Effect of substituents on the competition between several mechanisms of nucleophilic vinylic substitution[1]

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In an attempt to encourage vinylic substrates to undertake an $S_{RN}1$-like nucleophilic substitution route, a process that requires acquisition of one electron, a series of stilbene halides bearing one electron-withdrawing substituent on the double bond has been synthesized. Determination of the reduction potential of these substrates confirmed an increased tendency to acquire electrons. However, this effect was so strong that in the reaction of substrates **1**–**3** with the pinacolone enolate ion under typical $S_{RN}1$ conditions, two consecutive electron-transfer steps occurred, ultimately producing diphenylacetylene **6** without any $S_{RN}1$ products. Evidence was also gathered for a relevant contribution from an ionic halophilic route to the formation of **6**. The structurally similar propenal derivative **4** gave instead a novel ionic deformylation process, presumably initiated by a nucleophilic addition of the enolate ion to the aldehydic carbonyl and followed by bromide loss. The fluorenylidene derivative **5** although it has a very favourable redox potential, reacted by an ionic addition–elimination route. Competition by other routes thus hampers the occurrence of the $S_{RN}1$ process and comparison with cases of other vinyl halides analogously undergoing multiple reaction pathways is made.

Competition between several mechanistic routes in nucleophilic vinylic substitution is a common phenomenon.[2,3] The type of the competing mechanisms strongly depends on the nature of the substituents. In a recent search[4] for an authentic vinylic $S_{RN}1$ process ($S_{RN}V$ in Scheme 1, where Y^- is a nucleophilic

$$VyX \xrightarrow{\text{initiation}} VyX^{\bullet -} \quad (1)$$

$$VyX^{\bullet -} \longrightarrow Vy^{\bullet} + X^- \quad (2)$$

$$Vy^{\bullet} + Y^- \longrightarrow VyY^{\bullet -} \quad (3)$$

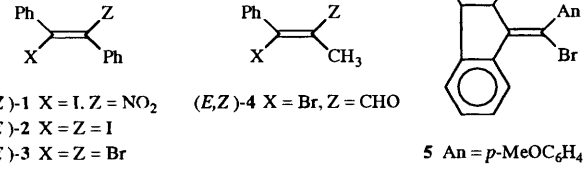
$$VyY^{\bullet -} + VyX \longrightarrow VyY + VyX^{\bullet -} \quad (4)$$

$$Vy^{\bullet} + SH \longrightarrow VyH + S^{\bullet} \quad (5)$$

Scheme 1

anion, SH is a hydrogen donor and VyX is a vinylic substrate carrying an appropriate leaving group X) several substrates, which were potential candidates to follow the $S_{RN}V$ mechanism, reacted simultaneously or exclusively *via* common ionic nucleophilic vinylic substitution (S_NV) routes,[2] chiefly by elimination–addition. Nevertheless, we were able to find an authentic example of an unequivocal $S_{RN}V$ route in a system possessing suitable structural features. Prominent among these is the absence of vinylic or allylic C–H bonds,[4] in order to prevent α,α-, α,β- or α,β′-elimination–addition pathways,[2] and the presence of an aromatic substituent on the double bond. This substituent plays an important role in stabilizing the radical anion of the vinylic substitution product [$VyY^{\bullet -}$ in reaction (3)]. Consequently, in the competitive reactions of the radical $Vy^{\bullet}$, formed in step (2), with the anion Y^- [step (3)] or with the hydrogen donating solvent [step (5)], the former can take over, thus making the propagation cycle of the substitution feasible [steps (2)–(4)].[4]

The $S_{RN}1$ route is initiated by a transfer of an electron to the substrate in step (1).[5] It is therefore expected that the presence of electron-withdrawing substituents on the vinylic system should increase the affinity of these substrates for the electrons. While this may spur the $S_{RN}V$ reaction and favour it with respect to alternative ionic or radical routes, it should be borne in mind that alternative routes, such as nucleophilic addition–elimination, may also be accelerated by these substituents. It was therefore of interest to investigate the effect of electron-withdrawing groups on the mechanism of substitution for substrates where both $S_{RN}V$ and other routes can take place. Hence, a series of vinyl halides bearing one electron-withdrawing group (Z) has been synthesized (**1**–**4**; Z being NO_2, I, Br, CHO, respectively). In order to comply with the structural features identified above, which are beneficial to the $S_{RN}V$ route,[4] compounds **1**–**4** lack vinylic or allylic hydrogens and carry one or two aryl substituents on the double bond.



(*E*,*Z*)-**1** X = I, Z = NO_2
(*E*)-**2** X = Z = I
(*E*)-**3** X = Z = Br

(*E*,*Z*)-**4** X = Br, Z = CHO

5 An = *p*-$MeOC_6H_4$

A preliminary electrochemical study has been carried out in order to confirm the expectation of an increased electron affinity of substrates **1**–**4** and to delineate possible reaction pathways. This study had also included 9-(α-bromo-*p*-methoxybenzylidene)fluorene (**5**), whose measured redox potential suggests that it may react *via* the $S_{RN}V$ route under appropriate conditions. Compound **5** is of special interest since it has been shown previously that it reacts either by an exclusive vinylic S_N1 route or by an exclusive vinylic addition–elimination route under different conditions.[2,6] As a typical $S_{RN}1$ process,[5] the reaction of substrates **1**–**5** with a ketone enolate ion has been studied under photostimulation or under ferrous ion catalysis.[7]

The results reported here for compounds **1**–**5** are compared with previous experimental data concerning nucleophilic substitutions carried out on other vinylic systems.

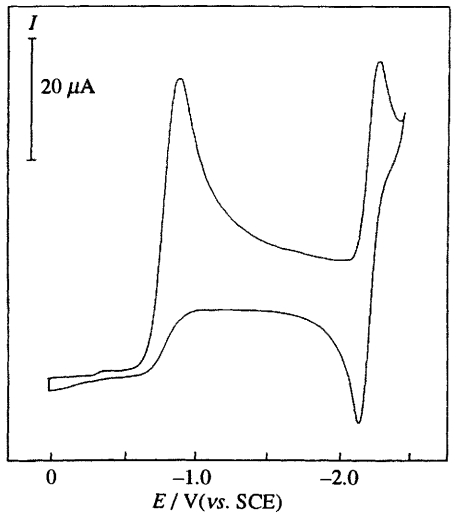


Fig. 1 Cyclic voltammetry of **1** (2 mmol dm^{-3}) in THF containing 0.37 mol dm^{-3} $Bu_4N^+BF_4^-$, at a gold electrode: scan rate, 500 mV s^{-1}; temperature, 25 °C

Table 1 Reduction potentials in THF containing 0.37 mol dm^{-3} $Bu_4N^+BF_4^-$

Compound[a]	E^p/V (*vs.* SCE; at 500 mV s^{-1})[b]
1	−0.94
(*E*)-**2**	−0.97
(*E*)-**3**	−1.69
4	−1.43[c]
5	−1.35
9	−1.86
(*E*)-**10**	−2.31
6	−2.26[d]
7	−1.73[d]
8	−1.66[d]

[a] Concentration: 2 mmol dm^{-3}. [b] Gold working electrode; typical uncertainty, ±10 mV. [c] Platinum working electrode. [d] Reversible potential (E°).

Results and discussion

Electrochemical characterization

The reduction potentials of the substrates were determined by cyclic voltammetry in anhydrous tetrahydrofuran (THF) under an argon atmosphere; the concentration of the substrate was 2 mmol dm^{-3}, while that of the supporting electrolyte, *i.e.* $Bu_4N^+BF_4^-$, was 0.37 mol dm^{-3}. The working electrode was a gold disc (0.5 mm diameter) and the auxiliary electrode was a platinum wire (1 cm^2 surface area). All redox potentials are relative to the saturated calomel electrode (SCE). A representative cyclic voltammogram of compound **1** is shown in Fig. 1. Similar voltammograms were obtained for compounds (*E*)-**2** and (*E*)-**3**.

Salient features of the voltammograms of **1**–**3** are (*i*) an irreversible, two-electron wave (E^p −0.94, −0.97, −1.69 V, respectively, for **1**, **2** and **3**, Table 1) followed by (*ii*) a reversible one-electron wave at a more negative potential. The first wave was irreversible over the range of potential scan rates from 500 mV s^{-1} to 20 V s^{-1}.† We attribute this wave, which depends on the structure of **1**–**3**, to the electrodehalogenation of the substrates, leading to diphenylacetylene (**6**) *via* the radical anions of **1**–**3** (Scheme 2), as it is supported by experimental

† The reduction wave of 2-bromo-2-nitrostyrene, a compound structurally comparable to **1**, is reported[8] to become reversible at a 10^2 V s^{-1} scan rate.

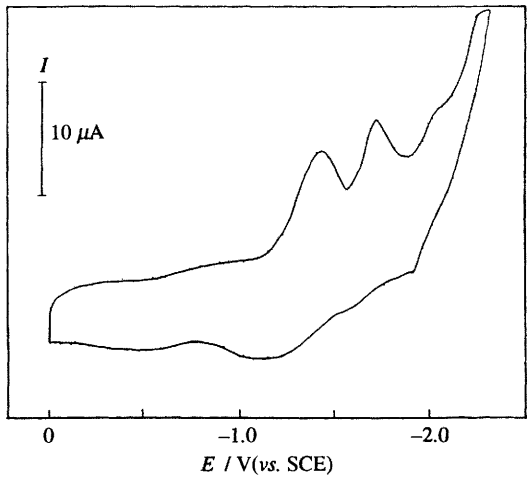
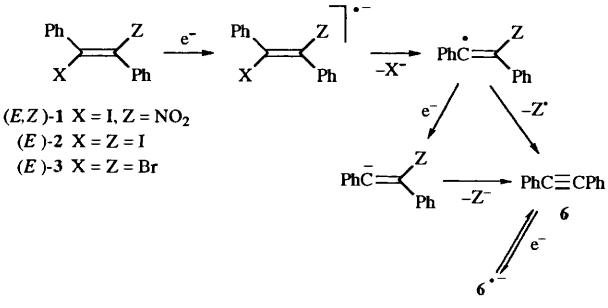


Fig. 2 Cyclic voltammetry of **4** (2 mmol dm^{-3}) in THF containing 0.37 mol dm^{-3} $Bu_4N^+BF_4^-$, at a platinum electrode: scan rate, 500 mV s^{-1}; temperature, 25 °C

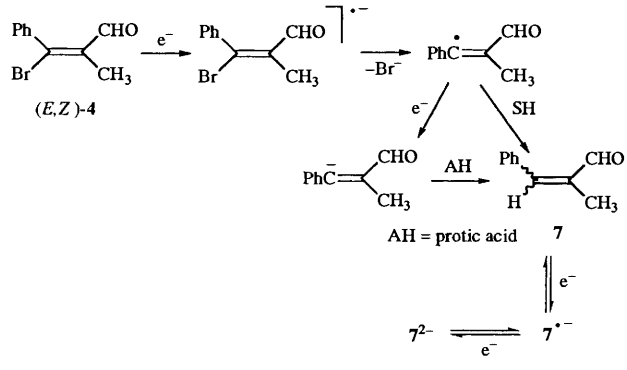


Scheme 2

evidence presented below and by the literature for similar vinylic substrates.[9] The second reversible wave corresponds to the one-electron reduction of **6** (E° −2.26 V) to its radical anion. Independent reduction of **6** under the same experimental conditions gives a similar voltammogram, thus confirming the above assignment.

In Scheme 2 a possible mechanistic dichotomy is delineated. In fact, once the vinyl radical is formed following the first electron acquisition, it can be reduced by a second electron to a vinyl carbanion, from which **6** is produced by loss of Z^-. Alternatively, however, **6** could be directly formed by loss of $Z^\bullet$ from the vinyl radical; reduction of $Z^\bullet$ to Z^- by a second electron would explain the finding of a two-electron reduction wave.

For compound **4** (Fig. 2), the voltammogram presented two waves: the first is the two-electron irreversible reduction of **4** to the hydrodebrominated product **7** (Scheme 3), while the second



Scheme 3

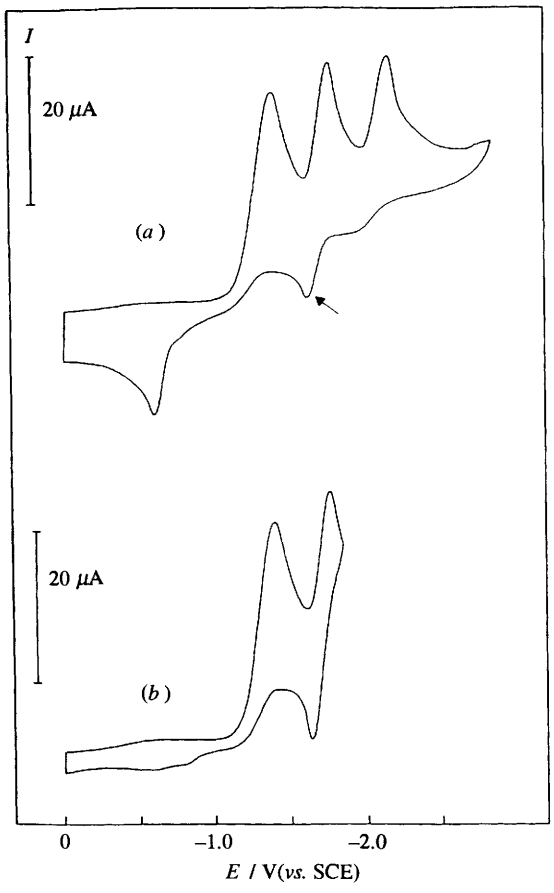


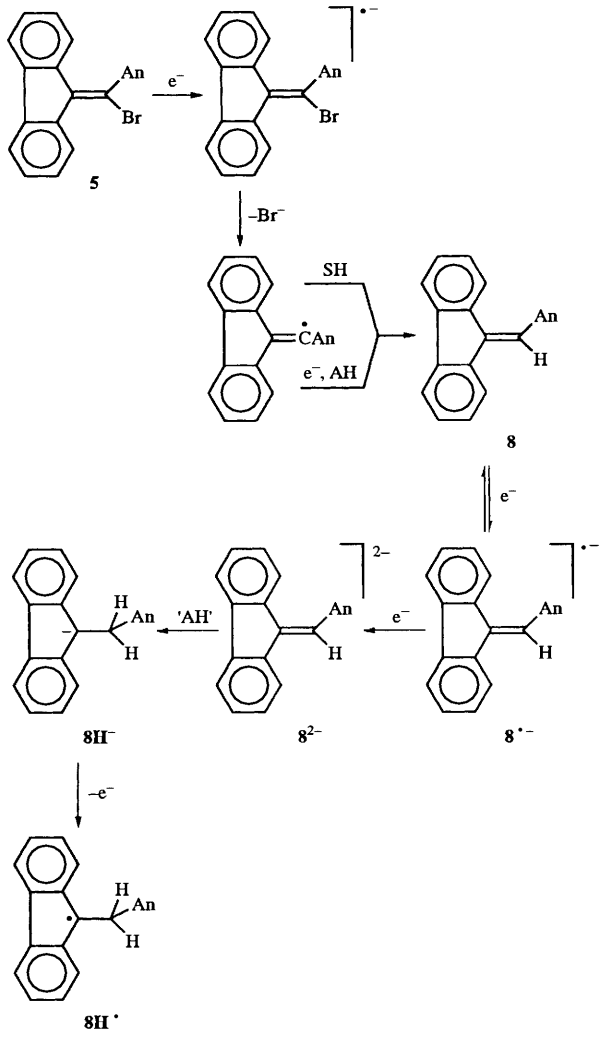
Fig. 3 (*a*) Full cyclic voltammogram of **5** (2 mmol dm^{-3}) in THF containing 0.37 mol dm^{-3} $Bu_4N^+BF_4^-$, at a gold electrode: scan rate, 500 mV s^{-1}; temperature, 25 °C. (*b*) When the potential scan does not exceed −1.8 V, the second wave becomes reversible (see text).

wave is the one-electron reduction of **7** to its radical anion (E° −1.73 V).‡ This is confirmed by the voltammogram of an authentic sample of **7** which, when reaching potentials more negative than −2.1 V, revealed also an irreversible wave at −2.36 V. This is likely to be the further reduction of $\mathbf{7}^{\bullet-}$ to $\mathbf{7}^{2-}$, as is reported[10] for cinnamaldehyde. Synthetic electrochemical evidence,[11] in general, points to a preliminary cathodic reduction of the C=C group of enones or enals, conducive to products of C–C coupling unless steric hindrance at C-3 is present;[11] this is followed by reduction of the C=O group at a much more negative potential.[10] In contrast, addition of solvated electrons to propenal in liquid NH_3 gives EPR signals typical of a radical anion of the ketyl kind.[12]

Even in the case of **4**, a possible alternative to the formation of **7** *via* the vinyl carbanion is suggested in Scheme 3. It is a hydrogen atom abstraction from the solvent SH by the vinyl radical; the resulting S$^\bullet$ species would be reduced to S^- by a second electron.

The voltammogram was more complex for **5**, which showed four potential-dependent waves (Fig. 3). The first is due to an irreversible, two-electron reduction of **5** to the hydrodebrominated product **8** (Scheme 4).[13] The second wave is the one-electron reduction of **8** to $\mathbf{8}^{\bullet-}$, as confirmed with an authentic specimen:[6] it is reversible (E° −1.66 V) provided that the potential scan does not exceed the value of −1.8 V. For a potential scan exceeding −1.8 V, this wave became partially reversible and a third irreversible wave appeared, possibly due

‡ This value is obtained from the voltammogram of a pure sample of **7**, where the reduction wave became reversible at a 20 V s^{-1} scan rate.



Scheme 4

to further reduction of $\mathbf{8}^{\bullet-}$ to $\mathbf{8}^{2-}$ (E^p −2.10 V). Finally, in the *oxidation* mode, a fourth irreversible wave appeared whenever the scan of the potential had reached values more negative than −1.8 V in the reduction mode; this is likely to be due to the oxidation of $\mathbf{8H}^-$, produced by protonation of $\mathbf{8}^{2-}$, to give $\mathbf{8H}^\bullet$ (E^p −0.47 V). The peculiar electrochemical behaviour of **5** was independent of the scan rate.

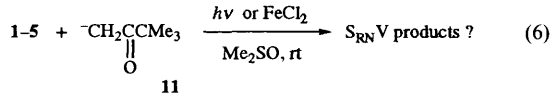
The redox potentials of compounds **1**–**5** are taken in all cases as the E^p of the first reduction wave and as such are reported in Table 1 for a 500 mV s^{-1} scan rate, along with the E° of compounds **6**–**8**. It is possible to observe that the iodo derivatives **1** and (*E*)-**2** present the more positive reduction potentials in the series, which is consistent with typical trends of the aryl halides (ArI > ArBr > ArCl);[14] in addition, the presence of a strong electron-withdrawing Z group in substrates of comparable structure, *i.e.* **1** *vs.* **2** and **4** *vs.* **3**, makes the reduction potential even more positive. As for the bromo derivative **5**, the high stabilization conferred by aromaticity of a negatively charged fluorenylidene moiety, makes the reduction potential of **5** very much closer in value to those of the iodo derivatives.

The reduction potentials of 1-bromo-1,2,2-triphenylethene (**9**) and of β-bromostyrene (**10**) were determined under the same conditions for comparison purposes (Table 1); these had been described[13] as giving irreversible *two-electron* reduction waves, as **1**–**5** do. Compound **9** has been found previously to substitute unambiguously *via* the $S_{RN}V$ route,[4] whereas compound **10**

reacts partially by this route[4,15] (owing to competition by an elimination–addition route) and they present a redox potential more negative than those of compounds **1**–**5**; therefore, owing to the latter feature, **1**–**5** did appear to be very prone to react in an $S_{RN}V$ substitution cycle. As shown below, this turned out not to be the case owing to competition by other routes, some of which were already anticipated by the electrochemical survey.

Reaction of compounds 1–5 with pinacolone enolate ion under $S_{RN}1$ conditions

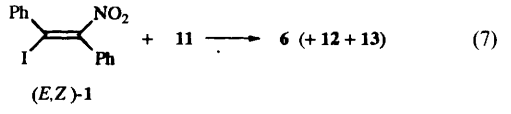
Each of the substrates **1**–**5** reacted with a three-fold excess of the enolate ion (**11**) of 3,3-dimethylbutan-2-one (pinacolone) in Me_2SO solution at room temperature [reaction (6)], which are suitable conditions with which to obtain $S_{RN}1$ products.[4,7]



The enolate ion was generated *in situ*[4,16] from the parent ketone (pK_a 27.7)[17] by the use of an almost stoichiometric amount of Bu^{t}OK (pK_a 32.2).[17] The reaction was induced either by $FeCl_2$ catalysis,[7]§ (at 40% molar with respect to the vinyl halide) or in a photochemical reactor. The experiments were run under N_2 and the product composition was monitored by gas chromatography on samples withdrawn during the reaction. In no case were the $S_{RN}V$ products obtained; the results are summarized in Table 2 and each system is discussed separately below.

α-Iodo-β-nitrostilbene (1)

Under both photostimulation and ferrous ion catalysis (expts. 1 and 2) substrate **1** had completely disappeared after only 10 min reaction time [reaction (7)] and the only product obtained from

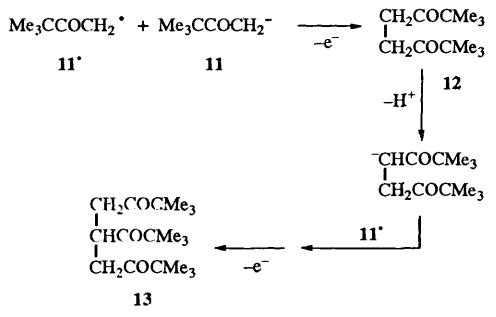


it was **6**, accompanied by small amounts of the dimer (**12**) and the 'trimer' (**13**) of pinacolone.

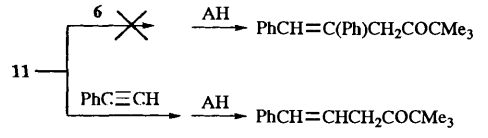
The dimer **12** had been previously obtained[16,19] in $S_{RN}1$ reactions characterized by sluggish reactivity; its formation, as well as that of the novel compound **13**, is likely to be due to radical-anion coupling steps, as depicted in Scheme 5.

No vinylic substitution product of **1** incorporating the pinacolone moiety was detected. A control experiment (expt. 3) indicates that the enolate of pinacolone does not add to **6** under the reaction conditions; in contrast, we had shown previously[4] that the pinacolone anion **11** does add to phenylacetylene (Scheme 6).

However, the recovery of **6** from expt. 3 is only partial, which



Scheme 5

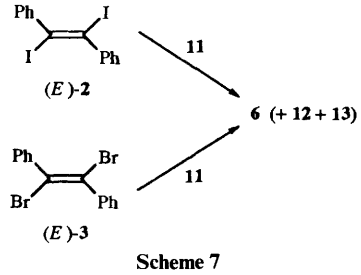


Scheme 6

suggests that part of it is lost, perhaps by polymerization, and justifies the low mass balance of expts. 1 and 2. No significant difference in the yield of **6** was observed on changing the induction technique or by addition of the radical scavenger *p*-dinitrobenzene (expt. 4).

α,α′-Diiodostilbene [(*E*)-2] and α,α′-dibromostilbene [(*E*)-3]

Reaction of (*E*)-**2** with **11** under photostimulation (expt. 5) provided a higher yield of **6** (Scheme 7) than in the reaction



Scheme 7

where **1** was the substrate. Again, not even traces of a vinylic substitution product were found, while small amounts of **12** and **13** were detected.

Partial inhibition of the formation of **6** occurred in the presence of *p*-dinitrobenzene (expt. 6). On the other hand, (*E*)-**3** provided a photostimulated yield of **6** (expt. 7) which was comparable with that from (*E*)-**2** (Scheme 7): even after only 1 min reaction time, 50% of **6** had already been formed. However, the yield of **6** was lower (expt. 8) under $FeCl_2$ stimulation. Interestingly, the reaction of (*E*)-**3** with Bu$^tO^-$ as the nucleophile in the absence of pinacolone left 10% of unreacted substrate after 10 min and gave a 44% yield of **6** (expt. 9), a yield comparable to those from expts. 4 and 6.

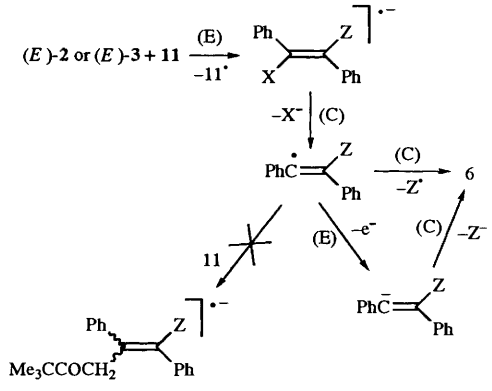
We conclude that the enolate **11** transfers an electron efficiently to (*E*)-**2** or (*E*)-**3** both under photostimulation and under ferrous ion stimulation and reduces them to the radical anions. This is followed by fragmentation with loss of halide ion. In compliance with the electrochemical evidence (Scheme 2), the electron affinity of the intermediate halovinyl radical is so high that a further rapid electron donation to form a halovinyl carbanion, stabilized by the electron-withdrawing group Z, occurs before any capture of the radical by **11** may take place and give the vinylic substitution product (Scheme 8). The successful occurrence of the coupling between the intermediate radical and a nucleophile, in competition with further electron donation (or with hydrogen atom abstraction from the medium),[4] is instead the key point for the reaction of

§ Recent electrochemical determinations in our laboratory give 0.1 V (*vs.* SCE) for the redox couple Fe^{3+}/Fe^{2+} in Me_2SO, while for the oxidation potential of $^-CH_2COCMe_3$ in Me_2SO we obtain E^p −0.15 V (*vs.* SCE, at 500 mV s^{-1}). We are presently engaged in the determination of the oxidation potentials for a wide series of nucleophiles and the relationship between these electrochemical data and the nucleophilic reactivity in $S_{RN}1$ aromatic processes will be described in a future paper. Similar investigations along this direction have already been published.[8,18] The relevance of these data for a more precise assessment of the role of ferrous ion in initiating the $S_{RN}1$ process is currently under evaluation. Anyhow, it has already been reported[7a] that Fe^{II} and $^-CH_2COCMe_3$ provide a successful initiation procedure to the aromatic $S_{RN}1$ reaction even with aryl halides endowed with reduction potential as negative as −2.3 V.

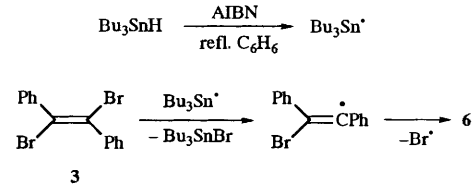
Table 2 Products and yields of the reactions of pinacolone enolate ion (**11**) with compounds **1**–**5** in Me_2SO at room temperature[a]

Expt. no	Substrate (VyX)	Conditions	Reaction time/min	VyX left (%)	Yield (%)[b] Product	Others
1	**1**	*hv*	10	**1** (0)	**6** (32)	**13** (tr)
			60	**1** (0)	**6** (54)	**13**
2	**1**	$FeCl_2$	10	**1** (0)	**6** (35)	**12** (tr) **13**
			60	**1** (0)	**6** (52)	**12** **13**
			180	**1** (0)	**6** (56)	**12** **13**
3	**6**	$FeCl_2$	10	**6** (42)		
			60	**6** (22)		
4	**1**	$FeCl_2$[c]	10	**1** (0)	**6** (37)	
			60	**1** (0)	**6** (42)	
5	**2**	*hv*	10	**2** (0)	**6** (79)	**13**
			60	**2** (0)	**6** (72)	**13**
			180	**2** (0)	**6** (58)	**13**
6	**2**	*hv*[c]	10	**2** (0)	**6** (45)	
			60	**2** (0)	**6** (67)	
7	**3**	*hv*	1	**3** (0)	**6** (50)	**12** **13**
			10	**3** (0)	**6** (82)	**13**
			60	**3** (0)	**6** (71)	**13**
8	**3**	$FeCl_2$	10	**3** (0)	**6** (45)	**12** **13**
9	**3**	Bu^tO^- only[d]	10	**3** (10)	**6** (44)	
10	**4**	*hv*	15	**4** (0)	**14** (75)	
11	**4**	$FeCl_2$	15	**4** (0)	**14** (75)	
12	**4**	—	15	**4** (0)	**14** (75)	
13	**5**	*hv*	15	**5** (10)	**17** + **18** (36)	**8** (6)
14	**5**	*hv*[c]	15	**5** (11)	**17** + **18** (50)	**8** (3)
15	**5**	—	3	**5** (49)	**17** + **18** (29)	**8** (4)
			15	**5** (32)	**17** + **18** (48)	**8** (6)

[a] Typical conditions: VyX, 0.5 mmol; **11**, 1.7 mmol; $FeCl_2$, 0.22 mmol; Me_2SO, 25 cm^3. [b] By GLC; typical uncertainty ±4%. [c] In the presence of 0.2 mmol of the radical scavenger *p*-dinitrobenzene. [d] 2.3 mmol.



Scheme 8



Scheme 9

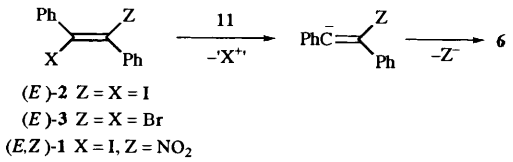
9 (and in part **10**)[4] *via* the $S_{RN}1$ route as also, more generally, with the aryl halides.[20]

The α-halovinyl carbanion then loses Z^- to form the elimination product **6** in what is overall an ECEC (electrochemical–chemical–electrochemical–chemical) process. The efficient donation of electrons from **11** to the substrate, either photostimulated or ferrous-ion induced, gives rise to a sufficiently high concentration of radicals of pinacolone (**11**•) to create a reasonable opportunity for their further transformation to **12** and **13** (Scheme 5). While the ECEC mechanism is reasonable and is supported by a similar pathway leading to benzyne (*vide infra*) in nucleophilic reactions of *ortho*-dihalobenzenes,[21] the ECC mechanism anticipated in Scheme 2 has also to be taken into account. We have indeed verified that in reaction with a stoichiometric amount of Bu_3SnH, induced by azoisobutyronitrile (AIBN) in boiling benzene (Scheme 9), (*E*)-**3** is extensively consumed (*ca.* 70%) with concomitant formation of **6**. This supports the feasibility of a spontaneous elimination of $Z^•$ [*i.e.* $Br^•$ in the case of (*E*)-**3**] from the intermediate vinyl radical,¶ either when produced in the preliminary bromine abstraction step by the tin radical or when generated by the ECC route (Scheme 2).

Clearly, under the 'reducing environment' provided by the $S_{RN}1$ conditions, competition of the ECEC route for the ECC route becomes likely with (*E*)-**2** and (*E*)-**3**, even though not necessarily exclusive (Scheme 8).

Finally, both the ECEC and the ECC routes are multi-step eliminations, initiated by steps (1) and (2) of Scheme 1; thus, inhibition by a radical scavenger should be observed. Since conversion to **6** does occur, however, although to a lesser extent (compare expts. 5 and 6), even in the presence of the scavenger, the existence of an alternative ionic route to **6**, which is not inhibited by the scavenger, is inferred. One possibility is a halophilic reaction[2,22] of the basic enolate ion **11** or of the

¶ One of the referees has suggested that removal of the second bromine atom from the bromovinyl radical (in Scheme 9) may be assisted by another $Bu_3Sn^•$. This seems unlikely since **3** and Bu_3SnH were in equimolar amounts: if removal of both bromine atoms from **3** would require $Bu_3Sn^•$, *no more* than 50% of **3** should have to be consumed. This is not the case, 71% of **3** having been consumed (see Experimental), without any significant formation of either bromostilbene or of stilbene. More generally, since it is likely that the radical species are present at low concentration, this would disfavour more a bimolecular reaction such as that between PhC(Br)=C(•)Ph and $Bu_3Sn^•$, rather than the unimolecular unassisted cleavage of PhCBr=C(•)Ph.



Scheme 10

slight excess of the Bu^tO^- (expt. 9) on the halogen with removal of species 'X^+' from (*E*)-**2** [or from (*E*)-**3**] (Scheme 10). The same intermediate anion of the previous route (Scheme 8) is formed and it loses the Z^- nucleofuge.

Similar behaviour is shown by the vinyl iodide **1**. The invariance of the yield of **6** with or without the scavenger (expt. 2 *vs.* 4), suggests that an 'I^+' removal step from **1**, which gives a carbanion highly stabilized by the nitro group, is the major if not the exclusive pathway in this case. It is known, in fact, that the electron transfer steps of an $S_{RN}1$ process are strongly impeded in nitroaryl halides, where the nitro group acts as a sink for electrons.[5,23] Consequently, donation of an electron to **1** would produce a 'stable radical anion $1^{\bullet-}$' which, being unable to fragment at the C–I bond with ensuing loss of I^-, should be able to revert effectively back to **1**. Only this reversibility,[8] coupled with a sluggish C–I bond cleavage, will ensure that the competing reaction of the neutral **1** with the nucleophile **11** available in solution will lead to the halophilic attack with formation of **6** *via* the non-SET-initiated route Scheme 10.

The reaction pattern of the dihalo substrates (*E*)-**2** and (*E*)-**3** (Scheme 8) represents a spectrum of pathways not observed, in general, with the *meta*- and *para*-dihalobenzenes which, following the photoinduced $S_{RN}1$ route[5,24] in liquid NH_3, or also under $FeCl_2$ induction[7a] in Me_2SO, give rise to the radical anion of the monosubstituted product (Scheme 11); it partitions

$$XC_6H_4X^{\bullet-} \longrightarrow XC_6H_4^{\bullet} + X^-$$

$$XC_6H_4^{\bullet} + Y^- \longrightarrow XC_6H_4Y^{\bullet-}$$

$$XC_6H_4Y^{\bullet-} + XC_6H_4X \longrightarrow \underset{\text{monosub.}}{XC_6H_4Y} + XC_6H_4X^{\bullet-} \quad \text{(oxidation)}$$

$$XC_6H_4Y^{\bullet-} \longrightarrow X^- + {}^{\bullet}C_6H_4Y \quad \text{(cleavage)}$$

$${}^{\bullet}C_6H_4Y + Y^- \longrightarrow YC_6H_4Y^{\bullet-}$$

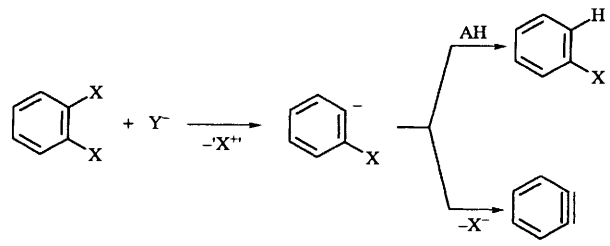
$$YC_6H_4Y^{\bullet-} + XC_6H_4X \longrightarrow \underset{\text{disub.}}{YC_6H_4Y} + XC_6H_4X^{\bullet-}$$

Scheme 11

between oxidation (yielding the mono-substitution product) and cleavage (eventually conducive to the disubstitution product). Incursion of hydrodehalogenation step(s) is not recorded (liquid NH_3 is a worse H-atom donor than Me_2SO).[25]

On the other hand, with *ortho*-dihalobenzenes and without photostimulation, an halophilic route was documented: it was followed by competitive protonation and benzyne formation (Scheme 12).[21] The strong stabilizing effect of *ortho* halogen substituents on phenyl anions was taken as responsible[22b] for the incursion of this ionic process; compounds (*E*)-**2** and (*E*)-**3** are structurally similar to *ortho*-dihalobenzene and the same stabilizing effect on the intermediate vinylic carbanion could play a relevant role (Scheme 8)

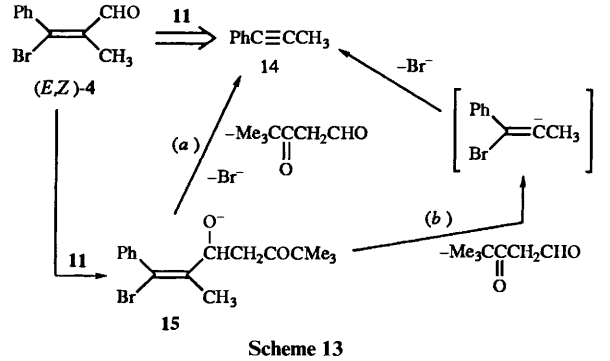
Finally, we should not forget the efficient competition of an halophilic route with an elimination–addition route in the case of oligohalobenzenes, which led to the so called 'halogen dance' by the action of Bu^tO^- or carbanions as nucleophiles.[22b]



Scheme 12

3-Bromo-2-methyl-3-phenylpropenal (4)

While hydrodebromination to give **7** is the outcome of the electrochemical experiment (Scheme 3), the unexpected alkyne **14** is obtained from the reaction of **4** with **11** both under photostimulation and by ferrous ion induction, as well as in the absence of any induction (expts. 10–12; Scheme 13). The



Scheme 13

reaction is over in 15 min and no precursor **4** is recovered at the end.

Since the CHO group, at variance with the NO_2, I or Br groups of **1**–**3**, is an inconceivable anionic leaving group (see Schemes 2, 8 or 10 for compounds **1**–**3**), neither of the above mentioned routes can apply in this case. A reasonable, though tentative, explanation for the formation of **14** could be a nucleophilic attack of **11** on the carbonyl carbon of the enal **4** to give the bromovinyl alkoxide **15**. Then **15** could form **14** by two alternative ways: (*a*) by a concerted loss of Br^- and of a neutral β-keto aldehyde, or less likely (*b*) by a two step process of elimination of the β-keto aldehyde with formation of an α-bromovinyl carbanion intermediate, followed by Br^- departure.

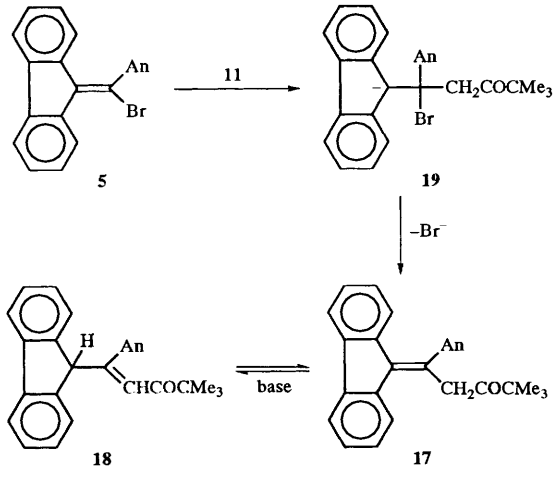
Consistent with an ionic pathway is the lack of formation of **12** or **13**, as well as the finding that the ferrous ion catalyst is not required (expt. 12). These results support a non-SET nature for the product determining step. The postulated β-keto aldehyde would be lost during work-up owing to its presumably high solubility in water, which is deduced from keto aldehydes of comparable structure.

We know of no precedents[26] for a similar 'deformylation' from alkenes of comparable structure, although it bears some resemblance with a Grob-type fragmentation.[26a] Reaction of an analogue of **4**, *i.e.* PhC(Cl)=C(Ph)CHO (**16**), with other nucleophiles,[27] not including carbanions, took the 'normal' addition–elimination substitution route. The dissimilarity between the two cases may arise from a different extent of $\pi_{(C=C)}$–$\pi_{(C=O)}$ conjugation in the enals. The carbonyl stretching frequencies suggest an extensive conjugation with the double bond of **16** (1680 cm^{-1}),[27] while in the case of **4** (1733 cm^{-1}) it appears in the range ascribed[28a] to non-conjugated enals: this could cause a preferential addition of the enolate ion to the C=O group (Scheme 13). Alternatively, it is known that soft nucleophiles attack in general the C-3 of an enal, thereby giving a predominant 1,4-addition; however, alkaline enolates loosely

associated in ion pairs predominantly attack at the carbonylic carbon.[28a] Potassium enolates form loose ion pairs in Me_2SO,[29] and this could support a 1,2-nucleophilic addition and therefore our rationalization (Scheme 13).

Compound 5

This is the only substrate investigated here which had given substitution of the halide with the pinacolone moiety (expt. 13). However, in spite of the favourable electron affinity of **5**, its interaction with **11** apparently does not proceed by an $S_{RN}1$ pathway, since no appreciable inhibition by the *p*-dinitrobenzene scavenger is verified (expt. 14). Similar yields of **17**, **18** and **8** are obtained with or without photostimulation (expt. 15) and **12** and **13** are not formed. Since the reaction occurs at room temperature, a vinylic S_N1 process is excluded,[6] but a nucleophilic addition–elimination route, favoured by the aromaticity of the fluorenylidene moiety of the intermediate carbanion **19** (Scheme 14) seems likely.[2,6,30]



Scheme 14

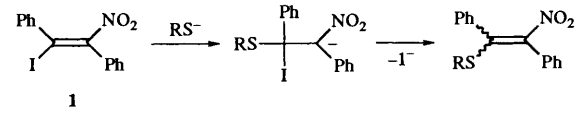
This route was previously observed in the presence of other promising SET-nucleophiles, *e.g.* thiolate ions.[6]

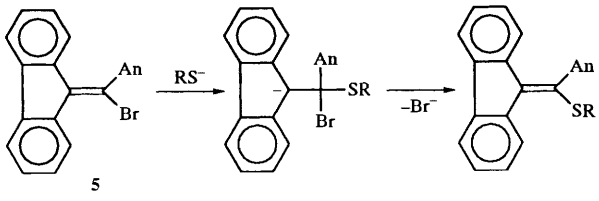
A partial tautomerization of the 'direct' substitution product **17** to its allylic isomer **18** occurs in the basic medium. The two positional isomers have very similar GC retention times but, fortunately, under preparative conditions predominance of the one or the other tautomer was obtained by modulating the concentration of Bu^{t}OK in the medium. The modest amount of the hydrodebromination product **8** can be attributed to a minor incursion of a SET pathway (Scheme 4), which is terminated by hydrogen transfer from the solvent to the radical, rather than by its capture by **11**, or by further reduction of the radical to form a carbanion and subsequent protonation.

Competition of S_NV mechanisms: comparison with other vinylic systems

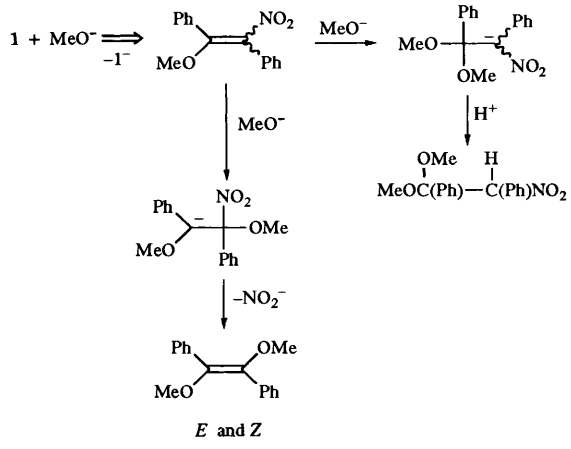
Nucleophilic substitution processes by the good electron donors RS^- have been studied with both compounds **1** and **5** and nucleophilic addition–elimination (Scheme 15) was the observed pathway.[6,31,32]

With alkoxides as the nucleophiles, the addition–elimination route is accompanied by further reactions, such as substitution of the nitro group by another MeO^- nucleophile, leading to PhC(OMe)=C(OMe)Ph from **1**[27] or addition to the nitrovinyl ether (Scheme 16),[33] but also by an halophilic reaction which leads to **6**.[34] We have already given evidence of an exclusive halophilic route with **1** (expt. 9) when using Bu$^tO^-$ as the nucleophile. On the other hand, with (*E*)-**2** and (*E*)-**3**, when using the enolate **11** as the nucleophile, ECEC and ECC routes, accompanied by the halophilic one, are observed. Finally,



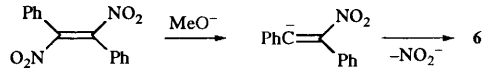


Scheme 15



Scheme 16

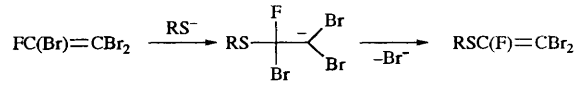
reaction of MeO^- or $CF_3CH_2O^-$ with the closely analogous substrate[34] PhC(NO_2)=C(NO_2)Ph also gave **6** (Scheme 17),



Scheme 17

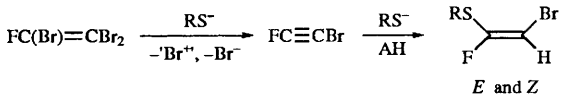
presumably by a route similar to the halophilic reaction, but initiated in this case by nucleophilic attack on one of the nitro groups.[35]

Other examples of more mildly activated alkenes which undergo multiple reaction pathways are polyhalogenated vinylic systems. Nucleophiles such as F^- or RS^- are considered to react *via* addition–elimination pathways (Scheme 18)[36] or



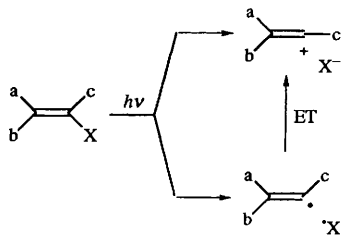
Scheme 18

elimination–addition *via* a halophilic-initiated route (Scheme 19).[36] Finally, the irradiation of vinylic halides provides a



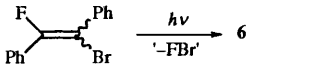
Scheme 19

convenient method with which to generate vinyl cations, either by direct heterolysis or by homolysis followed by electron transfer (Scheme 20).[37]



Scheme 20

In the case of a compound structurally analogous to our precursors, this led to **6** [reaction (8)],[38] which may introduce another competing mechanistic variant to those listed so far.



(8)

It is clear from the present and the previous work that evaluation of the scope of the $S_{RN}1$ reaction and the conditions under which it will compete with other routes, requires a comprehensive study involving gradual changes in the structure, in the leaving group, in the nature and bulk of the nucleophile and in the solvent. The previous work[4] had emphasized the role of elimination–addition routes, even though the nucleophilic addition–elimination route has always to be kept in mind; the present work has added the halophilic reaction as a serious competitor in the case of activated alkenes, all in a potential competition with the $S_{RN}V$ route. The borders between the various routes are delicate, since all are initiated by electron transfer, but to a different reaction centre of the ambident electrophilic alkene in the various cases. A single electron is transferred to the π MO in the initiating step[4] of the $S_{RN}V$ route, whereas two electrons are transferred from the nucleophile to the vinylic carbon, to a hydrogen or to a halogen in the nucleophilic addition–elimination, in the elimination–addition and in the halophilic routes, respectively.

In trying to discern a rationale behind the competition of the various routes already observed in the reactions of stilbenes activated by electron-withdrawing groups, as well as for future planning, salient features such as nucleophilicity, basicity and hard–soft character of the nucleophiles should be considered. The strongly nucleophilic but weakly basic RS^- reacts by addition–elimination with **1** in protic solvents,[31,32] but the strongly basic and sterically demanding Bu^tO^- mounts halophilic attack in dipolar aprotic medium (since vinylic hydrogens are not available; expt. 9). The MeO^- and $CF_3CH_2O^-$ ions are both nucleophilic and basic and the two processes co-exist.[32,34] The soft enolate ion, besides being a nucleophile and a base, has also a reducing capability and, consistently, the SET route begins to contribute, but its softness may also enhance an halophilic route toward the heavier halogens.

Conclusions

The results collected for compounds **1–5** compel us to conclude that the domain of existence of the $S_{RN}V$ mechanism is more limited than that of the corresponding $S_{RN}1$ with aromatic halides.[5] As a result of 'the rich mechanistic world of nucleophilic vinylic substitution' routes,[2] the presence on the vinyl moiety of electron-withdrawing substituents, some of which are easily tolerated by the aromatic $S_{RN}1$ route,[5] causes other mechanisms to take over. Notable is the halophilic competition with **1** and with the dihalo derivatives (*E*)-**2** and (*E*)-**3** (Scheme 10) or the addition–elimination route with **5** (Scheme 14). It is also noteworthy that the favourable reduction potentials of **1–5** indicate that the first SET step [*i.e.* (1) in Scheme 1] should easily take place and this is indeed the case, at least with (*E*)-**2** and (*E*)-**3**. However, the radical formed has other low-energy favourable routes, which occur preferentially (Scheme 8) and impede the $S_{RN}V$.

From the present investigation we have learned that Scheme 1 of the $S_{RN}1$ route has to be expanded to include, in a more general formulation (and at least for vinylic halides), three additional aspects (Scheme 21): (*i*) the reversibility of step (1), in

$$VyX + Y^- \overset{\text{initiation}}{\rightleftharpoons} VyX^{\bullet -} + Y^\bullet \quad (1)$$

$$VyX^{\bullet -} \longrightarrow Vy^\bullet + X^- \quad (2)$$

$$Vy^\bullet + Y^- \longrightarrow VyY^{\bullet -} \quad (3)$$

$$Vy^\bullet \xrightarrow{\text{'e}^-\text{'}} Vy^- \quad (9)$$

$$Vy^\bullet + SH \longrightarrow VyH + S^\bullet \quad (5)$$

$$Y^\bullet + Y^- \longrightarrow Y\text{-}Y^{\bullet -} \quad (10)$$

$$VyY^{\bullet -} + VyX \longrightarrow VyY + VyX^{\bullet -} \quad (4)$$

$$Y\text{-}Y^{\bullet -} + VyX \longrightarrow Y\text{-}Y + VyX^{\bullet -} \quad (11)$$

Scheme 21

the case of substrates whose radical anion is cleaved slowly[8,23] (*cf.* the nitro derivative **1**), (*ii*) fast electron transfer to the intermediate radical to give a carbanion [step (9)] before capture by the nucleophile [step (3)] or by the hydrogen donor solvent [step (5)], can take place,[8,20] (*iii*) simple or multiple coupling steps [step (10)] of the nucleophile Y^- with the radical species $Y^\bullet$ deriving from it after electron loss in the initiating step (see Scheme 5).

In addition, evidence is provided here (Scheme 9) for loss of a radical leaving group from a vinyl radical, resulting in the formation of a triple bond system, while in the previous paper[4] we also gave evidence for a rearrangement occurring on the vinyl radical and leading to a rearranged substitution product.

The work described here should be supplemented by a study of the $S_{RN}1$ route with *electron-donating* aryl-substituted alkenes. Indeed, the observation[4] of this route for 1-bromo-1,2,2-triphenylethene **9** encourages extension in this direction. Competition from a vinylic S_N1 route is possible for this range of substituents, as was reported[6] with **5** and many triaryl vinyl halides.[39] We are presently engaged in such studies which will be reported in due course.[40]

Experimental

Instrumentation

Most of the instrumentation has been described previously.[4] A Rayonet RPR-100 reactor, equipped with 16 lamps emitting in the 350 nm region (Pyrex filtered) was employed in the photostimulated reactions. Cyclic voltammetry determinations were carried out with a homemade potentiostat with positive feedback ohmic drop compensation[41] and a PARC Model 175 function generator; the voltammograms were recorded with a Nicolet 310 storage oscilloscope. HRMS determinations were carried out on a Bruker Apex TM47e FTMS spectrometer equipped with an external ion source and a cyclindrical 'infinity cell' and operating at 4.7 T. NMR spectra were taken in $CDCl_3$ on a Bruker AC 300 instrument.

Materials

Reagent grade diphenylacetylene (**6**; Aldrich) and 1-phenylprop-1-yne (**14**; Aldrich) were used as received. Compound **8** was available from a previous investigation.[6] Pinacolone was distilled from anhydrous K_2CO_3; freshly sublimed Bu^{t}OK was used to generate the enolate ion from pinacolone. Ferrous chloride was dried in a drying pistol over P_2O_5 at 110 °C under vacuum.[4] Tetrabutylammonium tetrafluoroborate was prepared[42] from $Bu_4N^+HSO_4^-$ (Aldrich) and $Na^+BF_4^-$ (Fluka) in water, recrystallized from ethyl acetate–light petroleum (40–70 °C) and dried under vacuum (10^{-2} Torr) at 60 °C for 6 h. Commercial Me_2SO (C. Erba RPE, 99.5%) was thoroughly purged with argon for 1 h prior to use in order to remove volatile acidic impurities, while distillation from CaH_2 proved to be less satisfactory.[4] For electrochemical measurements, THF was distilled from the benzophenone radical anion, stored and transferred under argon.‖

Synthesis of reactants

α-Iodo-β-nitrostilbene (**1**) was prepared according to Stevens and Emmons:[44] mp 175–178 °C (lit.,[44] 175–176 °C); it was an (*E*):(*Z*) mixture (*ca.* 1:1 by GLC). α,α′-Diiodostilbene [(*E*)-**2**] was prepared according to Suzuki:[45] mp 207 °C (lit.,[46] 204 °C for *E*[45]). Compound **5** was prepared according to Rappoport and Gal:[6] mp 152–154 °C (lit.,[6] 152–154 °C).

α,α′-Dibromostilbene (**3**) was prepared[47] by Br_2 addition to diphenylacetylene (**6**) dissolved in AcOH containing 0.1 mol dm^{-3} LiBr. Following the addition of salted water at the end of the reaction, the *E*-isomer [(*E*)-**3**, 97% pure by GLC] was precipitated as a white solid (52% yield), mp 210–212 °C (lit.,[48] 210–211 °C).

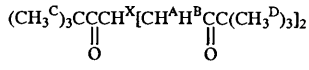
3-Bromo-2-methyl-3-phenylpropenal (**4**) was prepared[49] by bromination of 40 cm^3 (0.29 mol) of (*E*)-2-methyl-3-phenylpropenal (**7**; Aldrich) with 15 cm^3 of Br_2 (0.29 mol) in 200 cm^3 of CH_2Cl_2; subsequent dehydrobromination of the dibromo derivative (90 g, 0.29 mol) was carried out[50] with 39 g of KOH powder (0.6 mol) and 0.7 g 18-crown-6 (2.7 mmol) in 250 cm^3 of light petroleum at *ca.* 40 °C for 8 h. Extensive decarbonylation and tar formation occurred while removing the solvent from the crude reaction product. The residue (20 g) was chromatographed on silica gel with 5:1 hexane–diethyl ether as eluent, then with hexane and finally on alumina with 9:1 hexane–diethyl ether as eluent, giving 400 mg (2% yield) of pure **4** as a 5:1 *E*:*Z* mixture: ν/cm^{-1} 1733 (C=O); δ_H 10.2 [17% of 1 H, s (*Z*)-**4** CHO], 9.4 [83% of 1 H, s, (*E*)-**4** CHO], 7.4–7.3 (5 H, bs, Ph), 2.1 [83% of 3 H, bs, (*E*)-**4** Me] and 1.8 [17% of 3 H, bs, (*Z*)-**4** Me]; δ_C 194.3 [(*Z*)-**4** CHO], 188.9 [(*E*)-**4** CHO], 147.9 (=CCHO), 139.2 (Ph*C*=), 138.6, 130.0, 129.9, 128.3, 16.2 [(*E*)-**4** Me] and 14.8 [(*Z*)-**4** Me]. We have deduced the ^1H NMR assignments of the *E*,*Z* isomers from literature data[27] for the comparable substrate **16** and from the ^1H NMR of commercial (*E*)-**7**: δ_H 9.5 (1 H, s, CHO), 7.6–7.3 (5 H, m, Ph), 7.2 (1 H, s, vinylic H), 2.1 (3 H, s, CH_3); the ^{13}C NMR assignments we have given are consistent with these models. *m*/*z* 223.9828; $C_{10}H_9O^{79}Br$ requires 223.9831.

Synthesis of products

2,2,7,7-Tetramethyloctane-3,6-dione (12) and 2,2,8,8-tetramethyl-5-(2,2-dimethylpropanoyl)nonane-3,7-dione 13. A mixture of pinacolone (2.7 cm^3, 22 mmol), Bu^{t}OK (3.4 g, 30 mmol) and (*E*)-**3** (2.37 g, 7 mmol) in 44 cm^3 Me_2SO was irradiated in the photochemical reactor for 2 h and the reaction quenched by the addition of salted water. The solution was extracted with toluene, washed with water, dried (Na_2SO_4) and evaporated to give a mixture (2.3 g) which was flash chromatographed on silica gel with light petroleum (40–70 °C) and subsequently with graded mixtures of light petroleum (40–70 °C)–diethyl ether. Diphenylacetylene **6** was obtained in quantitative yield (1.25 g), accompanied by **12** (0.12 g, 18% yield) and **13** (0.47 g, 68% yield).

Compound **12**:[19] ν/cm^{-1} 1701 (C=O); δ_H 2.75 (4 H, s, CH_2) and 1.2 (18 H, s, CH_3); *m*/*z* 198 (M^+, 1), 141 (M^+ − Bu^t, 64), 113 (M^+ − COBu^t, 100) and 57 ($^tBu^+$, 77).

Compound **13**: mp 91–94 °C. ν/cm^{-1} 1695 (C=O). δ_H 2.76–2.68 and 2.49–2.41 (4 H, doublet of dd, CH^AH^B), 1.18 (9 H, s, CH_3^C) and 1.07 (18 H, s, CH_3^D); J_{AB} = 18.0 and J_{AX} = J_{BX} = 6.6 Hz. The ^1H NMR spectrum was well simulated by the program Daisy.[4] δ_C 218.7 ($COCH^X$), 213.3 (CO), 44.6



13

(CMe_3^C), 43.9 (CMe_3^D), 38.9 (CH_2), 36.1 (CH), 27.4 (CH_3^D) and 26.9 (CH_3^C); *m*/*z* (M^+ + 1) 297.2418; $C_{18}H_{33}O_3$ requires 297.2424.

Fluorenylidene derivatives 17 and 18. A mixture of 1.14 g of Bu^{t}OK (0.01 mol), 1.25 cm^3 pinacolone (0.01 mol) and 0.9 g of **5** (2.5 mmol) in 30 cm^3 Me_2SO was kept for 1 h under N_2 at room temperature. After a conventional work-up with diethyl ether, a solid (1 g) was obtained; crystallization from toluene gave 0.9 g (93% yield) of **17**, mp 143–146 °C. ν/cm^{-1} 1708 (C=O); δ_H 7.6–6.1 (12 H, m, Ar), 4.1 (2 H, s, CH_2), 3.7 (3 H, s, CH_3O) and 1.0 (9 H, s, CMe_3); δ_C 211.0 (*C*=O), 159.2 (C^{OMe}_{ipso}), 140.0 (C^{An}_{para}), 139.7, 139.3, 138.3 (Ar_2C=), 136.4, 136.0 [=*C*(An)-CH_2CO], 129.3, 127.2, 126.8, 126.5, 124.7, 124.0, 119.6, 119.0, 114.3, 55.2 (CH_3O), 46.8 (CH_2), 44.7 (CMe_3) and 26.4 (CH_3); *m*/*z* 382.1898; $C_{27}H_{26}O_2$ requires 382.1927.

This reaction was run again on a smaller scale with a smaller base–substrate ratio: 0.14 g Bu^{t}OK (1.2 mmol), 0.16 cm^3 pinacolone (1.2 mmol) and 0.17 g of **5** (0.47 mmol) in 3 cm^3 Me_2SO were kept for 2 h to give, after work-up, 100 mg of a mixture of a low melting solid and a liquid. The liquid was separated by suction with a Pasteur pipette. Obtained in this way were 50 mg of 85% of **18** admixed with 15% of **17** (33% yield), as a low-melting yellow liquid. ν/cm^{-1} 1671 (C=O); δ_H 7.8–7.2 (8 H, m, Ar), 7.0 (1 H, s, vinylic H), 6.7–6.5 (4 H, m, Ar), 3.9 (1 H, s, =CHCO), 3.6 (3 H, s, CH_3O), 1.4 (9 H, s, CMe_3); δ_C 206.8 (*C*=O), 159.6 (C^{OMe}_{ipso}), 155.2 (*C*=CH–CO), 145.9, 141.2, 132.3 (C=*C*H–CO), 129.3, 128.0 (C^{An}_{para}), 127.0, 126.9, 124.9, 119.9, 113.2, 54.8 (CH_3O), 49.6 (Ar_2CH), 44.3 (CMe_3) and 26.8 (CH_3).

General substitution procedure. Details on the ferrous stimulated or photostimulated reactions have been given before.[4] Quantitative GC analyses were performed by the internal standard (*i.e.* biphenyl) method and the yields are the average of at least three injections (typical error ±4%). In general, 2.3 mmol of Bu^{t}OK, 1.7 mmol of pinacolone, 0.22 mmol of $FeCl_2$ (whenever present) and 0.5 mmol of substrate in 25 cm^3 Me_2SO reacted at room temperature. Samples of the reaction mixture were taken at proper times, a known amount of standard was added and the sample was extracted with diethyl ether, washed with brine and dried (Na_2SO_4) before being injected.

Radical dehalogenation

A solution of 18 mg of (*E*)-**3** (0.049 mmol), 6 mg AIBN (0.04 mmol) and 14 μl Bu_3SnH (0.052 mmol) (1 μl = 1 mm^3) in 0.14

‖ Use of THF instead of Me_2SO was preferred in the reduction mode in order to avoid interference from depronotation of the solvent owing to the electrogeneration of strongly basic species (*i.e.* $Ar^{\bullet} \longrightarrow Ar^-$), followed by interaction of the conjugate base of the solvent with the substrate.[43]

cm^3 benzene was refluxed for 4 h;[51] direct GLC analysis (no work-up) of the reaction mixture revealed extensive consumption (71%) of **3**, coupled with 40% formation of **6**, only trace of a product consistent (GC–MS) with α-monobromostilbene, no stilbene, a modest amount of Bu_3SnBr (GCMS) and an appreciable amount of an unidentified peak featuring some MS fragments that are consistent with the stilbene moiety.

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