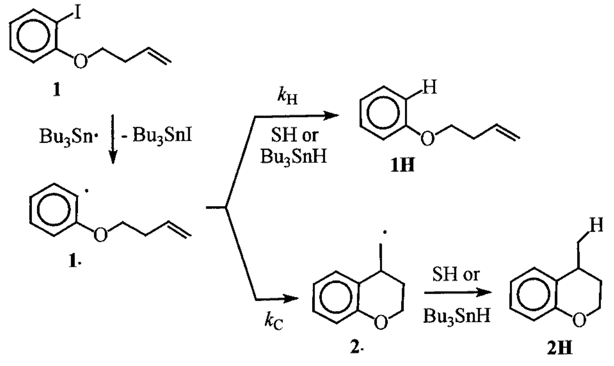
Results and Discussion

Determination of H-Abstraction Rates with Phenyl-Type Radical Clock **1**$^{\cdot}$

In a previous investigation,[12] *o*-(but-3-enyloxy)iodobenzene (**1**) had been employed as a radical clock, and a $4.2 \cdot 10^8$ s^{-1} intramolecular rate constant for the involved phenyl-type intermediate **1**$^{\cdot}$ (k_C in Scheme 2) was obtained at 25 °C,[13–15] by calibration with respect to H abstraction (k_H) from Bu_3SnH in benzene solution.[15] This k_C value was now exploited in turn for the determination of the k_H values for two H-donating solvents: Me_2SO and CH_3CN.



Scheme 2

Reactions of **1** were run in the chosen solvent at 25 °C with the AIBN/Bu_3SnH system,[16] by photochemical induction of the homolytic cleavage of initiator AIBN at 350 nm. The presence of Bu_3SnH ensured the perpetuation of an efficient radical chain process as according to Scheme 2, with intermediate **1**$^{\cdot}$ partitioning between cyclisation, ultimately affording **2H**, and H abstraction, giving **1H**. Under the adopted conditions, however, there were two H-donor species to **1**$^{\cdot}$: the solvent of interest (SH) and Bu_3SnH. Formation of **1H** should therefore follow Equation (1).

$$d[\mathbf{1H}]/dt = k_H \cdot [SH] \cdot [\mathbf{1}^{\cdot}] + k_{SnH} \cdot [Bu_3SnH] \cdot [\mathbf{1}^{\cdot}] = k'_H \cdot [\mathbf{1}^{\cdot}] \qquad (1)$$

For the two solvents investigated here, the reactions were performed in the presence of four different initial concentrations of Bu_3SnH. The molar amounts of the open-chain reduction product **1H** and of the cyclisation product **2H** were determined by GC analysis and used to calculate k'_H from Equation (2), from knowledge of the k_C value reported above.[13–15]

$$k_C/k'_H = [\mathbf{2H}]/[\mathbf{1H}] \qquad (2)$$

Equation (2) should hold whenever both the competing processes of Scheme 2 are of the same kinetic order. This was indeed the case here, because the formation of **2H** (with k_C) derived from a monomolecular first-order event, and H abstraction from the solvent, affording **1H** (with k_H), was a pseudo-first-order event. With reference to Equation (1), we used $7.8 \cdot 10^8$ $M^{-1} \cdot s^{-1}$ (at 25 °C)[15] as the k_{SnH} rate constant for H abstraction from Bu_3SnH by radical **1**$^{\cdot}$. To ensure that even the latter step was taking place under pseudo-first-order conditions, the reaction times of the experiments were chosen so as to be short enough to result in only minute conversion into products. In this way, the concentration of Bu_3SnH, which was anyway larger than that of **1**, remained sufficiently constant throughout the experiments, and the pseudo-first-order requirement was met. From the k'_H values obtained under these conditions, it was possible to obtain the k_H value of the solvent graphically, according to Equation (3), from the intercept of the plot at the various initial concentrations of Bu_3SnH. An example is provided in Figure 1 for the case of CH_3CN.

$$k'_H = k_H \cdot [SH] + k_{SnH} \cdot [Bu_3SnH] \qquad (3)$$

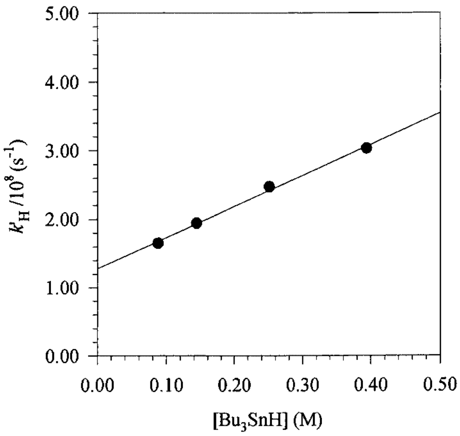


Figure 1. Determination of k_H by Equation (3); the case of acetonitrile is shown

Table 1. Rate constants of H-atom abstraction (k_H) by radicals **1**$^{\cdot}$ and **3**$^{\cdot}$ at 25 °C, by the use of radical clock precursors **1** and **3**, in the presence of Bu_3SnH (see Scheme 2 and Equations 1–3)

Radical	Solvent, SH	[Bu_3SnH]	k'_H [s^{-1}]	[SH][a]	k_H [$M^{-1} \cdot s^{-1}$]
1$^{\cdot}$	Me_2SO	0.299	$3.29 \cdot 10^8$	14.09	$2.76 \cdot 10^6$
		0.199	$2.26 \cdot 10^8$		
		0.142	$1.68 \cdot 10^8$		
		0.086	$1.28 \cdot 10^8$		
1$^{\cdot}$	CH_3CN	0.393	$3.03 \cdot 10^8$	19.19	$6.67 \cdot 10^6$
		0.251	$2.47 \cdot 10^8$		
		0.145	$1.94 \cdot 10^8$		
		0.088	$1.65 \cdot 10^8$		
3$^{\cdot}$	Me_2SO	0.287	$3.82 \cdot 10^8$	14.09	$6.37 \cdot 10^6$
		0.149	$2.48 \cdot 10^8$		
		0.091	$1.79 \cdot 10^8$		

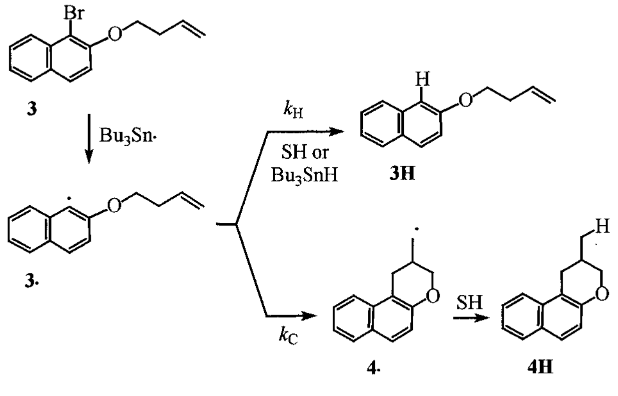
[a] Molarity of the neat solvent.

Table 1 reports the second-order rate constant k_H, calculated allowing for the effective concentration of the neat solvent, from its density and molecular weight.

This appears to be the first reliable determination of k_H from Me_2SO by a phenyl-type radical.[17] Our obtained k_H value for CH_3CN ($6.7 \cdot 10^6$ $M^{-1} \cdot s^{-1}$) was 2.4 times higher than that for Me_2SO ($2.8 \cdot 10^6$ $M^{-1} \cdot s^{-1}$), in keeping with analogous results by Savéant et al. ($1.4 \cdot 10^6$ and $6.0 \cdot 10^5$ $M^{-1} \cdot s^{-1}$ for CH_3CN and Me_2SO, respectively),[17] obtained with the 9-anthryl radical in an electrochemical investigation. The higher H donicity of CH_3CN than of Me_2SO towards aryl radicals explains why the former is a worse solvent than the latter in $S_{RN}1$ substitution processes,[18] in which the formation of aryl radicals as product-leading intermediates is a necessary requirement (see below).

The H-Atom Abstraction Rate of Naphthyl Radical

In our recent investigation,[12] we were puzzled to find that the reported k_H from Me_2SO by 1-naphthyl radical ($7.1 \cdot 10^6$ $M^{-1} \cdot s^{-1}$)[17] was one order of magnitude higher than that reported for the structurally analogous 9-anthryl radical ($6.0 \cdot 10^5$ $M^{-1} \cdot s^{-1}$),[17] both data having been obtained at 25 °C. Was there any error behind this discrepancy? As 1-bromo-2-naphthol is commercially available, the radical clock precursor **3**, structurally similar to **1**, could easily be synthesized. Treatment of **3** with the AIBN/Bu_3SnH system in Me_2SO solution with photostimulation at 25 °C (Scheme 3), had to give **3**$^{\cdot}$, the cyclisation of which to **4**$^{\cdot}$ would reasonably have to occur with the same k_C value as for the **1**$^{\cdot}$ → **2**$^{\cdot}$ process above, both being *6-exo-trig* processes.[19]



Scheme 3

On such treatment of **3**, run as above at different initial concentrations of Bu_3SnH, the expected **3H** and **4H** products were indeed obtained. Their molar amounts, combined with the k_C value of $4.2 \cdot 10^8$ s^{-1}, gave a k_H value for naphthyl radical **3**$^{\cdot}$ from Me_2SO of $6.4 \cdot 10^6$ $M^{-1} \cdot s^{-1}$. This rate constant agreed well with the determination of Savéant.[17] Since, though, the corresponding k_H value for 9-anthryl radical has been corroborated,[20] the difference in H-abstraction ability between 1-naphthyl and 9-anthryl radicals did appear to be real. Our own determination (Table 1) of k_H for the phenyl-type radical **1**$^{\cdot}$ was more in keeping with that for the 1-naphthyl radical, so that a *lower* reactivity of the 9-anthryl radical in H abstraction from Me_2SO was indeed confirmed, even though we cannot offer a sound and/or simple explanation for this experimental finding.

Competition Between Nucleophilic Attack and H-Atom Abstraction of the Phenyl Radical

Rate constants for the reactions between 1-naphthyl or 9-anthryl radicals and an enolate ion (k_Y in Scheme 1) in $S_{RN}1$ nucleophilic aromatic substitution have recently been reported.[12] In an $S_{RN}1$ process (Scheme 4),[21] a photostimulated electron transfer from the nucleophile generates the radical anion of precursor RX, which rapidly fragments.

$$RX \xrightarrow{Y^-/h\nu} RX^{\cdot -}$$

$$RX^{\cdot -} \rightarrow R^{\cdot} + X^-$$

$$R^{\cdot} + Y^- \rightarrow RY^{\cdot -}$$

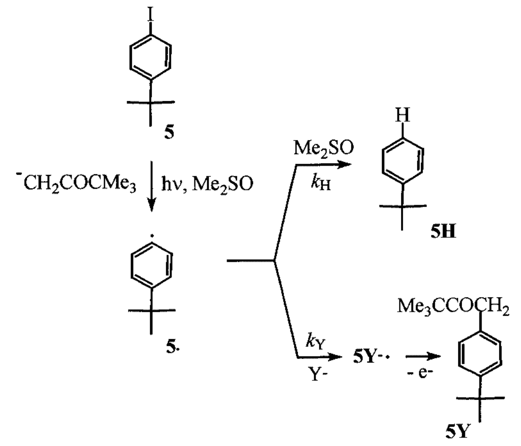
$$RY^{\cdot -} + RX \rightarrow RY + RX^{\cdot -}$$

Scheme 4. RX = ArX of VyX

The intermediate radical R$^{\cdot}$ may partition between combination with the nucleophile or H abstraction from the solvent (Scheme 1), and if k_H is known, the competing k_Y value can be calculated by product analysis.[12] The current determination of k_H from Me_2SO by the phenyl-type radical **1**$^{\cdot}$ (Table 1) has enabled us to extend our study of nucleophilic reactivity in $S_{RN}1$ reactions to the phenyl radical intermediate itself. If, however, an unsubstituted phenyl halide were taken as the precursor, its reduction product (i.e., benzene) would be too volatile to be precisely determined by gas chromatography. A higher boiling reduction product had to be found, and to this end 4-(*tert*-butyl)iodobenzene (**5**) was synthesized. No steric interference from the bulky *t*Bu group in the *para* position could be envisioned with respect to either of the competing processes of intermediate **5**$^{\cdot}$ (Scheme 5), while the higher boiling point of the *tert*-butylbenzene reduction product (**5H**) could reasonably be expected to ensure precise quantification. A photostimulated $S_{RN}1$ reaction between the enolate of pinacolone ($Y^- = Me_3CCOCH_2^-$) and **5** was performed in Me_2SO at 25 °C under standard conditions.[12]

Products **5H** and **5Y** were detected and, by use of Equation (4) and knowledge of the k_H value from Me_2SO (Table 1), the rate of reaction of the phenyl-type radical **5**$^{\cdot}$ with $Me_3CCOCH_2^-$ ion was obtained as $k_Y = 3.3 \cdot 10^9$ $M^{-1} \cdot s^{-1}$ (see Exp. Sect.).

$$\frac{k_H}{k_Y} = \frac{\ln \dfrac{[SH]_o - [Ph_2C{=}CHPh]_t}{[SH]_o}}{\ln \dfrac{[Y^-]_o - [Ph_2C{=}CYPh]_t}{[Y^-]_o}} \qquad (4)$$

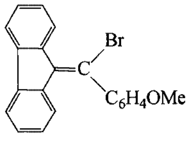


Scheme 5. Y = CH_2COCMe_3

This long-sought rate constant, with all the problems we had so far endured in order to obtain it,[12] has a value consistent with those of the reactions between 1-naphthyl and 9-anthryl radicals and pinacolone enolate ion ($2.9{\cdot}10^9$ and $4.4{\cdot}10^8$ $M^{-1}{\cdot}s^{-1}$, respectively),[12] and is similar to, or slightly larger than, the k_Y rate constants of other nucleophiles investigated in our study of the aromatic $S_{RN}1$ process.[12] This confirms that aryl radicals are both thermodynamically and kinetically efficient in their reaction with the enolate ions, with rate constants approaching the diffusion limit (ca. 10^{11} $M^{-1}{\cdot}s^{-1}$)[22] in these solvents.

Determination of H-Abstraction Rate Constants with Vinyl Radicals

Structurally analogous to aryl radicals ($Ar^{\cdot}$),[8b] vinyl radicals ($Vy^{\cdot}$) play a crucial role in the vinylic counterpart of the aromatic $S_{RN}1$ reaction (Scheme 4).[23] Once again, the efficiency of the substitution process depends on the relative rates of nucleophilic addition (k_Y) and of H-abstraction (k_H, Scheme 1). Unfortunately, there was no quantitative information relating to the reactivity of vinyl radicals with solvents or other H-atom donors,[24] let alone with nucleophiles. For these reasons we attempted to determine k_H values for several solvents and H-atom donors in the case of the vinyl radicals deriving from vinyl halides **6** and **7**, which had previously been investigated by us.[23] To perform these determinations, time-resolved laser flash photolysis and competition experiments were employed.



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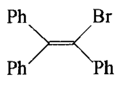

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a) Laser Flash Photolysis Determinations

a1) k_H Value of $6^{\cdot}$ from Bu_3SnH

A solution of precursor **6** in a 40:60 (v/v) CH_3CN/CH_3OH mixed solvent was purged with argon and irradiated at 248 nm, and the spectrum was recorded. Two transients, absorbing at λ_{max} = 300 and 340 nm, respectively (Figure 2, a), were observed. The 300-nm species reacted rapidly with oxygen (Figure 2, b).

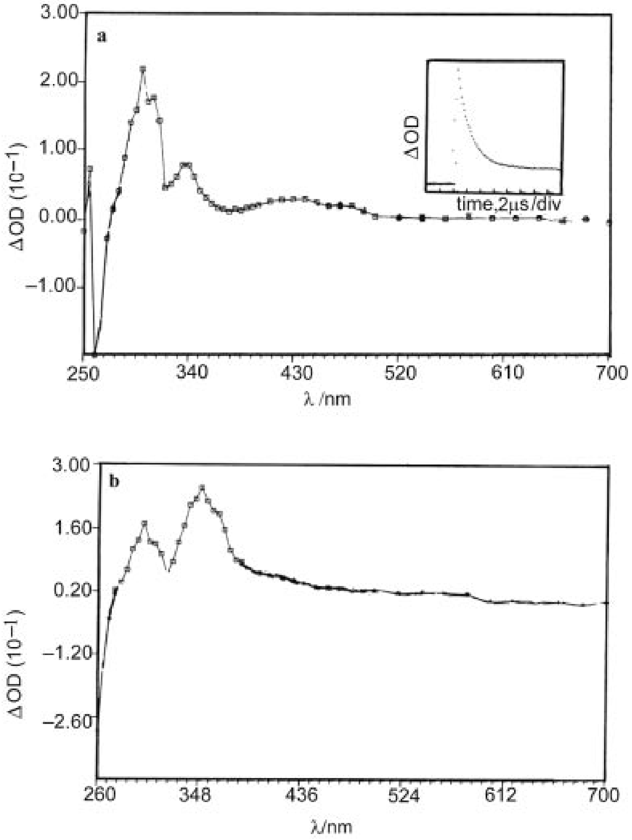
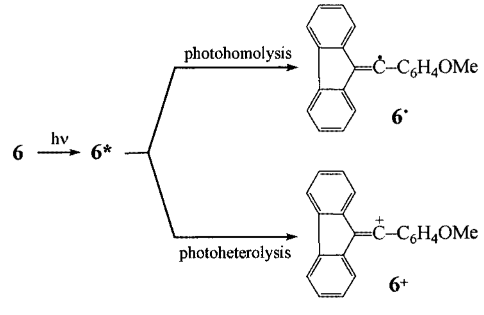


Figure 2. Absorption spectrum observed on photolysis (at 248 nm) of **6** (40 μM) in CH_3CN/CH_3OH (40:60, v/v) solution; a) in Ar-saturated solution and recorded 0.6 μs after the pulse; inset: decay of the absorption of vinyl radical $6^{\cdot}$ at 300 nm; b) in O_2-saturated solution and recorded 0.15 μs after the pulse

In keeping with previous results,[25] the structures of radical $6^{\cdot}$ and of cation 6^{+}, deriving from photohomolysis and photoheterolysis of the C−X bond of **6**, are suggested for the 300- and the 340-nm species, respectively (Scheme 6).



Scheme 6

In the presence of Bu_3SnH, added as a H-atom donor, the rate of decay of the 300-nm species was observed to increase, thus supporting the radical nature of $6^{\cdot}$.[26] The rate of decay of **6**$^{\cdot}$ was then measured in the presence of increasing amounts of Bu_3SnH, and a plot of the observed rate constant (k_{obs}, s^{-1}) against [Bu_3SnH] provided the value of $3.7 \cdot 10^8\ \text{M}^{-1} \cdot \text{s}^{-1}$ for the H-abstraction process by **6**$^{\cdot}$ from Bu_3SnH (Figure 3).

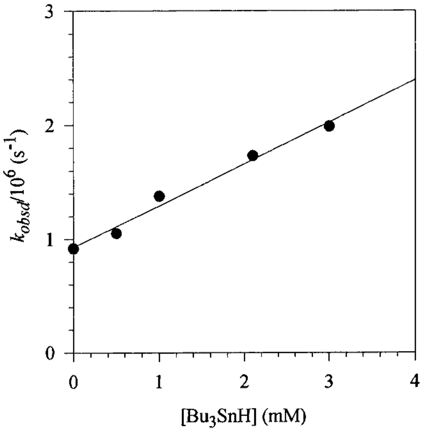


Figure 3. Plot of k_{obs} of vinyl radical **6**$^{\cdot}$ vs. [Bu_3SnH]

This value confirms the determination by Ingold et al. ($3.8 \cdot 10^8\ \text{M}^{-1} \cdot \text{s}^{-1}$)[24] for H abstraction from Bu_3SnH by vinyl radical $CH_3(CH_3)_5CH{=}CH_2^{\cdot}$ remarkably well, and is only a factor of two lower than the corresponding k_H value ($7.8 \cdot 10^8\ \text{M}^{-1} \cdot \text{s}^{-1}$)[15] for the phenyl-type radical **1**$^{\cdot}$. The consistency of these values provided a sort of internal check to the reliability of our determinations.

a2) k_H of 7$^{\cdot}$ from CH_3CN

Photolysis of precursor **7** in CH_3CN solution at 248 nm gave two absorption bands with λ_{max} = 270 and 320 nm, respectively (Figure 4, a).

The presence of oxygen suppressed only the formation of the 270-nm absorption (Figure 4, b). In contrast, in a 40:60 (v/v) CH_3CN/CH_3OH mixed solvent it was the 320-nm absorption that was partially depleted (Figure 4, c).

These results enabled us to identify the 270-nm species as the radical $Ph_2C{=}CPh^{\cdot}$ (**7**$^{\cdot}$) and the 320-nm species as the cation $Ph_2C{=}CPh^+$ (**7**$^+$), deriving from photohomolysis and photoheterolysis, respectively, of the C−Br bond of precursor **7** (Scheme 7).

From the rate of decay of the 270-nm absorbance in CH_3CN, we were able to measure the k_H value from this solvent by **7**$^{\cdot}$ as $1.2 \cdot 10^5\ \text{M}^{-1} \cdot \text{s}^{-1}$. This value is *sixty times lower* than the corresponding k_H value ($6.7 \cdot 10^6\ \text{M}^{-1} \cdot \text{s}^{-1}$) obtained for the phenyl-type radical **1**$^{\cdot}$ in CH_3CN (Table 1).

b) Competition Reactions in Photostimulated Experiments

b1) k_D of 7$^{\cdot}$ from CD_3CN

Precursor **7** had previously provided an unambiguous example of a vinylic $S_{RN}1$ process (Scheme 4) in Me_2SO solution, through the intermediacy of **7**$^{\cdot}$ as the reactive intermediate.[23b] This prompted us to develop a set of competitive reactions according to Scheme 1, in order to determine k_Y from product analysis, if the k_H (or k_D) were known, or vice

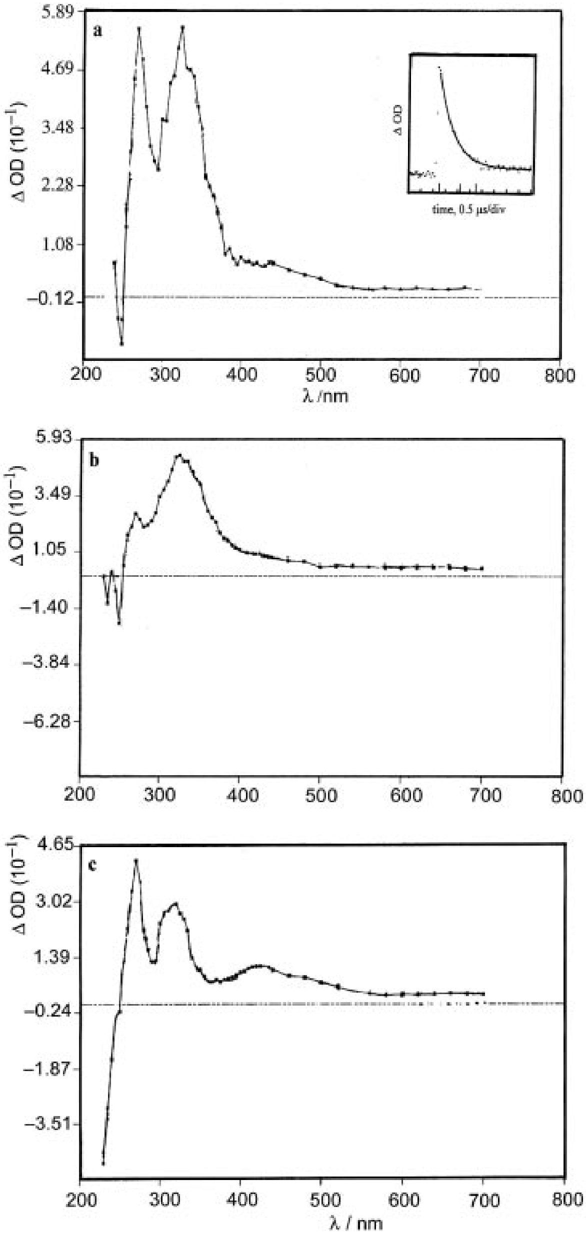
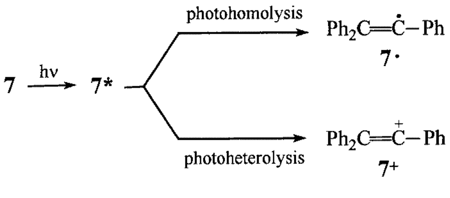
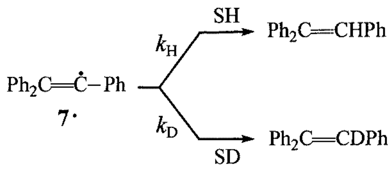


Figure 4. Absorption spectrum of the transients produced from photolysis (at 248 nm) of **7** (0.21 mM); a) in Ar-saturated CH_3CN solution, recorded 0.30 μs after the pulse; inset: decay of the absorption of vinyl radical **7**$^{\cdot}$ at 270 nm; b) in O_2-saturated CH_3CN solution, recorded 0.30 μs after the pulse; c) in Ar-saturated CH_3CN/CH_3OH (40:60, v/v) solution, recorded 1.5 μs after the pulse



Scheme 7

versa. Photostimulation of **7** in the presence of $(EtO)_2PO^-$ as the nucleophile was carried out in CH_3CN (i.e., SH), containing a known amount of its deuterated analogue CD_3CN (i.e., SD). Photostimulated electron transfer from the nucleophile (Scheme 4) had to produce **7**$^{\cdot-}$ and, from the subsequent cleavage of the C−Br bond, **7**$^{\cdot}$. The latter would be able to react with the nucleophile, or to abstract either H atom or D atom from the SH/SD mixed solvent, to give $Ph_2C{=}CHPh$ or $Ph_2C{=}CDPh$, respectively (Scheme 8). The molar amounts of these two reduction products were determined by GC-MS and GC analyses, and used to calculate the k_H/k_D ratio by use of a modified Equation (4), where $[SH]_0$ and $[SD]_0$ are the initial concentrations of the two solvents, while $[Ph_2C{=}CHPh]_t$ and $[Ph_2C{=}CDPh]_t$ are the concentrations of the two reduction products formed at time *t*, see Equation (5).



Scheme 8

$$\frac{k_H}{k_D} = \frac{\ln \dfrac{[SH]_o - [Ph_2C{=}CHPh]_t}{[SH]_o}}{\ln \dfrac{[SD]_o - [Ph_2C{=}CDPh]_t}{[SD]_o}} \qquad (5)$$

Equation (5) should hold whenever the intermediate radical **7**$^{\cdot}$ has no other side-reactions. Accordingly, we chose sampling times *t* short enough to minimize the occurrence of the competing substitution process with $(EtO)_2PO^-$. The value of k_H obtained in *a2)* for CH_3CN ($1.2{\cdot}10^5$ $\text{M}^{-1}{\cdot}\text{s}^{-1}$) enabled us to calculate the competing k_D rate constant for CD_3CN by Equation (5) as $2.3{\cdot}10^4$ $\text{M}^{-1}{\cdot}\text{s}^{-1}$ (Entry 1, Table 2).

b2) k_H of 7$^{\cdot}$ from Me_2SO

By a similar approach, a photostimulated reaction between $(EtO)_2PO^-$ and **7** was performed in a mixture of Me_2SO and CD_3CN. Determination of the k_H/k_D ratio as above, enabled us to obtain the k_H value from Me_2SO ($1.1{\cdot}10^5$ $\text{M}^{-1}{\cdot}\text{s}^{-1}$; Entry 2, Table 2) by using k_D from CD_3CN as the relay value. Even this k_H rate constant for **7**$^{\cdot}$ proved to be *lower* than the corresponding k_H value for the phenyl-type radical **1**$^{\cdot}$ ($2.8{\cdot}10^6$ $\text{M}^{-1}{\cdot}\text{s}^{-1}$, Table 1). Other rate constants of **7**$^{\cdot}$ (in $\text{M}^{-1}{\cdot}\text{s}^{-1}$, Table 2) similarly obtained by this approach were: k_D from $[D_6]Me_2SO$ ($2.0{\cdot}10^4$) in a mixture of CH_3CN and $[D_6]Me_2SO$ (Entry 3), k_H from Bu_3SnH ($7.5{\cdot}10^8$) in a mixture of CD_3CN and Bu_3SnH (Entry 4), and k_H from $(Me_3Si)_3SiH$ ($1.6{\cdot}10^9$) in a mixture of CD_3CN and $(Me_3Si)_3SiH$ (Entry 5).

Competition Between Nucleophilic Attack and H-Atom Abstraction for a Vinyl Radical

The k_H values obtained for the vinyl radical **7**$^{\cdot}$ enabled us to calculate the k_Y rate constants (Scheme 1) with a few nucleophiles for photostimulation of **7** in Me_2SO solution. As we had done for aryl radical **5**$^{\cdot}$ (see above, Scheme 5), the relative amounts of reduction and substitution products were determined and, by use of Equation (4), the k_H/k_Y ratios were calculated for each nucleophile. The k_Y values reported in Table 3 were finally obtained by use of the appropriate k_H relay value.

The vinylic k_Y rate constants for the three nucleophiles [reactivity order: $Me_3CCOCH_2^- > PhS^- > (EtO)_2PO^-$] are lower than the corresponding k_Y values obtained with a phenyl-type radical. This is particularly true for $(EtO)_2PO^-$, the k_Y of which is $2.8{\cdot}10^6$ $\text{M}^{-1}{\cdot}\text{s}^{-1}$ vs. **7**$^{\cdot}$ and $2.5{\cdot}10^9$ $\text{M}^{-1}{\cdot}\text{s}^{-1}$ vs. **1**$^{\cdot}$.[12]

Table 2. Rate constants of H abstraction (k_H) and D abstraction (k_D) by vinyl radical **7**$^{\cdot}$ at 25 °C, by competition experiments under photostimulation at 350 nm

Entry	SH or H-atom donor	SD	Time [s]	$Ph_2C{=}CHPh$ [yields, %]	$Ph_2C{=}CDPh$ [yields, %]	$Ph_2C{=}CBrPh$ [recovd., %]	k_H/k_D	k_H or k_D [M^{-1} s^{-1}][a]
1[b]	CH_3CN	CD_3CN	40	1.7	0.3	89	5.3	$k_D = (2.3{\pm}0.2){\cdot}10^4$
2[b]	Me_2SO	CD_3CN	30	45	10	38	4.7	$k_H = (1.1{\pm}0.1){\cdot}10^5$
			60	47	10	17		
			90	47	10	10		
3[b]	CH_3CN	$[D_6]Me_2SO$	30	23	3	70	6.0	$k_D = (2.0{\pm}0.2){\cdot}10^4$
			60	28	3	65		
			90	24	3	52		
4[c]	Bu_3SnH	CD_3CN	600	50	1	40	$3.3{\cdot}10^4$	$k_H = (7.5{\pm}0.8){\cdot}10^8$
			1200	56	1	38		
5[c] [d]	$(Me_3Si)_3SiH$	CD_3CN	30	37	0.2	34	$6.7{\cdot}10^4$	$k_H = (1.6{\pm}0.1){\cdot}10^9$
			60	59	0.2	21		

[a] The k_H or k_D values are an average from the various sampling times. The relay value in Entry 1 is $k_H = 1.2{\cdot}10^5$ from CH_3CN. [b] Initiation of the process was by photostimulated electron transfer from $(EtO)_2PO^-$ ion. [c] Initiation of the process was by photoinduced cleavage of initiator AIBN. [d] The addition product $Ph_2C{=}C(Ph)SiMe_3$ was also identified by GC-MS, and estimated to be formed in ca. 30% yield.

Table 3. Rate constants (k_Y) for reaction of vinyl radical **7**$^{\cdot}$ with the nucleophiles (Y^-) in Me_2SO solution at 25 °C

Entry	Nucleophile (Y^-)	Time [s]	$Ph_2C{=}CHPh$ [yield, %]	$Ph_2C{=}CYPh$ [yield, %]	$Ph_2C{=}CBrPh$ [recovd., %]	k_H/k_Y	k_Y [M^{-1} s^{-1}][a]
1[b]	$(EtO)_2PO^-$	300	75	8	12	0.04	$(2.8{\pm}0.1){\cdot}10^6$
		900	71	8	12		
2[c]	$Me_3CCOCH_2^-$	30	20	15	50	19	$(3.9{\pm}0.4){\cdot}10^7$
		60	22	20	39		
		90	18	15	25		
3[b] [d]	PhS^-	1200	56	15	29	0.006	$(1.9{\pm}0.1){\cdot}10^7$

[a] k_Y is an average at the various sampling times. [b] Relay value is k_H from Me_2SO ($1.1{\cdot}10^5$ M^{-1} s^{-1}). [c] In the presence of Bu_3SnH as the H donor; [Bu_3SnH] = 5.7 mm; k_H = $7.5{\cdot}10^8$ M^{-1} s^{-1}. [d] At 40° C.

Semiempirical Calculations

The vinyl radical $Ph_2C{=}C(^{\cdot})Ph$ (**7**$^{\cdot}$) showed lower reactivity than a phenyl-type radical in H abstraction both from CH_3CN and from Me_2SO (Table 2), as well as with nucleophiles and, in particular, towards $(EtO)_2PO^-$ ion (Table 3). This could be explained in terms of a difference in stability between vinyl and phenyl radicals. The phenyl radical accommodates the odd electron in an sp^2 orbital perpendicular to the π system of the benzene ring, and consequently no delocalization of it is possible. Vinyl radicals possessing π-type substituents α to the carbon atom bearing the odd electron, on the other hand, have been found to be linear (i.e., with sp hybridization[11,27]). For such vinyl radicals, the π system of the substituent is orthogonal to the vinylic π system, but colinear with the p orbital hosting the odd electron. Delocalization of the latter into the π system of the substituent then becomes possible, and stabilization of the vinyl radical ensues. Radical $Ph_2C{=}C(^{\cdot})Ph$ (**7**$^{\cdot}$), with an α-Ph substituent, is expected (and found)[28] to be linear, with the α-phenyl ring perpendicular to the vinyl plane. In an attempt to determine any stabilization arising from this α-Ph substituent, calculation of the $\Delta H°_f$ of radical $H_2C{=}C(^{\cdot})Ph$, taken as a simplified model of radical **7**$^{\cdot}$, was carried out by a semiempirical method (AM1), with imposition of a perpendicular (⊥) conformation with respect to the π-vinyl system on the α-Ph substituent. The obtained $\Delta H°_f$ value, of 70.4 kcal/mol, can be compared (Table 4) with the $\Delta H°_f$ values for radicals $CH_2{=}CH^{\cdot}$, $Ph^{\cdot}$, and $PhCH{=}CH^{\cdot}$, obtained by the same semiempirical method, as well as with that of $H_2C{=}C(^{\cdot})Ph$, in which the α-Ph system was imposed as collinear (//) to the π-vinyl system. Available experimental data are 71.7 kcal/mol for $CH_2{=}CH^{\cdot}$,[29] and 81.1 kcal/mol for $Ph^{\cdot}$,[30] and the reasonable agreement with these data supports the reliability of our semiempirical calculations.

Table 4. Enthalpies of formation ($\Delta H°_f$) of radicals and neutrals of interest; the calculated BDE_{C-H} values of the RH species are also provided

RH	$\Delta H°_f$(RH) [kcal/mol][a]	R$^{\cdot}$	$\Delta H°_f$(R$^{\cdot}$) [kcal/mol][a]	BDE_{C-H} [kcal/mol][b]
PhH	22	$Ph^{\cdot}$	73	103
$CH_2{=}CH_2$	16	$CH_2{=}CH^{\cdot}$	60	96
$CH_2{=}CHPh$	39	$CH_2{=}C(^{\cdot})Ph$[c]	70	83
$CH_2{=}CHPh$	39	$CH_2{=}C(^{\cdot})Ph$[d]	78	91
$CH_2{=}CHPh$	39	$(^{\cdot})CH{=}CHPh$	82	95

[a] Calculated by the HyperChem program (AM1 level). [b] BDE_{C-H} = $\Delta H°_f(R^{\cdot})$ + $\Delta H°_f(H^{\cdot})$ − $\Delta H°_f(RH)$; $\Delta H°_f(H^{\cdot})$ = 52 kcal/mol. [c] The α-Ph is ⊥ to the vinylic plane (see text). [d] The α-Ph is // to the vinylic plane (see text).

In combination with the $\Delta H°_f$ value of $H^{\cdot}$ (52.1 kcal/mol),[31] the data in Table 4 enable the involved BDE_{C-H} values to be calculated.[22] The lower value of BDE_{C-H} (ca. 8 kcal/mol) corresponding to the ⊥ α-Ph-substituted $H_2C{=}C(^{\cdot})Ph$, in comparison both with the // α-Ph-substituted $H_2C{=}C(^{\cdot})Ph$ and also with $PhCH{=}CH^{\cdot}$, in which delocalization of the odd electron on the phenyl substituent is prevented, supports a stabilization of the ⊥ α-Ph-substituted vinyl radical. If an analogous stabilization were also present in the ⊥ α-Ph-substituted radical **7**$^{\cdot}$, it could explain the lower value of its k_H and k_Y rate constants (Table 3) in comparison to those of $Ph^{\cdot}$.

In the particular case of the reaction between **7**$^{\cdot}$ and $(EtO)_2PO^-$ ion, the low k_Y value (Table 3) could addition-

Table 5. Calculated $BDE_{C\text{-}Y}$ values of the vinylic substitution products, $CH_2{=}C(Ph){-}Y$

Y[a]	$\Delta H°_f[H_2C{=}C(Ph)Y]$ [kcal/mol][b]	$\Delta H°_f(Y^{\cdot})$ [kcal/mol][b]	$BDE_{C\text{-}Y}$ [kcal/mol][c]	k_Y [$M^{-1}{\cdot}s^{-1}$][d]
$(EtO)_2PO$[e]	−187	−165	92 (112)	$2.8{\cdot}10^6$
CH_3COCH_2[f]	−10	−6	74 (99)	$3.9{\cdot}10^7$
PhS	65	55	60 (81)	$1.9{\cdot}10^7$

[a] Taken from ref.[22] [b] Calculated from Benson's group increments.[22] [c] BDE_{C-Y} = $\Delta H°_f(CH_2{=}C\{^{\cdot}\}Ph)$ + $\Delta H°_f(Y^{\cdot})$ − $\Delta H°_f(CH_2{=}C\{Ph\}Y)$; $\Delta H°_f(CH_2{=}C\{^{\cdot}\}Ph)$ = 70 kcal/mol (from Table 4, the α-Ph is ⊥). The corresponding values from the aromatic homologues (i.e., Ph−Y) are given in parentheses.[22] [d] From Table 3, vs. **7**$^{\cdot}$. [e] $\Delta H°_f[(\{EtO\}_2PO)$ = −165 kcal/mol (calculated by the HyperChem program at AM1 level). [f] Taken as a model of Me_3CCOCH_2.

ally be due to steric congestion at the C_α carbon atom of $\mathbf{7}^\bullet$, owing to the presence of two "spectator" C_β-phenyl rings in the plane of the p orbital bearing the odd electron,[28] and also to the encumbrance of the diethyl phosphite anion.[22] The energy of the C−Y bond (BDE_{C-Y}) of the vinylic $H_2C{=}C(Ph)Y$ substitution products (Table 5), evaluated by recourse to Benson's group increments approach,[22,32] confirms weaker vinylic BDE values than in the corresponding aromatic case (i.e., for Ph−Y).[22] In particular, the $BDE_{(C-P)}$ value of $H_2C{=}C(Ph){-}P(O)(OEt)_2$ (92 kcal/mol), considerably lower than that of $Ph{-}P(O)(OEt)_2$ (112 kcal/mol), combined with the unfavorable entropic contribution for the addition of the $(EtO)_2PO^-$ ion,[22] could support the experimentally observed smaller tendency of the vinylic C−P bond of product $Ph_2C{=}C(Ph){-}P(O)(OEt)_2$ to be formed.

Experimental Section

General Remarks: Photochemical reactions were conducted in a Rayonet RPR-100 reactor equipped with 16 "350-nm" lamps (Pyrex-filtered). A water-jacketed Pyrex flask (10 mL capacity) was designed in order to perform thermostatted photochemical experiments;[12] the dimensions of this flask fitted to the hole of the RPR-100 reactor, and connection to an external thermostat was provided by appropriate tubes. Characterization of the structures of reaction products was by NMR at 200 and 300 MHz with Bruker instruments, and by GC-MS with an HP 5972 MSD at 70 eV. Chemical shifts are reported in the δ scale in ppm relative to residual nondeuterated solvent signals ($CDCl_3$). GC-MS and GC analyses were run on methylsilicone capillary columns. HRMS determinations were performed with a Bruker Apex TM47e FTMS. Semiempirical calculations were carried out by use of the HyperChem package.

Materials: Commercial chemicals (Aldrich) were used without further purification. Benzene was dried over sodium wires, while Me_2SO was distilled from CaH_2 and stored over activated molecular sieves (4 Å) under argon. Acetonitrile was distilled from anhydrous K_2CO_3. Deuterated solvents (Aldrich) were dried over activated 4 Å molecular sieves. Pinacolone, PhSH, and $(EtO)_2PHO$ were distilled prior to use; freshly sublimed *t*BuOK was used to generate the corresponding anions in the photostimulated experiment in Me_2SO.[21]

Synthesis of Precursors: Precursor **1** was synthesized from potassium *o*-iodophenoxide and 4-bromo-1-butene as previously described.[12] Precursor **3** was similarly obtained in 45% yield by treatment of 1-bromo-2-naphthol (Aldrich), KOH (powder), and 4-bromo-1-butene in CH_3CN solution at 60 °C for 48 h. ^1H NMR ($CDCl_3$): δ = 8.12−7.40 (m, 6 H, ArH), 6.0−5.9 (m, 1 H, CH=), 5.2−5.1 (dd, 2 H, $=CH_2$), 4.25 (t, 2 H, OCH_2), 2.55 (q, 2 H, $CH_2CH{=}CH_2$) ppm. ^{13}C NMR ($CDCl_3$): δ = 152 (C^{Ar}_{ipso}-O), 137 (CH=), 130−118 (aromatic carbons), 115 ($=CH_2$), 107 ($C^{Ar}_{ipso}-Br$), 69 (CH_2OAr), 33 ($CH_2CH{=}CH_2$) ppm. MS: *m/z* = 276−278 [M^+], 222−224 [$M^+ - CH_2CH_2CH{=}CH_2$]. HRMS: calcd. for $C_{14}H_{13}{}^{79}BrO$ 260.0146; found 276.0169. Precursor **5** was obtained in 40% yield by conventional iododediazoniation of commercial 4-*tert*-butylaniline: ^1H NMR ($CDCl_3$): δ = 7.65−7.55 and 7.15−7.10 (dd, 4 H, ArH), 1.3 (s, 9 H, CMe_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 151 (C^{Ar}_{ipso}-*t*Bu), 138−128 (aromatic carbon atoms), 91 ($C^{Ar}_{ipso}-I$), 35 (CMe_3), 31 (Me) ppm. MS: *m/z* = 260 [M^+], 245 [$M^+ - 15$], 118 [245 − I]. HRMS: calcd. for $C_{10}H_{13}I$ 260.0058; found 260.0047.

Synthesis of Products: *tert*-Butylbenzene (**5H**) is commercially available (Aldrich). Samples of **1H** and **2H** were available from the previous investigation.[12] An analytical sample of **3H** was obtained by alkylation of β-naphthoxide ion with 4-bromo-1-butene,[12] and purified by flash chromatography (benzene/hexane, 1:1) to give a waxy, low-melting solid that was used for the determination of the GC response factor. ^1H NMR ($CDCl_3$): δ = 7.8−7.1 (m, 7 H, ArH), 6.0−5.9 (m, 1 H, CH=), 5.25−5.10 (dd, 2 H, $=CH_2$), 4.15 (t, 2 H, OCH_2), 2.60 (q, 2 H, $CH_2CH{=}CH_2$) ppm. ^{13}C NMR ($CDCl_3$): δ = 157 ($C^{Ar}_{ipso}-O$), 135 (CH=), 129−119 (C_{Ar}), 117 ($=CH_2$), 67 (CH_2OAr), 34 ($CH_2CH{=}CH_2$) ppm. MS: *m/z* = 198. Product **4H** was synthesized on an analytical scale (for the determination of the GC response factor) by means of a photoinduced reaction between **3** and AIBN/Bu_3SnH in benzene, followed by flash chromatography (benzene/hexane, 1:3), to give an oil. ^1H NMR ($CDCl_3$): δ = 7.80−6.95 (m, 6 H, ArH), 3.80 (d, 2 H, OCH_2), 2.65−2.60 (bd, 2 H, $ArCH_2$), 2.05−1.90 (m, 1 H, $ArCH_2{-}CH{-}Me$), 0.93−0.90 (d, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 154 ($C^{Ar}_{ipso}-O$), 138−129 (aromatic carbon atoms), 108 ($C^{Ar}_{ipso}-CH_2$), 72 (OCH_2), 32 ($ArCH_2$), 31 ($ArCH_2CHMe$), 17 (CH_3) ppm. MS: *m/z* = 198. Product **5Y** was obtained by photostimulation (at 350 nm) of **5** (1.15 mmol) with Me_3CCOCH_3 (3.4 mmol) and *t*BuOK (3.6 mmol) in 10 mL of Me_2SO for 40 min. Workup with brine and diethyl ether gave an organic phase that was thoroughly washed with brine and dried (Na_2SO_4). Removal of the solvent gave a residue that was chromatographed on silica gel first with hexane, and then with hexane/diethyl ether (30:1), to give 30 mg of pure **5Y** as an oil (11% yield). ^1H NMR ($CDCl_3$): δ = 7.4−7.1 (dd, 4 H, ArH), 3.76 (br. s, 2 H, $ArCH_2$), 1.3 (s, 9 H, $ArCMe_3$), 1.2 (s, 9 H, $COCMe_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 213 (C=O), 149 (C^{Ar}_{ipso}−*t*Bu), 132 ($C^{Ar}_{ipso}-CH_2$), 130−125 (aromatic carbon atoms), 44 ($COCMe_3$), 34 ($ArCMe_3$), 31 ($ArCMe_3$), 26 ($COCMe_3$) ppm. MS: *m/z* = 232 [M^+], 147 [$M^+ - 85$], 117, 85 [$COCMe_3{}^+$], 57 [$CMe_3{}^+$]. HRMS: calcd. for $C_{16}H_{24}O$ 232.1822; found 232.1814. Further elution of the column provided 25 mg (6% yield) of the disubstitution compound **(5)₂Y**, i.e., 1,1-bis(*p*-*tert*-butylphenyl)-3,3-dimethyl-2-butanone; m.p. 176−177 °C. HRMS: calcd. for $C_{26}H_{36}O$ 364.2757; found 364.2719. Synthesis of $Ph_2C{=}CDPh$: Under a stream of argon, *t*BuOK (243 mg, 2.16 mmol), $(EtO)_2POH$ (185 μml, 1.44 mmol), and **7** (155 mg, 0.462 mmol) were added to 5 mL of [D₆]Me₂SO. The reaction mixture was irradiated at 350 nm for 120 min, and then quenched with water and extracted with ethyl acetate. Removal of the solvent gave a residue that was chromatographed on silica gel first with petroleum ether, and than with cyclohexane, to give finally 10 mg of $Ph_2C{=}CDPh$ (98% pure by GC analysis, 9% yield). ^1H NMR (CD_3Cl): δ = 6.97−7.28 (m, 15 H) ppm. MS: *m/z* = 257 [M^+], 256,255, 254, 253, 242, 241, 240, 180, 179.120.

General Procedure for the Determination of k_H by the Radical Clock Approach: Precursor **1** (0.06 mmol) was irradiated for 30−60 min at 350 nm in the chosen solvent (2.5 mL) in the presence of a known amount of Bu_3SnH (e.g., 0.21 mmol) and azobis(isobutironitrile) (AIBN; 0.06 mmol), while the flask was maintained at 25 °C by means of the glass jacket connected to an external thermostat. An internal standard (biphenyl) was added at the end of the irradiation and, after conventional workup with diethyl ether, analysis by GC and GC-MS provided the molar quantities of the open-chain reduction product **1H** and of the cyclic reduction product **2H**. Reactions were similarly repeated at different initial concentrations of Bu_3SnH. Use of Equation (2) allowed k'_H values to be obtained as a function of the amount of tin hydride present; by use of Equation (3), the required k_H value of the solvent under investigation was obtained as the intercept in a k'_H vs. [Bu_3SnH] plot (see Figure 1).

Reaction Between 3 and the AIBN/Bu_3SnH System in Me_2SO: Under a stream of argon, substrate **3** (46 mg, 0.165 mmol) in an Me_2SO (2.5 mL) solution of Bu_3SnH (e.g., 104 mg, 0.36 mmol) containing AIBN (30 mg) was irradiated at 350 nm at 25 °C for 60 min. Addition of an internal standard (biphenyl), workup with diethyl ether, and concentration to a small volume preceded GC determination of the molar amount of products **3H** and **4H**. The reaction was then repeated in the presence of different initial concentrations of Bu_3SnH. As before, the k_H value was obtained as the intercept in a k'_H vs. [Bu_3SnH] plot; see Equation (3).

The Photostimulated $S_{RN}1$ Reaction: Under a stream of argon, substrate **5** (0.14 mmol) was added to a flask containing a solution of Me_3CCOCH_3 (0.44 mmol) and *t*BuOK (0.66 mmol) in Me_2SO (7 mL). The mixture was stirred under argon and irradiated with 16 "350-nm" lamps, while the flask was thermostatted at 25 °C. After 1 min, the irradiation was switched off, brine and crushed ice were added, along with a suitable amount of the internal standard (biphenyl), and the mixture was worked up with diethyl ether. Concentration to a small volume, and analyses by GC and GC-MS, gave the molar quantities of the products formed (i.e., 0.021 mmol of **5Y** and 0.004 mmol of **5H**). Use of Equation (4) allowed k_Y to be calculated (as $3.3\cdot10^9$ $\text{M}^{-1}\cdot\text{s}^{-1}$), taking 14.1 M for the concentration of neat Me_2SO (i.e., SH) and k_H as being $2.76\cdot10^6$ $\text{M}^{-1}\cdot\text{s}^{-1}$.

Laser Flash Photolysis Experiments

General: Solutions of **6** in CH_3CN/CH_3OH (40:60, v/v) and of **7** in CH_3CN were prepared at initial concentrations suitable for obtaining OD of ca. 1−2 cm^{-1}, and were purged with argon before and during the experiment. The solutions were flowed in a 2 mm (in the direction of the laser beam) by 4 mm (in the direction of the analysis light) Suprasil quartz flow cell (flow rates ca. 1−2 mL/min), and photolyzed with 20-ns pulses of 248-nm light (ca. 2−40 mJ/pulse) from a Lambda-Physik EMG103MSC excimer laser. The peak optical density changes (ΔOD) of the light-induced optical transmission changes were of the order of 0.1−0.6, depending on substrate concentration and pulse power; the rise time was 1−2 ns. The light-induced optical transmission changes were digitized by Tektronix 7612 and 7912 transient recorders interfaced with a DEC LSI11/73$^+$ computer that also controlled the apparatus and the online preanalyzed data. Final data analysis was performed with a Microvax I connected to the LSI.

Procedures for the Determination of k_H and k_Y with Vinyl Radical $7^{\cdot}$

i) Determination of H-(or D-)Abstraction Rate Constant k_H (or k_D) by Vinyl Radical $7^{\cdot}$ from SH (or SD) Solvents: Under an inert gas, [*t*BuOK] = 98 mM, [$(EtO)_2POH$] = 62 mM, and [**7**] = 21 mM were added to a mixture of SH and SD solvents (1:1, v/v). The reaction mixture was irradiated at 350 nm at 25 °C. Sampling times were chosen to minimize as much as possible the formation of the substitution product [i.e., $Ph_2C{=}C(Ph)P(O)(OEt)_2$; see Table 2]. The irradiation was switched off during each sampling. Addition of an internal standard (biphenyl), quenching with water, extraction with diethyl ether, and GC analysis were carried out for each sampling. GC yields were determined by the internal standard method. The relative amounts of $[Ph_2C{=}CHPh]_t$ and $[Ph_2C{=}CDPh]_t$ were determined by GC-MS as described in the Appendix. Equation (5) allowed the k_H/k_D ratio to be calculated. Whenever k_H was known, it was possible to calculate k_D, and vice versa (Table 2).

ii) Determination of H-Abstraction Rate Constant k_H by Vinyl Radical $7^{\cdot}$ from Bu_3SnH [or $(Me_3Si)_3SiH$]: Under a stream of argon, **7** (3.25 mg, 9.69 μmol), Bu_3SnH {or $(Me_3Si)_3SiH$} (99 μmol) and initiator AIBN (4.58 mg, 27.9 μmol) were added to 2 mL of CD_3CN. The reaction mixture was irradiated at 350 nm at 25 °C. The irradiation was switched off during each sampling. Addition of an internal standard (biphenyl), quenching with water, extraction with diethyl ether, and GC analysis were carried out for each sampling. GC yields were determined by the internal standard method. The relative amounts of $[Ph_2C{=}CHPh]_t$ and $[Ph_2C{=}CDPh]_t$ were determined by GC-MS as described in the Appendix. Use of Equation (5) allowed k_H to be calculated, by taking 19.1 M for the concentration of neat CD_3CN (i.e. $[SD]_0$) and k_D as being $2.3\cdot10^4$ $\text{M}^{-1}\cdot\text{s}^{-1}$.

iii) Determination of Rate Constant k_Y for the Reaction of Vinyl Radical $7^{\cdot}$ with a Nucleophile: *t*BuOK (62 mg, 0.553 mmol), the parent acid of a nucleophile (0.388 mmol), and **7** (42 mg, 0.125 mmol) were added to 6 mL of Me_2SO under a stream of argon. The reaction mixture was irradiated at 350 nm at 25° C. The irradiation was switched off during each sampling. Addition of an internal standard (biphenyl), quenching with water, extraction with diethyl ether, and GC analysis were carried out for each sampling. GC yields were determined by the internal standard method. Equation (4) allowed k_Y to be calculated, by taking 14.1 M for the concentration of neat Me_2SO (i.e. $[SH]_0$) and k_H as being $1.1\cdot10^5$ $\text{M}^{-1}\cdot\text{s}^{-1}$.

Appendix

To determine the relative amounts of $Ph_2C{=}CHPh$ (256) and $Ph_2C{=}CDPh$ (257), we measured the intensities of the corresponding molecular ion peaks (i.e., i_{256} and i_{257}) by GC-MS, assuming that the intensity of each peak was directly proportional to the concentration of product present in the reaction mixture [Equation (6)].

$$i_{256}/i_{257} = [Ph_2C{=}CHPh]/[Ph_2C{=}CDPh] \qquad (6)$$

From independent GC analysis, we obtained the total concentration of the reduction products (i.e., $[Ph_2C{=}CHPh] + [Ph_2C{=}CDPh]$), which, by partition according to the i_{256}/i_{257} ratio [Equation (6)], had to provide the separate values of $[Ph_2C{=}CHPh]$ and $[Ph_2C{=}CDPh]$. Unfortunately, the mass spectrum of $Ph_2C{=}CDPh$ also presented a fragment peak with m/z = 256, the intensity of which was ca. 44% of the corresponding molecular ion peak (i.e., m/z = 257). This hampered the above determination of $[Ph_2C{=}CHPh]$ and $[Ph_2C{=}CDPh]$. To overcome this problem, a calibration curve was made, by plotting the i_{256}/i_{257} ratios determined by GC-MS vs. the molar fraction $x_H = [Ph_2C{=}CHPh]/([Ph_2C{=}CHPh] + [Ph_2C{=}CDPh])$ from solutions containing *known* amounts of $Ph_2C{=}CHPh$ and $Ph_2C{=}CDPh$ (Figure 5).
In each solution, the total concentration C_o is determined by Equation (7).

$$C_o = x_H[Ph_2C{=}CHPh] + (1 - x_H)[Ph_2C{=}CDPh] \qquad (7)$$

The intensities of the m/z = 256 and m/z = 257 peaks are set equal to Equations (8) and (9), respectively, where i_{256} $([Ph_2C{=}CHPh]_o)$ and i_{257} $([Ph_2C{=}CHPh]_o)$ are the intensities of the m/z = 256 and m/z = 257 peaks in a solution containing *only* $Ph_2C{=}CHPh$ at a concentration equal to C_o, whereas i_{256} $([Ph_2C{=}CDPh])_o$ and i_{257} $([Ph_2C{=}CDPh)])_o$ are the intensities of the m/z = 256 and m/z =

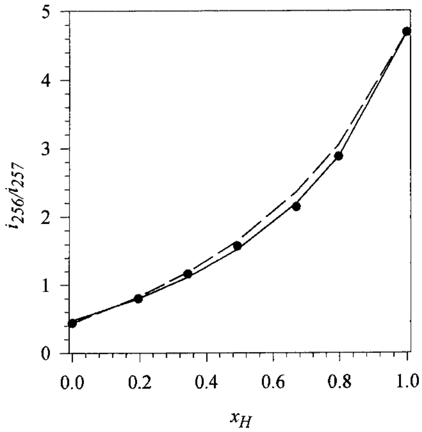


Figure 5. Calibration plot of i_{256}/i_{257} vs. x_H from a solution containing known amounts of $Ph_2C{=}CHPh$ and $Ph_2C{=}CDPh$; full line: from Equation (11); broken line: from Equation (10)

257 peaks in a solution containing *only* $Ph_2C{=}CDPh$ at a concentration equal to C_o.

$$i_{256} = x_H\ i_{256}([Ph_2C{=}CHPh]_o) + (1 - x_H)\ i_{256}([Ph_2C{=}CDPh]_o) \qquad (8)$$

$$i_{257} = x_H\ i_{257}([Ph_2C{=}CHPh]_o) + (1 - x_H)\ i_{257}([Ph_2C{=}CDPh]_o) \qquad (9)$$

From Equations (8) and (9), the ratio i_{256}/i_{257} as a function of the molar fraction x_H [Equation (10)] was obtained:

$$i_{256}/i_{257} = (a + bx_H)/(1 + cx_H) \qquad (10)$$

where

$$a = i_{256}([Ph_2C{=}CDPh]_o)/i_{257}([Ph_2C{=}CDPh]_o) = 0.436$$

$$b = \{i_{256}([Ph_2C{=}CHPh]_o) - i_{256}([Ph_2C{=}CDPh]_o)\}/i_{257}([Ph_2C{=}CDPh]_o) = 1.486$$

$$c = \{i_{257}([Ph_2C{=}CHPh]_o) - i_{257}([Ph_2C{=}CDPh]_o)\}/i_{257}([Ph_2C{=}CDPh]_o) = -0.5898$$

The fit of the calibration plot $i_{256}/i_{257} - x_H$ (Figure 5) to Equation (10) gave Equation (11) confirming the validity of Equation (10).

$$i_{256}/i_{257} = (0.4748 + 1.1314\,x_H)/(1 - 0.6568\,x_H) \qquad (11)$$

This enabled $[Ph_2C{=}CHPh]_t$ and $[Ph_2C{=}CDPh]_t$ to be determined [see Equation (5)] in the experimental samples. Each sample was analyzed by CG-MS to obtain the value i_{256}/i_{257}; the molar fraction x_H was calculated and averaged from Equations (10) and (11). From the total concentration of $Ph_2C{=}CHPh + Ph_2C{=}CDPh$ (determined by GC analysis) and the above x_H molar fraction, we finally obtained $[Ph_2C{=}CHPh]_t$ and $[Ph_2C{=}CDPh]_t$.

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