

Unequivocal $S_{RN}1$ Route of Vinyl Halides with a Multitude of Competing Pathways: Reactivity and Structure of the Vinyl Radical Intermediate

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ABSTRACT

Unambiguous examples of the vinylic $S_{RN}1$ reaction initiated by a single-electron transfer from an electron-donor anion (Y^-) to a suitable VyX substrate, and proceeding through a vinyl radical (Vy^{\cdot}) intermediate, are described. Competition by alternative substitution routes is extensive, but through a systematic modification of the structure of the substrate, unequivocal examples of the vinylic $S_{RN}1$ route are documented. The geometry of the Vy^{\cdot} and kinetic parameters for H-abstraction and coupling with Y^- are reported.

Introduction

The common $C_{(sp^2)}$ -halogen bond of aryl and vinyl halides stimulated an investigation aimed at unveiling analogies in reactions of these two families. The multiplicity of mechanisms for nucleophilic substitution (S_N) reactions with vinyl halides (VyX) exceeds that of aryl halides (ArX),¹ due to the intermediate position of vinylic systems between saturated and aromatic systems. The most common is the addition-elimination (Add-EI) route, initiated by nucleophilic addition to the double bond of VyX to yield a carbanion, which expels the nucleofuge. It is facilitated by electron-withdrawing groups (EWGs) on the double bond, or by good anionic nucleophiles. A single-step S_N2 -like route has been suggested.^{1b,2} Strongly basic anions may lead to elimination-addition (EI-Add) routes if VyX bears advantageously positioned C-H and C-X bonds: α,β -, α,α -, or α,β' -eliminations to an acetylene, a carbene, or an allene, respectively, are followed by nu-

cleophilic addition to the intermediate. Finally, suitable structural features lead to S_N1 reaction via a vinyl cation.³

We were interested in the vinylic counterpart of the extensively studied aromatic radical-nucleophilic substitutions ($S_{RN}1$),^{4,5} which are initiated either by spontaneous or photoinduced single-electron transfer (SET) from an electron-donor anion (Y^-) to the unsaturated system,^{5,6} proceeding by the reaction cycle delineated in Scheme 1 for a generic halide RX ($R = Ar$ or Vy).

The radical anion of RX is formed by SET in the initiation step (eq 1), fragmentation of $RX^{\cdot-}$ leads to a R^{\cdot} intermediate (eq 2) that couples with the nucleophile (eq 3) and yields the radical anion of the substitution product; ET to another RX gives the product RY and perpetuates the chain process (eq 4).^{5,6} Alternatively, R^{\cdot} can abstract an hydrogen from the solvent (SH) or another H-source (eq 3').⁷

$S_{RN}1$ processes had already been reported for a few VyX systems.⁸ If VyX and ArX react by parallel routes with electron-donor anions (Scheme 1), it would allow distinguishing effects due to the electrophilicity of VyX in ionic routes with nucleophilic anions, from effects due to the electron affinity of VyX toward reducing anions in ET routes. The possible competition between ionic and ET routes by suitable anions in many processes,^{9,10} including S_N2 reactions,¹¹ is well appreciated, thanks to a sizable body of experimental (electrochemical)¹² and theoretical^{9,13} contributions. Could evidence be achieved for the vinylic $S_{RN}1$ route, $S_{RN}1(V)$, despite the more frequently encountered nonradical nucleophilic ones? Could this route, where ET from a reducing anion generates the Vy^{\cdot} intermediate, be unambiguously distinguished from routes where the basic or nucleophilic character of the anion prevails? Could the $S_{RN}1(V)$ be distinguished from another route where, in the absence of reducing ions, C-X bond photolysis of VyX generates radical Vy^{\cdot} ,¹⁴ which yields the product via a nonnucleophilic nonchain ligand transfer? We know now that the $S_{RN}1(V)$ is not a common route, due to severe competition by other routes, but that it takes place with substrates with well-defined structures: our results have led to a better understanding of the subtle structural features that modulate competition among various nucleophilic vinylic substitution (S_NV) routes.

Preliminary Evidence

The first reported example of the $S_{RN}1(V)$ route was the photostimulated reaction of acetone enolate ion with β -bromostyrene (**1**) in liquid NH_3 .⁸ It gave the substitution product, $PhCH=CHCH_2COMe$ (**2a**), its base-isomerized tautomer, $PhCH_2CH=CHCOMe$ (**3a**), and the reduction product $PhCH=CH_2$ (**4**), formed by hydrogen-abstraction by the intermediate radical $PhCH=CH^{\cdot}$ from the medium (eq 3'). We performed an analogous reaction with the

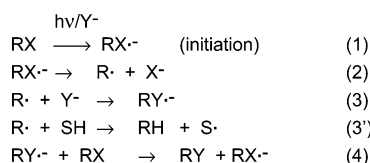
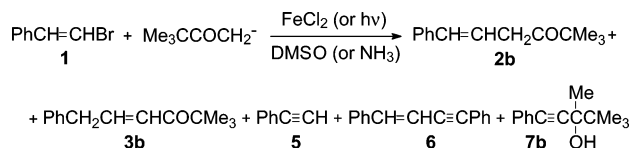
Carlo Galli was born in Rome in 1949, where he received the Laurea degree in Chemistry. Following postdoctoral research with Joe Bunnett at UCSC, he returned to the University "La Sapienza" in Rome, where he has been a Professor of Organic Chemistry since 1990. His research interests include ring-closure reactions, radical and electron-transfer processes, and the mechanism of enzymatic reactions.

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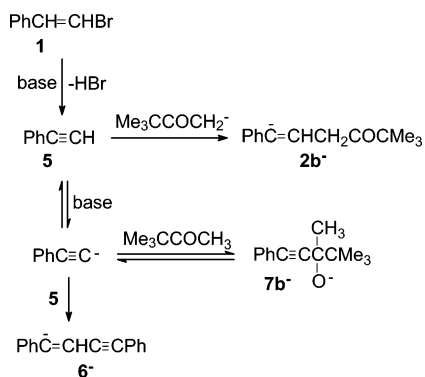
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Scheme 1. The S_{RN}1 Reaction Cycle (R = Ar or Vy)Scheme 2. Reaction of **1** with Me₃CCOCH₂⁻

Scheme 3. Reaction Mechanism



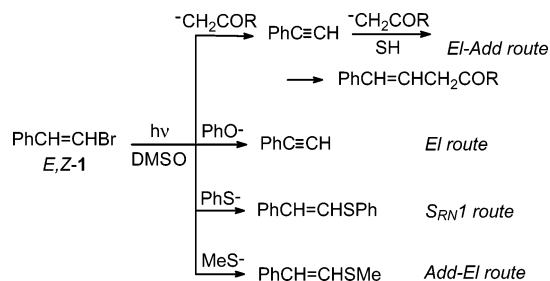
commercially available (9/1 *E/Z* mixture) **1** in DMSO, with the enolate ion of pinacolone (3,3-dimethyl-2-butanone) as the nucleophile (a well-known reducing anion),¹⁵ using FeCl₂ catalysis, a convenient alternative initiation to photostimulation.¹⁶ We obtained (Scheme 2) a somewhat different and richer product mixture than that of its literature analogue:⁸ **1** disappeared completely with formation of tautomeric substitution products **2b** and **3b**, plus phenylacetylene **5** and the enyne **6**, rather than the reduction product styrene **4**. Products **2b**, **3b**, and **6** were all richer in the *E*-isomer, but this was not pursued further. However, a major component of the reaction mixture was **7b**, an unexpected isomer of **2b** and **3b**. At shorter reaction times, **7b** predominated, but the amount of **2b** and **3b** increased at the expense of **7b** and **5** after a prolonged exposure to the basic reaction medium. We easily understand why the conceivable formation of the analogous **7a** from CH₃COCH₂⁻ could have been previously missed: isomers **3b** and **7b** have very similar GC retention times even on capillary columns, which were not standard equipment in 1976.⁸ The same holds true for **4** versus **5**. Our finding was the same when using the enolate of acetone (instead of pinacolone) in DMSO solvent^{15b} or when photostimulating the reaction rather than using ferrous-ion catalysis. Every explored source of difference between our experimental conditions and those originally employed provided the same results reported in Scheme 2. We were forced to conclude that the observed process was not an S_{RN}1(V) reaction but, rather, an α,β-EI-Add process (Scheme 3).¹⁵

Hence, when vinylic β-C-H and α-C-Br bonds are available, as in **1**, enolate ion basicity prevails over its

Table 1. Redox Potential (*E*_{Y⁻/Y⁻}), p*K*_{HY} and Nucleophilicity (*n*_{MeI}) Values of Anions Y⁻ Involved in the Study of the S_{RN}1 Route

Y ⁻	<i>E</i> _{Y⁻/Y⁻} (V vs SCE) ^a	p <i>K</i> _{HY} ^b	<i>n</i> _{MeI} ^c
MeCOCH ₂ ⁻	-0.04	26–28	
Me ₃ CCOCH ₂ ⁻	-0.15	26–28	
PhCOCH ₂ ⁻	-0.10	25	
PhS ⁻	0.04	10.3	9.9
(EtO) ₂ PO ⁻	0.34	15	7.0
PhO ⁻	0.25 (in MeCN)	18	5.8
EtS ^{-d}	0.6 (in THF) ^e	15	8.0 ^f
O ₂ NCH ₂ ⁻	ca. 0.5 ^e	17	
RO ^{-g}	ca. 0.6 ^e	29–31	6.3
NO ₂ ⁻	0.7 (in DMF) ^e	7.5	5.4
N ₃ ⁻	1.3 (in DMF) ^e	7.9	5.8
Cl ⁻	1.9 (in DMF) ^e	1.8	4.4

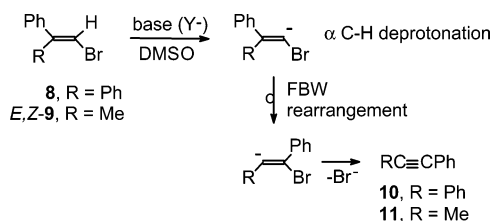
^a Data at 0.5 V/s in DMSO, from ref 20a. ^b Data in DMSO, from ref 18. ^c Data from ref 19. ^d Taken as representative of MeS⁻ and PhCH₂S⁻. ^e Data from ref 20b. ^f For HS⁻. ^g With R = primary alkyl group.

Scheme 4. Observed Routes with **1**

reducing character, leading to the α,β-elimination key intermediate **5**. Deprotonation of **5** and addition of PhC≡C⁻ to the neutral ketone to give anion **7b**⁻ is reversible, and the re-formed precursor species leads to **2b**, **3b**, and **6** (Scheme 2). Indeed, **2b**, **3b**, **6**, and **7b** were formed by the independent reaction of **5** with Me₃CCOCH₂⁻ under the same conditions.^{15a}

An analogous outcome was obtained in the reaction of **1** with the strongly basic anions PhCOCH₂⁻ and EtCOCH₂⁻CH₃.^{15b} The lack of depressing effect by added *p*-dinitrobenzene on the extent of the reaction (Scheme 2), which gave analogous products,^{15b} contrasts with the intervention of a S_{RN}1 route which should be suppressed by the electron scavenger,^{6a} due to the interception of electrons both in the initiation and propagation steps (eqs 1 and 4).

Our interpretation of the multiple potential role of the anion,¹⁷ in being a base,¹⁸ a nucleophile,¹⁹ and a reductant²⁰ (cf. Table 1), suggested an experiment which provided an unambiguous case of S_{RN}1(V) mechanism. Reaction of **1** with PhS⁻, a weaker base than Me₃CCOCH₂⁻ (p*K*_{HY} = 10.3 and 27.7, respectively)¹⁸ but still a decent reducing anion (*E*_{Y⁻/Y⁻} 0.04 and -0.15 V vs SCE, respectively, in DMSO),^{20a} provided the direct substitution product PhCH=CHSPh under photostimulation (Scheme 4) without side reactions.²¹ Its inhibited formation by added *p*-dinitrobenzene indicates the occurrence of an electron-induced substitution route (Scheme 1). The stereochemistry was consistent with the S_{RN}1 route: from an initial 9:1 *E/Z* composition, precursor **1** was partially

Scheme 5. Reaction of **8** or *E,Z*-**9** with Y⁻ = Me₃CCOCH₂⁻

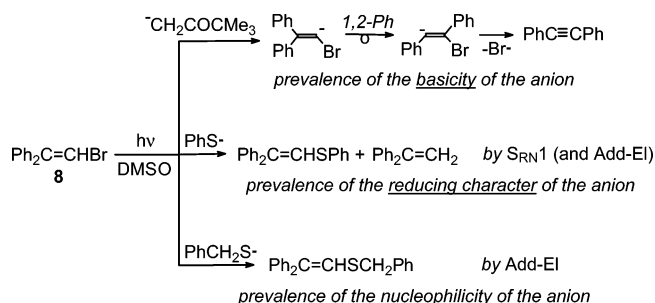
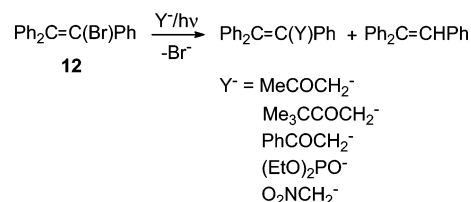
recovered from the photostimulated reaction with PhS⁻ as a 3:1 *E/Z* mixture. *E*-**1**, being slightly easier to reduce than *Z*-**1**,²² is plausibly more reactive and more extensively consumed in the ET route, whereas in the E2 route *Z*-**1** would be more reactive.¹ At variance with the S_{RN}1 route of PhS⁻ with **1**, the stronger base (p*K*_{HY} = 18)¹⁸ but weaker reductant PhO⁻ ion (*E*_{Y⁻/Y⁻} 0.25 V vs SCE)^{20a} yielded **5** by an α,β-elimination pathway.²¹ Product **5** was not converted further to any addition product, possibly because “hard” oxygen nucleophiles do not add efficiently to “soft” carbon centers. Similarly, the even stronger base *t*-BuO⁻ (p*K*_{HY} = 32)¹⁸ gave **5** from **1**, without any addition product.²¹ The thio-nucleophile MeS⁻, which is as basic (p*K*_{HY} ca. 15)¹⁸ as PhO⁻, but less reducing (*E*_{Y⁻/Y⁻} ca. 0.6 V vs SCE)^{20b} than PhS⁻, gave the substitution product from **1** by an exclusive Add–El route in DMSO.²³ The evidence includes complete retention of configuration for both isomers of **1**, an element effect *k*_{Z–Br}/*k*_{Z–Cl} of 1.0 in 95:5 DMSO:CD₃OD, the nonobservation of **5**, the slow addition of MeS⁻ to **5**, and no effect of the radical scavenger TEMPO when added to *Z*-**1**–Br first, followed by MeS⁻.²³ These observations are summarized in Scheme 4.

Varying the Structure of VyX

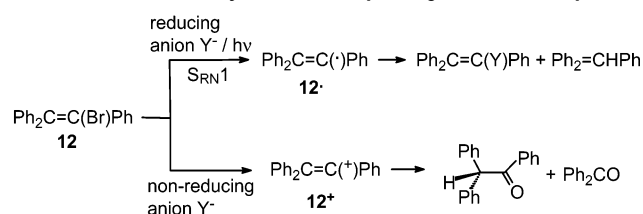
Because a β-C–H bond predisposes a vinyl halide to elimination with a basic enolate ion, we searched for the S_{RN}1(V) mechanism with precursors having only an α-C–H bond. With substrates **8** and *E,Z*-**9**, an alkyne (**10** or **11**) was, however, obtained via a Fritsch–Buttenberg–Wiechell rearrangement (FBW, in Scheme 5).²¹ Once again, the basic character of Me₃CCOCH₂⁻ ion (Y⁻), combined with the presence of the vinylic C–H bond, favors the operation of a new ionic pathway over the occurrence of the S_{RN}1(V) process.

An example of a S_{RN}1(V) reaction is the reaction of **8** with PhS⁻ ion (cf. also Scheme 4), although a minor contribution from the Add–El pathway could not be excluded (Scheme 6).²¹ The latter route takes over in the reaction of **8** with the nucleophilic but less reducing (*E*_{Y⁻/Y⁻} ca. 0.6 V vs SCE)^{20b} PhCH₂S⁻ ion, where depression of the substitution product by added *p*-dinitrobenzene was not observed.²¹ This many-sided reactivity of anions¹⁷ displays a delicate balance among the predominance of either the basic, or reducing, or nucleophile character of an anion over the possible observation of an unequivocal S_{RN}1(V) reaction. We conclude that the presence of both β-C–H and α-C–H bonds should be avoided with an enolate ion as the potential nucleophile.²¹

A plausible precursor lacking vinylic or allylic C–H bonds and fully substituted by phenyl rings is triphenylvi-

Scheme 6. Observed Routes with **8**Scheme 7. S_{RN}1 Reactions with **12**

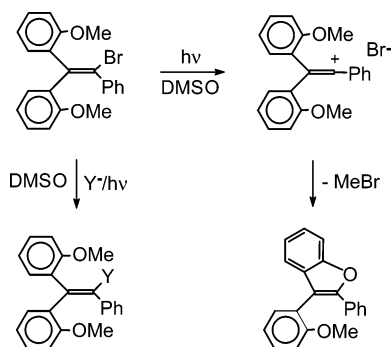
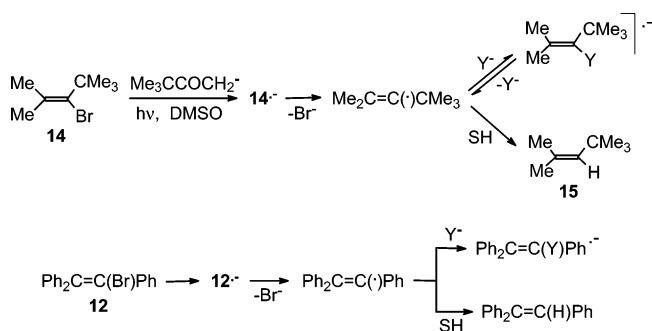
Scheme 8. Dichotomy of Routes Depending on the Nucleophile



nyl bromide **12**. With Me₃CCOCH₂⁻ under photostimulation in DMSO, it gave substitution and reduction products (Scheme 7), accounted for by an S_{RN}1(V) process.^{5c,15b,24} Other triarylvinyl halides, such as An₂C=C(Br)An (**13**) (An = *p*-MeOC₆H₄),²¹ or else bearing combinations of Ph and *p*-An groups,^{25,26} all reacted by S_{RN}1(V) processes with this anion. Competition from a vinylic S_N1 route was excluded since this route was extremely slow in 80% EtOH at high temperature.²⁷

By using **12** as a reference substrate,^{15b,24} the S_{RN}1(V) route was additionally documented with other reducing Y⁻ ions (for *E*_{Y⁻/Y⁻} values in V vs SCE, see Table 1), such as MeCOCH₂⁻ (–0.04), PhCOCH₂⁻ (–0.1), O₂NCH₂⁻ (ca. 0.5) and (EtO)₂PO⁻ (0.3) (Scheme 7). Different VyY/VyH product ratios were always formed by competition of reaction 3' with 3 (Scheme 1) of the intermediate Vy[•] originated in reactions 1 and 2.^{24b} Formation of both products was strongly depressed by added *p*-dinitrobenzene. Conversely, the photostimulated reaction of **12** with nonreducing anions (NO₂⁻, Cl⁻, N₃⁻, RO⁻; *E*_{Y⁻/Y⁻} = 0.6–1.9 V vs SCE) gave cleavage products (Scheme 8) probably arising from capture by traces of water of the intermediate vinyl cation (Vy⁺), generated from direct C–X bond photolysis.²⁶

Whenever initiation of the S_{RN}1(V) process (eq 1) is lethargic,^{6a,20a} since the anion is not a sufficiently good electron-donor under photostimulation,^{14a} C–X bond photolysis can compete favorably and afford solvolysis/rearrangement/cleavage products in a photoinduced S_N1 process.^{14b,26,28,29} Direct photohomolysis of the C–X bond may also compete with the photolysis

Scheme 9. Competition of C–Br Photoheterolysis vs S_{RN}1 (Y⁻ = Me₃CCOCH₂⁻)Scheme 10. Stabilization of VyY⁻: Reactions of **14** vs **12**

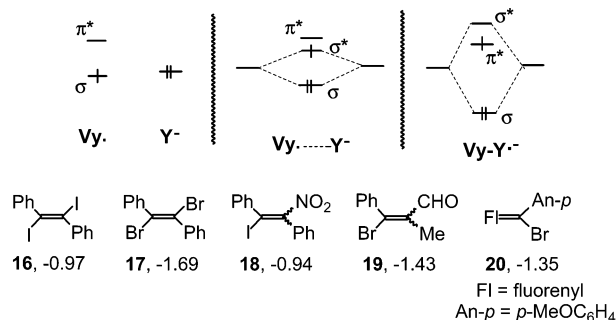
(vide infra), giving the Vy^{*} and leading to minor amounts of the hydrodehalogenated product (VyH).²⁶

Further on this dichotomy, intramolecular capture of a Vy⁺ formed from an appropriate triarylvinyllg (LG = leaving group) on photoheterolysis was found in the absence of an electron-donor anion (Scheme 9).²⁶ Conversely, with the reducing enolate ion (Y⁻ = Me₃CCOCH₂⁻), the more efficient S_{RN}1(V) process took over the direct C–X bond photoheterolysis.²⁶

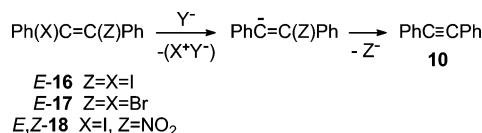
Other Structural Effects of VyX

Although the photostimulated reaction of an enolate ion with **12** did occur through the S_{RN}1(V) route,^{15b,24} it was puzzling that vinyl bromide **14**, also lacking vinylic C–H bonds, gave only the reduction product **15** (Scheme 10),^{15b} whose formation was significantly inhibited by *p*-dinitrobenzene, and no substitution product. We infer that photostimulated ET from the nucleophile to **14** did form Vy^{*} (eqs 1 and 2), but subsequent nucleophilic attack (eq 3) did not compete with the hydrogen transfer from the medium (eq 3'). This is explained by the ET events involved in a S_{RN}1(V) reaction (Scheme 11).^{15b,20a}

When a new σ bond begins to form between the sp² carbon-centered radical (Vy^{*}) and Y⁻, in a nascent two-center three-electron bond, the odd electron is at first in the low-energy σ* MO of the partially formed C–Y bond. As this new bond shortens, gradually approaching the normal C–Y bond length, the σ* MO energy increases gradually, and if a lower-energy π* MO is available, the odd electron may be transferred to it from the σ*.³⁰ This stabilizes the radical anion of the substitution product (VyY⁻), which would revert to Vy^{*} and Y⁻ in the absence

Scheme 11. Addition of Y⁻ to Vy^{*}: Energy Change of the MOs

Scheme 12. Product of the Halophilic Attack



of a suitable low energy π*.³¹ We assume that the VyY⁻ from **14**, which lacks a conjugative vinylic π-substituent, reverts reversibly to Vy^{*}, which gave irreversibly only the hydrogen abstraction product **15** (eq 3'). In contrast, precursor **12**, having three double bond π-substituents, did provide the substitution product VyY (Scheme 10).^{15b,24a}

Both semiempirical (HyperChem) and ab initio (Gaussian 90, 6-31G* basis set) calculations of the LUMO energy of the model compounds PhCH=CHCH₂CHO and MeCH=CHCH₂CHO show that the former, bearing a conjugative π-substituent, is lower in energy by ca. 1 eV than the latter, thereby supporting the rationalization based on Scheme 11.^{15b}

Further stabilization of the π* MO of VyY⁻, facilitating its formation and consequently promoting the S_{RN}1 pathway, could be provided by EWGs on the double bond. This would also increase the electron affinity of VyX, fostering its one-electron reduction in the initiation (eq 1). Consequently, vinyl halides **16**–**20** were investigated.³² Indeed, all their *E_p* data (in V vs SCE)³² are less negative than those of **12** (–1.86 V)³² and **13** (–2.14)²¹ that gave the S_{RN}1(V) reaction, thereby confirming their higher reduction propensity.

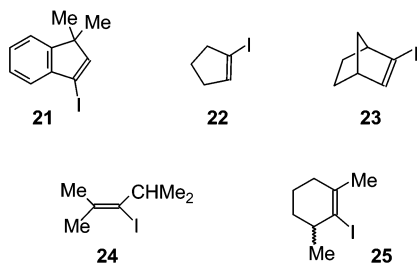
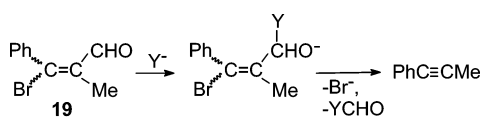
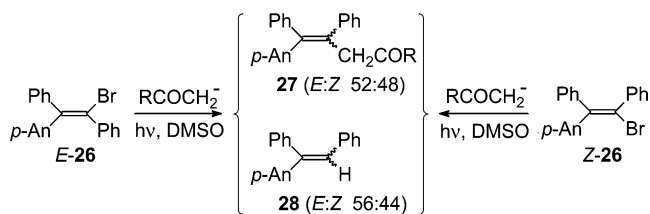
In contrast with our expectation, Me₃CCOCH₂⁻ (Y⁻) reacts with **16**–**20** through the ionic Add–El or halophilic routes (Scheme 12)^{1c,32} or gave substitution with rearrangement.³² In particular, Y⁻ anions (RCOCH₂⁻, RS⁻, ArS⁻, PhO⁻) were added to the carbonyl of carbonyl-substituted VyX, such as **19** or Ar(Cl)C=C(Me)CO₂Me,³³ followed by loss of both the nucleofuge and a neutral fragment, to yield an elimination product (Scheme 13).

Therefore, the facilitation of the SET by the EWGs was accompanied by an increased electrophilicity of the C_β and halogen moieties. Pathways where the anion nucleophilicity or the C–X bond polarization took over the S_{RN}1(V) route were consequently observed.

The S_{RN}1(V) mechanism was also previously suggested for the photostimulated reactions of PhS⁻ and MeCOCH₂⁻ with vinyl halides **21**–**23**.⁸

However, competition by non-S_{RN}1(V) routes, particularly for the unconjugated substrates bearing vinylic C–H

Scheme 13. Effect of a 1,2-Addition

Scheme 14. Stereoconvergence in S_{RN}1(V)

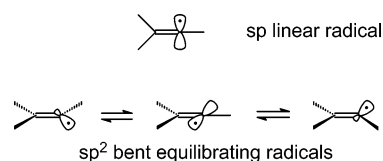
bond(s), cannot be unequivocally excluded, especially with the strong base MeCOCH_2^- , since the structural analogues **24** and **25** provided with the basic $\text{Me}_3\text{CCOCH}_2^-$ ion evidence of α,β' -elimination instead of the S_{RN}1(V) route.^{15b} With **25**, this elimination was followed by nucleophilic addition to the intermediate bent allene,^{1c} to give VyY . Competition by electron-induced hydrodeiodination reaction gave VyH in both cases, whereas coupling of Vy^* with Y^- was presumably prevented by the lack of stabilization of the VyY^- species, since both **24** and **25** are unconjugated VyX (cf. **14** vs **12** in Scheme 10).^{15b} However, the substitutions of **21–23** with the weaker base PhS^- , which did not proceed in the dark, could proceed via S_{RN}1(V).⁸

The S_{RN}1(V) route was invoked for a few other systems. The photostimulated reaction of $\text{R}'\text{SO}_2^-$ ion with $\text{R}_2\text{C}=\text{C}(\text{HgBr})\text{R}$ ($\text{R} = \text{Ph}$, alkyl) provided conjugated sulfones in a radical scavenger-inhibited reaction.³⁴ The photoinduced $\text{Co}_2(\text{CO})_8$ catalyzed carbonylation of some VyX , including **1**, was described as a S_{RN}1(V) reaction,³⁵ occurring by coupling of $\text{Co}(\text{CO})_4^-$ with the intermediate Vy^* . Since the mechanism was not studied in depth, a careful mechanistic scrutiny is essential for excluding the many alternative routes to the S_{RN}1(V) pathway.

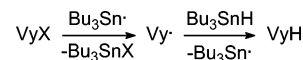
Geometry of the Vinyl Radical

The geometry of the reactive S_{RN}1(V) intermediate was probed by stereo-indicator substrates. The photostimulated reaction of $\text{Me}_3\text{CCOCH}_2^-$ with either pure **E-26** or **Z-26** led to a complete loss of the original stereochemistry, forming identical mixtures of both the substituted (**27**) and hydrodehalogenated (**28**) products (Scheme 14; $\text{R} = t\text{-Bu}$).²⁵ When this reaction was repeated in the presence of the electron scavenger, no products were

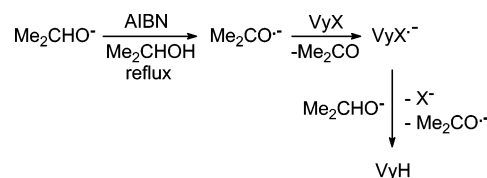
Scheme 15. Possible Structures of a Vinyl Radical



Scheme 16. Unambiguous Radical Hydrodehalogenation of a VyX



Scheme 17. Unambiguous ET-Induced Hydrodehalogenation of a VyX



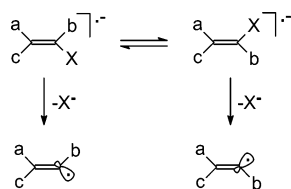
obtained, indicating that ET steps are instrumental for the process.²⁵

The complete stereoconvergence, which gave nearly 1:1 *E/Z* mixtures of **27** and **28**, excluded a configurationally stable bent structure for the intermediate vinyl radical $\text{Ph}(\text{An})\text{C}=\text{C}(\cdot)\text{Ph}$ (**26**). Instead, it is consistent either with a *sp* linear or with a pair of in-plane rapidly interconverting isomeric *sp*² bent radicals (Scheme 15). If the interconversion rate of the latter radicals significantly exceeds the capture rates of the nucleophile or of the hydrogen, the precursor configuration would be lost. Moreover, the configurations of recovered *E*- and *Z*-**26** were retained, and a configurational stability of the products was deduced by the time-invariance of the *E/Z* ratios of both **27** and **28**.²⁵ Consequently, the vinyl halide configuration was lost during the S_{RN}1 pathway.

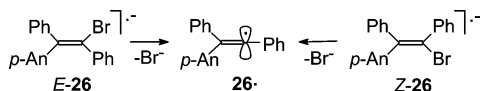
The intermediacy of radical **26** was shown by its independent unambiguous generation from the reaction of *E*- and *Z*-**26** with the Bu_3Sn^- radical formed from $\text{Bu}_3\text{SnH}/\text{AIBN}$ (Scheme 16).²⁵

The hydrodehalogenated product **28** was obtained from either *E*-**26** or *Z*-**26** in a *E/Z* ratio identical with that reported in Scheme 14, confirming that **26** is responsible for the common stereochemical outcome of both the radical (from the tin reduction) and the S_{RN}1(V) process.

An independently investigated ET-induced hydrodehalogenation,²⁵ which would proceed through the VyX^- species of isomeric precursors **26**, was the reaction of 2-propoxide ions with *E*- and *Z*-**26** (VyX in Scheme 17) in refluxing 2-propanol, with the radical initiator AIBN. The *E*-**28**/*Z*-**28** mixtures obtained from *E*- and *Z*-**26** were identical to that reported in Scheme 14, whereas the recovered precursors were nonisomerized. Consequently, $\text{E-26}^- \rightleftharpoons \text{Z-26}^-$ isomerization is slower than the cleavage of the radical anion. Configurational equilibration of vinylic radical anions had been documented,³⁶ with rate constants of $10^1\text{--}10^5 \text{ s}^{-1}$.²² If the radical anion of the substrate bears fissionable bond(s), fragmentation can compete with its configurational equilibration (Scheme 18).

Scheme 18. Configurational Equilibration vs Cleavage of a VyX⁻

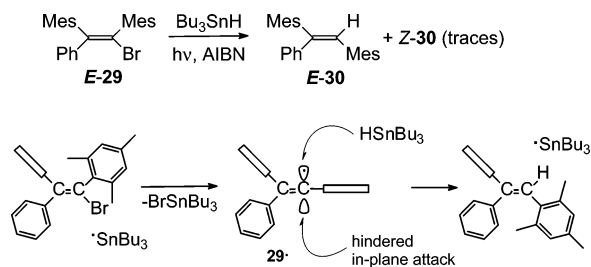
Scheme 19. Stereoconvergence in a Linear Vinyl Radical



The hypothesis that the *E*-**26**⁻ to *Z*-**26**⁻ equilibration rate is slower than that of C–Br bond cleavage is corroborated by the cleavage rate constant of *E*- α,α' -dibromostilbene radical anion (**17**⁻) of $> 10^8 \text{ s}^{-1}$.³⁷ Hence, the stereoconvergence obtained with *E*- and *Z*-**26**, which react via their radical anions (Scheme 19), is again rationalized by the intermediacy of either an *sp* linear or a *sp*² configurationally unstable radical **26**[•] (Scheme 15). Subsequent work demonstrated that the *sp* linear geometry for an α -arylviny radical is more likely.³⁸

The ratio of the captured products from either a statically linear *sp*, or fast equilibrating (i.e., average-linear) *sp*² radical intermediate, is determined by the relative steric environments of the two sides of the vinylic species. In **26**[•] they are sterically very similar, and the electronic difference between *p*-An and Ph is minor, which accounts for the ca. 1:1 product ratios obtained either for the S_{RN}1(V), from the tin-induced radical formation and from the ET-induced (RO⁻/AIBN) reactions of *E*- and *Z*-**26**.²⁵ Stereoelectronic effects play a role in the hydrodebromination of *E*-1,2-dimesityl-2-phenylvinyl bromide (*E*-**29**; Mes = Mesityl = 2,4,6-Me₃C₆H₂) under radical (Bu₃SnH/AIBN) conditions, since approaches from the two sides of the radical's SOMO are unequal.³⁹ Substrate **29** has a propeller-like conformation of the aromatic rings.^{39,40} Removal of bromine atom from *E*-**29** by a tin radical yields the α -mesitylviny radical **29**[•], calculated to have a *sp* linear structure with its SOMO in a plane orthogonal to the π -system of the C=C bond.³⁹ For steric reasons, the two β -aryl rings cannot be mutually in the C=C bond plane, and calculations show that in the preferred (ca. 9 kcal/mol) conformation, the β -Ph ring is almost completely conjugated and is in the C=C plane, whereas the β -Mes ring is almost perpendicular to this plane.³⁹ H-atom transfer to **29**[•] should take place in-plane from both sides, and since the β -Ph-including side is sterically more hindered than that including the tilted β -Mes ring, preferential attack from the latter face was expected. Indeed, the reduction of *E*-**29** (Scheme 20) gave a $\geq 9:1$ *E*-**30**/*Z*-**30** ratio, i.e., predominant formal inversion of configuration.³⁹ A similar, easier approach from the mesityl face had been reported previously with the analogous *sp*-hybridized ketene MesC(Ph)=C=O and vinyl cation MesC(Ph)=C⁺-Mes.⁴¹ Consequently, vinylic radical reactions appear to be similarly governed by steric effects.

The structural effects of α -substituents are also probed by calculations.³⁸ Vinyl radicals bearing the π -type α -sub-

Scheme 20. Stereoelectronic Effects on the Radical Hydrodehalogenation of *E*-**29**^a

^a Rings perpendicular to the C=C Plane are shown side-on as rectangles.

Table 2. Calculated Inversion Barrier (in kcal/mol) for Bent CH₂=C(•)R Radicals^a

R	barrier
H	3.3
Me	3.1
SH	4.7
Cl	11
OH	13
F	20

^a From ref 38.

stituents CH=CH₂, CHO, CN and Ph were calculated to be linear,^{38,42} as anticipated above (cf. **26**[•] and **29**[•]). The substituents's π system is orthogonal to the C=C bond's π system, and parallel to the radical center *p* orbital. Conversely, for vinyl radicals bearing the σ -type α -Me, SH, Cl, OH, and F substituents, the bent form was found to be the minimum energy structure,^{38,42} in accord with spectroscopic evidence.⁴³ The inversion barrier of the latter radicals markedly increases as the electronegativity of the group increases (Table 2).³⁸ With a small barrier, the bent α -substituted vinyl radical will rapidly invert, thus behaving as an “average-linear” vinyl radical (cf. Scheme 15), whereas with a high inversion barrier, the bent configuration should be stable. The prediction is that, in contrast to the complete stereoconvergence in the formation of **28** from the linear α -phenylvinyl radical intermediate (**26**[•]),²⁵ the reduction of a VyX bearing a strongly electronegative α - σ -type substituent should give a diverse stereochemical outcome. Hydrogen-abstraction by the intermediate α - σ -Vy[•] should be faster than isomerization of its *E,Z* bent forms, consequently affording a hydrodehalogenated product with a retained configuration. Calculations for the CH₂=C(•)F radical gave a high enough inversion barrier of ca. 20 kcal/mol to enable an unambiguous test of this prediction.³⁸ Indeed, reduction of *E*-**31** with Bu₃SnH/AIBN gave the retained configuration hydrodebrominated product *cis* β -fluorostyrene (**32**) as a *single* product (Scheme 21).³⁸

Kinetics Determinations

Partition of a vinyl radical between H-abstraction (eq 3') and coupling with a nucleophile (Y⁻) in the S_{RN}1 route (eq 3) has often been commented. Quantitative data concerning reactions of vinyl radicals are more scanty than for the corresponding aryl radicals.⁴⁴ The only available rate constant pertaining to hydrogen abstraction

Scheme 21. Hydrodehalogenation through a Configurationally Stable Bent Vinyl Radical

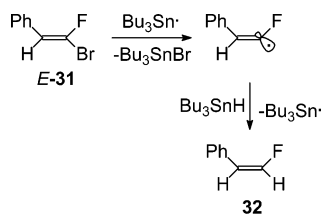


Table 3. Rate Constants (in M⁻¹ s⁻¹, at 25 °C) for Hydrogen Abstraction (*k_H*) and Capture by the Nucleophile (*k_Y*) of Ph· vs 12^{•a}

process	Ph·	12 [•]
<i>k_H</i> from DMSO	2.8 × 10 ⁶	1.1 × 10 ⁵
<i>k_H</i> from MeCN	6.7 × 10 ⁶	1.2 × 10 ⁵
<i>k_Y</i> with RCOCH ₂ ⁻	3.3 × 10 ⁹	3.9 × 10 ⁷
<i>k_Y</i> with (EtO) ₂ PO ⁻	2.5 × 10 ⁹	2.8 × 10 ⁶
<i>k_Y</i> with PhS ⁻	3.2 × 10 ⁸	1.9 × 10 ⁷

^a From ref 47.

(*k_H*) by an alkylvinyl radical is 3.8 × 10⁸ M⁻¹ s⁻¹ for H-abstraction from Bu₃SnH.⁴⁵ Additional *k_H* values are valuable for obtaining the *k_Y* value from the observed ratios of the competitive reduction (RH) and substitution (RY) products.⁴⁶

***k_H* Determination.** Laser flash photolysis enabled the direct determination of one necessary *k_H* value. Irradiation of Ph₂C=C(Br)Ph (**12**) at 248 nm in CH₃CN solution at 25 °C led to both C–Br homolysis and heterolysis.⁴⁷ Two transients, absorbing at λ_{max} 270 and 320 nm, were observed and ascribed to 12[•] and 12⁺, respectively. From the decay rate of 12[•] at 270 nm in CH₃CN, *k_H* = 1.2 × 10⁵ M⁻¹ s⁻¹ for H-abstraction from CH₃CN,⁴⁷ a 60-fold lower value than the corresponding *k_H* value (6.7 × 10⁶ M⁻¹ s⁻¹) obtained for phenyl radical in CH₃CN.⁴⁷

Photolysis of **12** in 50/50 (v/v) CH₃CN/CD₃CN yielded a mixture of Ph₂C=CHPh and Ph₂C=CDPh. From their molar ratio and the *k_H* value reported above, *k_D* = 2.3 × 10⁴ M⁻¹ s⁻¹ for D-abstraction from CD₃CN by 12[•].⁴⁷ By using this value and a similar approach, photolysis of **12** in 50/50 (v/v) DMSO/CD₃CN gives *k_H* = 1.1 × 10⁵ M⁻¹ s⁻¹ for H-abstraction from DMSO.⁴⁷

***k_Y* Determination.** Substrate **12** reacts by S_{RN}1(V) processes in DMSO (Scheme 7), through intermediate 12[•].^{15b,24} From the Ph₂C=C(Y)Ph/Ph₂C=CHPh ratios in photostimulated reactions of **12** in DMSO and the *k_H* value for 12[•] in DMSO, the competing *k_Y* values for 12[•] with Me₃CCOCH₂⁻, PhS⁻, and (EtO)₂PO⁻ are 3.9, 1.9, and 0.28 × 10⁷ M⁻¹ s⁻¹, respectively.⁴⁷ All these values are 50-fold lower than the corresponding *k_Y* values obtained with Ph·.^{46,48}

Semiempirical Calculations. The lower reactivity of 12[•] than that of Ph· in both H-abstraction from MeCN and DMSO, and in coupling with nucleophiles (Table 3), is ascribed to a stability difference between the two radicals.⁴⁷ The odd electron in Ph· is in a sp² orbital perpendicular to the π aromatic system, and consequently no delocalization is possible. In the linear α-Ph-substituted vinyl radical 12[•], the Ph π-system is parallel to the p orbital hosting the odd electron, delocalizes the latter and

stabilizes 12[•]. This explains the lower *k_H* and *k_Y* values for 12[•], compared with those of Ph·. AM1 calculations for H₂C=C(•)Ph, a simplified model of 12[•], conducted with the α-Ph group in a parallel (//) versus perpendicular (⊥) conformation to the π-vinyl system, gave ca. 8 kcal/mol stabilization of the latter conformation.⁴⁷

Concluding Remarks

There is probably no other family of substrates such as the VyX, for which so many diverse S_N routes are available.¹ Our systematic search for an unequivocal example of the S_{RN}1(V) route has delineated the role of the El-Add route as a serious competitor, particularly with the basic enolate ion as the nucleophile.^{15b} With electrophilic VyX, the Add–El and halophilic routes are other potential competitors.³² Finally, with electron-donor substituents, the photoinduced S_N1 route can also arise.²⁶ The borders between the various routes are delicate, since all are initiated by ET, but to different sites of the ambident electrophilic alkene. A SET from the nucleophile to the vinylic π MO initiates the S_{RN}1 route, whereas two electrons intrude to a vinylic hydrogen, halogen, or carbon, respectively, in the El-Add, the halophilic and the Add–El routes. In the photoinduced S_N1 route, vertical transfer of electron to an excited MO causes either C–X bond heterolysis or homolysis.^{14b,29,49} In trying to discern structural features of VyX exclusively conducive to the S_{RN}1 route, the delicate balance among the predominance of either the basic, reducing or nucleophilic character of the anion upon its reactivity was demonstrated.²¹

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