A Search for Unambiguous Vinylic $S_{RN}1$ Reactions

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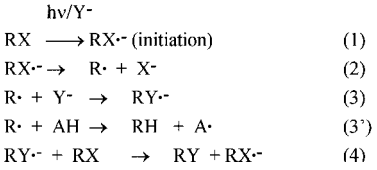
In a search for unambiguous examples of the vinylic $S_{RN}1$ route, vinyl bromides $Ph(CH_3)C{=}CHBr$ (**10**), $Ph_2C{=}CHBr$ (**15**), $An_2C{=}C(Br)An$ (**18**) and $An_2C{=}CBr_2$ (**20**) were treated with $Me_3CCOCH_2^-$ under photostimulation conditions in Me_2SO, whereas substrates $PhCH{=}CHBr$ (**2**), $Ph_2C{=}C(Br)Ph$ (**3**), **10** and **15** were similarly allowed to react with PhS^- and $PhCH_2S^-$. With the strongly basic enolate ion, the prevailing reactions were elimination/addition routes, α-deprotonation followed by 1,2-Ph shift and bromide ion elimination, or halophilic steps. With **18**, however, an $S_{RN}1$ route was obtained. The weakly basic but reducing anion PhS^- gave the $S_{RN}1$ route with **2**, **3** and **15**. The nucleophilic character of the $PhCH_2S^-$ anion instead prevailed with **15**, whereas with **3** a variety of behaviours was obtained. The mechanistic interpretations were supported by the electrochemically determined redox potentials of the substrates.

Introduction

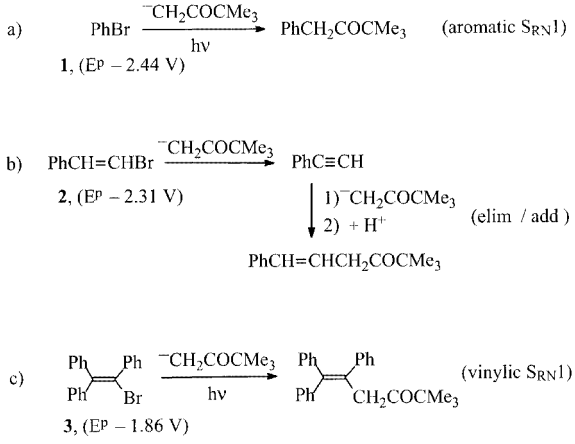
The common $C(sp^2)-$halogen bond in aryl halides and vinyl halides has provided the stimulus for investigations aimed at unveiling differences or similarities in behaviour for these two fundamental families. With respect to reactivity features in nucleophilic substitution reactions, the variety of mechanistic possibilities and the strong competition between reaction pathways presented by vinyl halides exceeds those presented by the aryl halides.[1]

We have observed this spectrum of pathways during an attempt to find a vinylic counterpart to the aromatic $S_{RN}1$ mechanism,[2] the reaction scheme of which is outlined in Scheme 1[3] (R stands for either an aryl or a vinyl residue, AH is a hydrogen donor and Y^- is a suitable nucleophile).

However, important differences were immediately recognized. Whereas, for example, bromobenzene (**1**) reacted with the enolate anion of a ketone (Y^-) by a photoinduced electron-transfer (ET) initiation (Scheme 1, step 1), the vinylogue β-bromostyrene (**2**) (Scheme 2)[2] reacted differently under the same conditions. This was surprising, since the two substrates had similar electron affinities ($E^p = -2.44$ and -2.31 V vs. SCE, respectively, in THF at 0.5 V/s),[4] that should make single-electron reduction and the ensuing fragmentation possible (steps 1 and 2 in Scheme 1). However, **2** underwent elimination/addition by an ionic mechanism, the basicity of the enolate ion prevailing over its reducing character,[2a] resulting in abstraction of a proton from the vinylic β-C−H group. Consistently with this, the absence of vinylic β-hydrogen atoms in $Ph_2C{=}C(Br)Ph$ (**3**) enabled it to undergo a vinylic $S_{RN}1$ reaction.[2]



Scheme 1



Scheme 2

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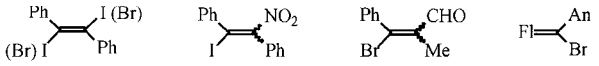
The situation can, however, be more complex. $Me_2C{=}C(Br)CMe_3$ (**4**), which also lacks vinylic hydrogen atoms, failed to give an $S_{RN}1$ reaction with the enolate ion.[2b] This was attributed to the lack of any substituent (e.g., Ph) capable of lowering (by conjugation) the energy of the expected radical anion of the substitution product formed (step 3).[2b,5] On the basis of this information, and in an attempt to promote the $S_{RN}1$ pathway, we even investigated vinyl halides bearing electron-withdrawing substituents (Scheme 3; Fl = fluorenyl, An = *p*-$MeOC_6H_4$).[4a]



5 (**6**), -0.97 (-1.69) **7**, -0.94 **8**, -1.43 **9**, -1.35

Scheme 3. E^p data (in V vs. SCE)

Despite the fact that these electron-withdrawing substituents should provide suitable stabilisation for the radical anion of the $S_{RN}1$ product, ionic processes such as addition/elimination or halophilic routes and substitution with structural rearrangement were again dominant.[4a] The room for a vinylic $S_{RN}1$ process did therefore appear to be rather limited, with competition from ionic pathways seemingly strongly linked to subtle structural features of the substrate.

Here we present the results of an investigation in which the structure of the vinyl halide was modified in a further attempt to make the vinylic $S_{RN}1$ process prevail over possible competing ionic pathways. Because the electron affinity of the substrate may be decisive in governing this competition between electron-induced (i.e., the $S_{RN}1$ route) and ionic processes, the redox potentials of the substrates were electrochemically determined, and the reported E^p data supported our mechanistic interpretation. As well as modifying the structure of the substrate, we also modified the nature of the anion, by changing either its reducing character, its nucleophilicity or its basicity, in order to be able to single out the most likely substrate/anion combination that would promote the onset of the vinylic $S_{RN}1$ reaction.

Results and Discussion

The Structure of the Substrate

Because the presence of a β-C−H bond appeared to shift the reactivity of a vinyl halide towards an elimination/addition process in the presence of an enolate ion,[2] we explored the feasibility of a vinylic $S_{RN}1$ reaction on a precursor bearing an α-C−H bond. Two substrates were synthesised, and their reactions with the enolate ion of 3,3-dimethyl-2-butanone (pinacolone), as the reference nucleophile (Y^-), were investigated. The vinyl halide was treated with a threefold excess of the nucleophile in Me_2SO solution at room temperature according to the general procedure in our previous investigations[2b,4] with irradiation by "350-nm"

Table 1. Yields in the described reactions, performed in Me_2SO at room temperature

Substrates, VyX[b][c]	Reaction conditions	Nucleophile, Y^-	Yields (%)[a] VyX, recvd.	VyY[d]	VyH[e]	Others
10	*hν*, 20 min	$Me_3CCOCH_2^-$	**10**, 17	**12**, 21; **13**, 59	–	**11**, 2
10	*hν*, 45 min	$Me_3CCOCH_2^-$	**10**, 1	**12**, 11; **13**, 73	–	**11**, 4
10 + scaven.	*hν*, 45 min	$Me_3CCOCH_2^-$	**10**, 3	**12**, 9; **13**, 71	–	**11**, 2
10	45 min	$tBuO^-$	**10**, 65	**14**, 8	–	**11**, 1
15	*hν*, 30 min	$Me_3CCOCH_2^-$	**15**, 64	–	**17**, 1	**16**, 23
15 + scaven.	*hν*, 30 min	$Me_3CCOCH_2^-$	**15**, 69	–	**17**, 1	**16**, 21
15	30 min	$tBuO^-$	**15**, 77	–	–	**16**, 7
18	60 min	$Me_3CCOCH_2^-$	**18**, 60	**19**, 32	–	–
18 + scaven.	60 min	$Me_3CCOCH_2^-$	**18**, 94	**19**, 1	–	–
20	*hν*, 20 min	$Me_3CCOCH_2^-$	**20**, 7	–	**22**, 36	**21**, 52
20 + scaven.	*hν*, 20 min	$Me_3CCOCH_2^-$	**20**, 51	–	–	**21**, 38
23	*hν*, 20 min	$Me_3CCOCH_2^-$	**23**, 74	–	**24**, 12	–
23 + scaven.	*hν*, 20 min	$Me_3CCOCH_2^-$	**23**, 93	–	–	–
25	*hν*, 20 min	$Me_3CCOCH_2^-$	**25**, 5	–	**15**, 68	**16**, 23
25 + scaven.	*hν*, 20 min	$Me_3CCOCH_2^-$	**25**, 6	–	**15**, 67	**16**, 19
3	*hν*, 30 min	PhS^-	**3**, 15	**26**, 29	**27**, 56	–
3 + scaven.	*hν*, 30 min	PhS^-	**3**, 53	**26**, 20	**27**, 17	–
15	*hν*, 30 min	PhS^-	**15**, 16	**28**, 46	**17**, 6	–
15 + scaven.	*hν*, 30 min	PhS^-	**15**, 58	**28**, 21	**17**, 1	–
3	*hν*, 30 min	$PhCH_2S^-$	**3**, 50	**29**, 10	**27**, 2	**30**, 2; **31**, 2
3 + scaven.	*hν*, 30 min	$PhCH_2S^-$	**3**, 61	**29**, 6	**27**, 1	**30**, 2; **31**, 2
15	*hν*, 30 min	$PhCH_2S^-$	**15**, 0	**32**, 99	–	–
15 + scaven.	*hν*, 30 min	$PhCH_2S^-$	**15**, 0	**32**, 99	–	–
2	*hν*, 30 min	PhS^-	**2**, 47	**33**, 25	–	–
2 + scaven.	*hν*, 30 min	PhS^-	**2**, 87	**33**, 0	–	–
2	*hν*, 30 min	PhO^-	**2**, 40	–	–	**34**, 49
2	30 min	$tBuO^-$	**2**, 0	–	–	**34**, 99

[a] GC yields. [b] Typical conditions: VyX, 0.2 mmol; Y^-, 0.7 mmol; Me_2SO, 5 mL. [c] The scavenger is 1,4-$(O_2N)_2C_6H_4$. [d] VyY = substitution product. [e] VyH = reduction product.

lamps. The enolate ion was generated in situ from pinacolone by use of an almost stoichiometric amount of *t*BuOK. The experiments were performed under argon, and the product compositions were monitored by gas chromatography and GC-MS analyses on samples withdrawn during the reaction. The reaction conditions, the products and their GC yields are given in Table 1 (VyX, VyY and VyH are the precursor halide, its substitution product and its reduction product, respectively; any other product formed is also indicated). The yields were calculated by the internal standard method (vs. biphenyl) and no attempts were made to optimise them.

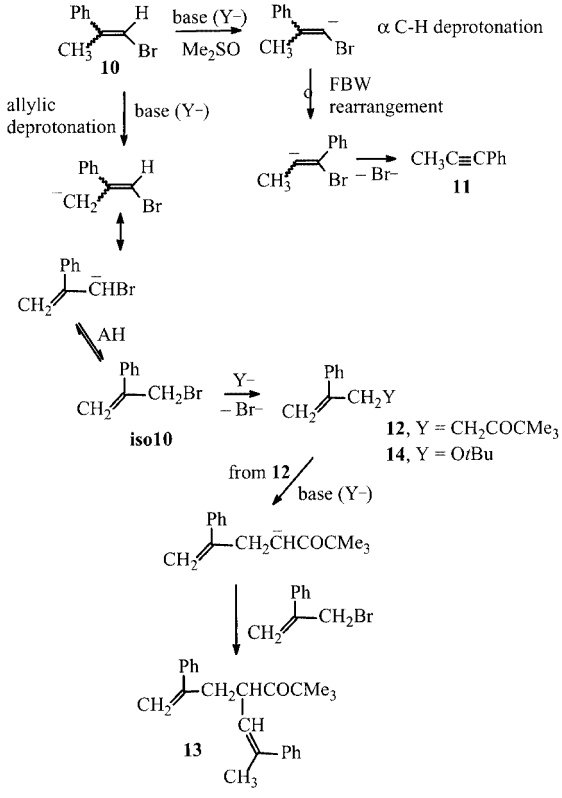
(*E*,*Z*)-β-Bromo-α-methylstyrene (10)

On treatment of **10** with the enolate ion, two minor products were obtained: methylphenylacetylene (**11**) and 6,6-dimethyl-2-phenyl-1-hepten-5-one (**12**) (Scheme 4). These were produced even in the absence of photostimulation or in the presence of *p*-dinitrobenzene, a well-known electron scavenger, implying the operation of an ionic pathway and *not that* of the $S_{RN}1$ mechanism. Deprotonation of **10** by the strongly basic enolate ion Y^- (pK_{HY} = 27.7)[6] gives a vinyl carbanion, which presumably gives **11** by a Fritsch−Buttenberg−Wiechell (FBW) rearrangement of the phenyl group,[7] followed by loss of a bromide ion. In competition with this α-vinyl deprotonation, an allylic deprotonation followed by migration of the double bond and reprotonation[1] could give the isomeric substrate **iso10**, featuring an allyl bromide functionality (Scheme 4). An easy allylic S_N2 reaction of **iso10** by the enolate ion would then give rise to **12**. The major product, however, was a higher molecular weight compound (**13**), the yield of which increased after a longer reaction time. Its MS and ^1H NMR spectra were consistent with a structure that could derive from deprotonation of **12** in the basic medium, followed by an S_N2 reaction of the resulting anion with the **iso10** formed in situ.

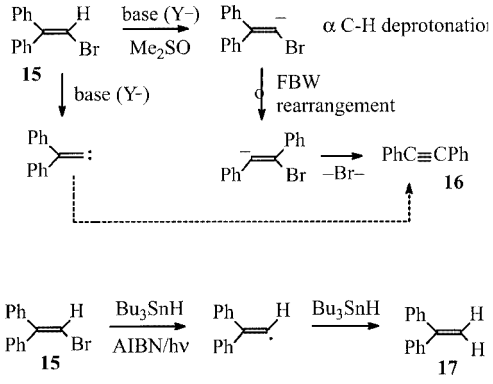
In order to confirm this ionic reaction scheme, **10** was treated with the strong base *t*BuOK (pK_{HY} = 32.2).[6] In keeping with the α-deprotonation/FBW rearrangement, **11** was indeed obtained, while 3-*tert*-butoxy-2-phenylpropene (**14**; i.e., the allylic S_N2 product of $tBuO^-$ on **iso10**) was also observed.

1-Bromo-2,2-diphenylethene (15)

Replacement of the methyl group of **10** by a phenyl group ought both to prevent the allylic deprotonation described in Scheme 4 and to stabilise slightly better − and hence enhance the formation of − the radical anion of the $S_{RN}1$ reaction product. In addition, **15** is slightly easier to reduce than **10** (E^p = −2.2 instead of −2.3 V vs. SCE), to the benefit of the $S_{RN}1$ initiation. In contrast to expectations, however, **15** gave only diphenylacetylene (**16**) on treatment with the pinacolone enolate ion (Y^-), most probably through the α-deprotonation/FBW rearrangement pathway (Scheme 5). It was considered possible that an electron-transfer process might co-exist, affording the intermediate vinyl radical (through loss of a bromide ion: Scheme 1, step 2), which would then undergo the FBW rearrangement. This could be ruled out, however, since the 2,2-diphenylvinyl radical, independently generated by use of $Bu_3Sn^{\cdot}$,[8] neither rearranged nor gave **16** (Scheme 5), but only provided 1,1-diphenylethene (**17**) by H abstraction. On replacement of the enolate ion by *t*BuOK, **16** was obtained, confirming the α-deprotonation route. Another route might be an α-elimination to a vinylidenecarbene that would rearrange to **16**.[7a,9] In an attempt to trap such an intermediate carbene[7a] by performing the reaction between **15** and *t*BuOK in the presence of a cycloalkene, no trace of any addition product of the postulated carbene onto the olefin was detected. Hence, an FBW rearrangement through the carbanion seems the most likely route.[7a] We concluded that neither α- nor β-vinylic hydrogen atoms should be pre-



Scheme 4

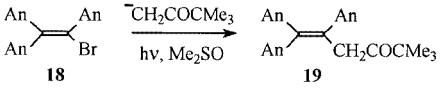


Scheme 5. Y = Me_3CCOCH_2

sent in the vinyl halide if an $S_{RN}1$ reaction with a nucleophile as basic as an enolate ion were sought (however, see below).

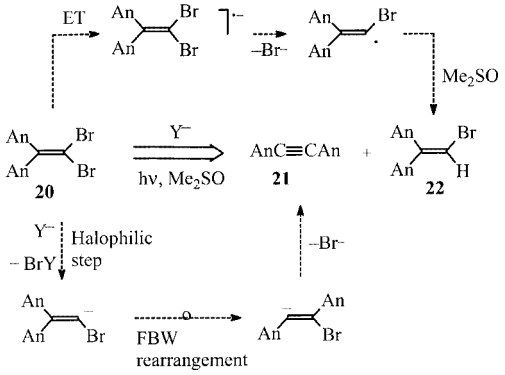
Redox Potentials of the Substrates

Another conceivable structural change was to investigate vinylic halides endowed with electron affinities *lower* than that of **3** ($E^p = -1.86$ V vs. SCE).[4a] Precursors with electron affinities *higher* than this value (Scheme 3) had been shown to be more susceptible to the incursion of ionic nucleophilic mechanisms than to the vinylic $S_{RN}1$ route.[4a] Starting with structure **3**, we progressively replaced the Ph moieties by the more electron-donating An (*p*-$MeOC_6H_4$) groups. Electrochemical measurements indicated that the reduction potentials became progressively more negative in the series (Table 2), both for the RX precursors and for their RH derivatives. Actually, we had already reported evidence of $S_{RN}1$ reactions with the pinacolone enolate ion for a monoanisyl derivative, (*E*)- or (*Z*)-An(Ph)C=C(Br)Ph,[10] and for the bis(*o*-anisyl) derivative (*o*-$MeOC_6H_4)_2$C=C(Br)Ph.[11] When we now tested the tris(*p*-anisyl) derivative **18** ($E^p = -2.14$ V), it gave 32% conversion into the pinacolyl derivative **19** under photostimulation conditions (Scheme 6).



Scheme 6

This finding showed that vinyl halides endowed with redox potentials almost as negative as (or approaching) that of an aryl halide such as **1** ($E^p = -2.4$ V in Scheme 2) could react by the $S_{RN}1$ mechanism, but this was not always the main factor and the situation might be more complex. Substrate $An_2C=CBr_2$ (**20**), with a redox potential ($E^p = -2.17$ V) similar to **18**, in fact gave different behaviour on treatment with the reference nucleophile (Scheme 7). A halophilic route,[1,12] followed by FBW rearrangement,[7] may explain the formation of AnC≡CAn (**21**), whereas an ET-induced dehalogenation followed by hydrogen abstraction (step 3′, Scheme 1) may explain the formation of $An_2C=CHBr$ (**22**).[2,10]



Scheme 7. Y = Me_3CCOCH_2

Consistently with this, the formation of **22** was suppressed in the presence of the electron scavenger *p*-dinitrobenzene, while that of **21** was not suppressed. In agreement with this explanation, the halophilic route was not in evidence with the precursor $An_2C=CCl_2$ (**23**, $E^p = -2.32$ V), Cl^+ being more difficult to abstract than Br^+,[13] whereas the ET-induced hydrodehalogenation to $An_2C=CHCl$ (**24**) was still observed, and was inhibited by addition of *p*-dinitrobenzene. Anyhow, no $S_{RN}1$ reaction occurred with the pinacolone enolate ion, perhaps because of insufficient stabilisation offered to the formation of the intermediate radical anion $RY^{\cdot-}$ by the spectator α-halogen. Finally, the photostimulated reaction of the enolate ion with the structurally comparable precursor $Ph_2C=CBr_2$ (**25**), despite its higher electron affinity ($E^p = -1.51$ V), gave only the halophilic route, followed by FBW rearrangement to give **16** (compare with Scheme 5), as well as protonation to give **15**, neither step being affected by the electron scavenger. This confirmed stronger incursion from ionic nucleophilic pathways when the redox potential of the vinyl halide was less negative than that of **3**,[4a] and also corroborated the stronger tendency of the An group (relative to Ph) to migrate in the FBW rearrangement.[7c,7d]

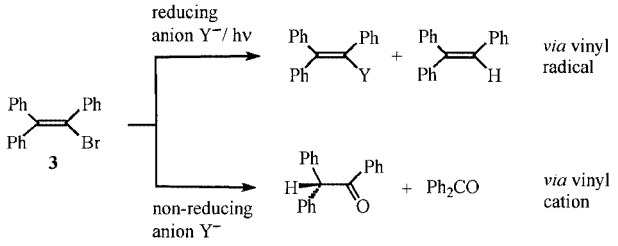
Table 2. Redox potentials of the precursors (VyX) and of their reduction products (VyH)

VyX	E^p (V vs. SCE)[a]	VyH	E^p (V vs. SCE)[a]
$Ph_2C=C(Br)Ph$ (**3**)	−1.86	$Ph_2C=C(H)Ph$ (**27**)	−2.19
An(Ph)C=C(Br)Ph	−1.92	An(Ph)C=CHPh	−2.26
An(Ph)C=C(Br)An	−2.00	An(Ph)C=CHAn	−2.37
$An_2C=C(Br)An$ (**18**)	−2.14	$An_2C=CHAn$	−2.46
$An_2C=CBr_2$ (**20**)	−2.17	$An_2C=CHBr$ (**22**)	−2.48
$An_2C=CCl_2$ (**23**)	−2.32	$An_2C=CH_2$	−2.7
$Ph_2C=CBr_2$ (**25**)	−1.51	$Ph_2C=CHBr$ (**15**)	−2.24
Ph(Me)C=CHBr (**10**)	−2.3		

[a] Values in THF at 0.5 V/s vs. SCE. The concentration of the substrate was 2 mM, while that of the supporting electrolyte, $Bu_4N^+BF_4^-$, was 0.37 M. The working electrode was a gold disc (0.5 mm diameter).

The Nature of the Nucleophile (Y^-)

The efficiency of some anions in the vinylic $S_{RN}1$ mechanism had been already investigated with the reference substrate **3** (Scheme 8).[2,11] The more reducing anions provided evidence for a photostimulated $S_{RN}1$ process in Me_2SO, consistent with their redox potentials.[14] Conversely, anions that were not reducing enabled the photoheterolysis of the vinyl C−X bond to take over, and cleavage products reasonably resulting from capture of the intermediate vinyl cation by water were obtained.[11,15]

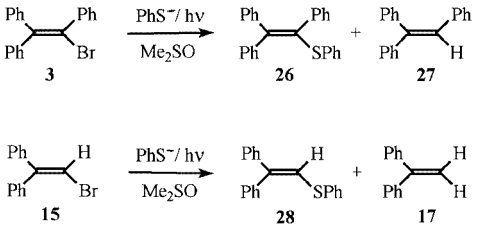


Scheme 8

This investigation was now implemented with two sulfur-centred anions, the first of which, PhS^-, is more reducing than the second, $PhCH_2S^-$ (0.1 and 0.6 V, respectively),[14,16] but less nucleophilic (pK_{HY} = 10.3 and 15.4).[6] Moreover, in view of the lower basicities of both of these thio anions relative to the enolate ion, the study could now also include **15** as a precursor.

Phenylthio Anion

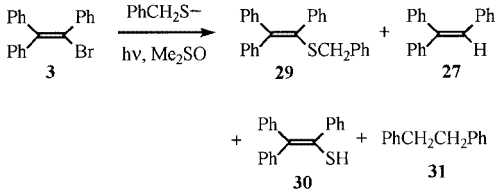
Under the usual conditions, the photostimulated reaction between PhS^- and **3** gave a 29% yield of the substitution product **26**, and 56% of the reduction product **27** (Scheme 9). In the presence of the electron scavenger, a larger percentage of **3** was recovered (53% vs. 15%) and a lower amount of **27** (17%) obtained, whereas the percentage of **26** was not substantially depressed (20%). This might indicate **27** deriving from an ET-induced hydrodehalogenation, with **26** deriving both from an ET-induced vinylic $S_{RN}1$ route and from a direct nucleophilic substitution route, not depressed by addition of *p*-dinitrobenzene. This would be consistent with the reaction between **15** and PhS^-, in which the substitution (**28**) and reduction (**17**) products were obtained, while the addition of the scavenger depressed, but did not wholly suppress, the formation of **28**. Such nucleophilic substitutions (either addition/elimination or even S_N2-like)[1,17] on unactivated vinylic substrates have precedents. It is worth emphasising that the lower basicity of PhS^- prevented the occurrence of the α-deprotonation/FBW rearrangement pathway observed with the enolate ion reaction of **15** (Scheme 5).



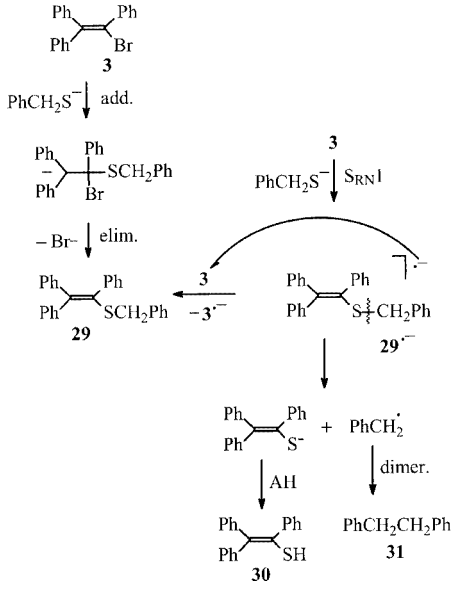
Scheme 9

α-Benzylthio Anion

The photostimulated reaction between this anion and **3** gave only modest amounts of the expected substitution (**29**) and reduction (**27**) products (Scheme 10), accompanied by an unexpected substitution product (**30**) and by 1,2-diphenylethane (**31**); 50% of unchanged **3** was recovered. The addition of the electron scavenger somewhat reduced the yield of substitution product **29** from 10 to 6%. It was conceivable that a vinylic $S_{RN}1$ route might account for a (minor) share of the conversion of **3**, while a larger share could be due to a direct nucleophilic substitution. Moreover, it is known that thio radical anions are prone to cleavage steps,[18] through which the origins of the stable[19] triphenylethenethiol **30** and of **31** could be traced (Scheme 11).

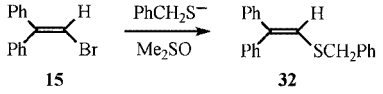


Scheme 10

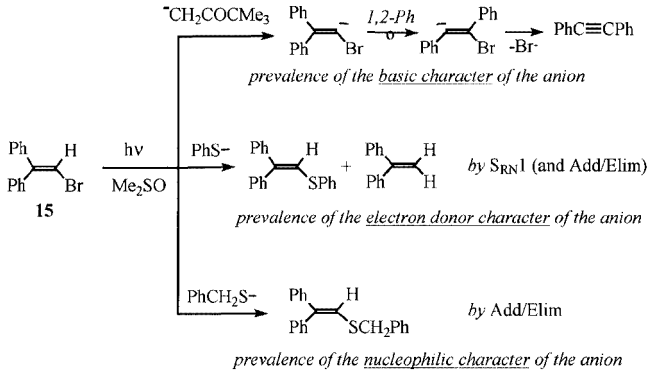


Scheme 11

Treatment of $PhCH_2S^-$ with **15** quantitatively gave the substitution product **32** without any cleavage or reduction products (Scheme 12), and with no depression of the yield on addition of electron scavenger. An ionic nucleophilic substitution, most probably an addition/elimination route,[20] therefore appeared likely. The results obtained with this precursor as a function of the nature of the anion are summarised in Scheme 13.

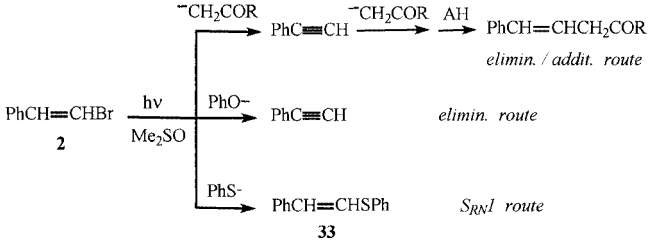


Scheme 12



Scheme 13

Finally, in view of the lower basicity of PhS^- relative to enolate ions, we attempted its reaction with **2**. The expected $S_{RN}1$ product (**33**) was indeed obtained under photostimulation conditions, in keeping with the good electron-donor character of the thio anion. Conversely, the more weakly electron-donating (E^0 = 0.25 V vs. SCE)[16] but sufficiently basic (pK_{HY} = 18)[6] PhO^- anion gave phenylacetylene (by the β-elimination route), also observed in the corresponding reaction with the enolate ion (Scheme 2). However, this elimination product did not convert further to any addition product, possibly because "hard" oxygen nucleophiles do not add efficiently to "soft" carbon centres.[21] The more strongly basic $tBuO^-$ anion behaved similarly, the results being summarised in Scheme 14.



Scheme 14

Conclusions

This study confirmed the wide spectrum of mechanisms of nucleophilic substitution available to vinyl halides. Despite this mechanistic variety, it was possible to document the unambiguous occurrence of the vinylic $S_{RN}1$ reaction in a few more instances (**19**, **26**, **28**, **29** and **33**), when an appropriate combination of substrate and nucleophile was present. It was also remarkable how the threefold nature of an anion may show at times a clear predominance variously of its nucleophile, its basic or its reducing character, depending in a delicate way on the reaction conditions, as shown in Schemes 2, 8, 13 and 14.

Experimental Section

General Remarks: Photochemical reactions were conducted in a Rayonet RPR-100 reactor equipped with a set of 16 "350-nm" lamps (Pyrex-filtered). Characterisation of the structure of the reaction products was performed 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 ppm on the δ scale, relative to residual nondeuterated solvent signals ($CDCl_3$). GC-MS and GC analyses were performed on methylsilicone (OV1) capillary columns. HRMS determinations were carried out with a Bruker Apex TM47e FTMS.[4a] Determination of the reduction potentials (E^p) of the compounds reported in Table 2 was conducted in THF (vs. SCE, at a 0.5 V/s sweep rate), as reported in a previous paper.[4a]

Materials: Commercial chemicals and compounds (*E*)-**2**, **11**, **16**, **17** and **31** (Janssen or Aldrich) were used without further purification. Benzene was dried with sodium wire, while Me_2SO was distilled from CaH_2 and stored over activated molecular sieves (4 Å). For the electrochemical measurements, THF was distilled from benzophenone radical anion.[4a] The conjugate acids of the anions were distilled prior to use; freshly sublimed *t*BuOK was used to generate the anions in Me_2SO.

Synthesis of Precursors: The following precursors were prepared according to the literature: triphenylvinyl bromide (**3**),[2b,22] tris(*p*-anisyl)vinyl bromide (**18**),[23] 1,1-bis(*p*-anisyl)-2,2-dibromoethene (**20**),[24] 1,1-bis(*p*-anisyl)-2,2-dichloroethene (**23**),[25] 1,1-dibromo-2,2-diphenylethene (**25**).[26]

(*E*,*Z*)-1-Bromo-2-phenylpropene (10): Bromination[2b,27] of commercial (Aldrich) α-methylstyrene (2.05 mL, 15.8 mmol), dissolved in CCl_4 (10 mL), with a solution of Br_2 (1 mL, 19.5 mmol) in 20 mL of CCl_4 for 18 h, followed by dehydrobromination[2b] of the dibromo derivative with KOH powder (2.68 g, 40.9 mmol) and 18-crown-6 (35 mg, 0.13 mmol) in boiling hexane (40 mL) for 36 h, gave a brown liquid, which was distilled (bp 104−108 °C at 28 Torr) to give 0.6 g (19%) of a 92:8 (*E*)/(*Z*) mixture of pure **10** as an oil: ^1H NMR: δ = 7.4−7.2 (m, 5 H, Ph), 6.45 [q, 1 H, =CH (*Z*) isomer], 6.23 [q, 1 H, =CH (*E*) isomer], 2.23 [d, 3 H, CH_3 (*Z*) isomer], 2.13 [d, 3 H, CH_3 (*E*) isomer] ppm. ^{13}C NMR: δ = 141.6 (Me*C*=), 140.3 (C^{Ph}_{ipso}C=), 128.2, 127.7 and 125.8 (C_{Ar}), 101.5 (=*C*Br), 25.0 (CH_3 *cis* to Br) ppm. HRMS: calcd. for $C_9H_9{}^{81}Br$ 197.9865; found 197.9852.

1-Bromo-2,2-diphenylethene (15): Bromination of commercial (Aldrich) 1,1-diphenylethene (**17**) (3.4 mL, 19.3 mmol), dissolved in CCl_4 (15 mL), was conducted analogously, with a solution of Br_2 (1 mL, 19.5 mmol) in CCl_4 (15 mL) for 20 h. Spontaneous dehy-

drobromination occurred during workup, and 4.2 g (85%) of the expected **15** was obtained as an oil. It was purified by distillation (bp 120−122 °C at 0.1 Torr): ^{1}H NMR: δ = 7.4−7.2 (m, 10 H, Ph), 6.76 (s, 1 H, =CH) ppm. ^{13}C NMR: δ = 146.8 (Ph_2C=), 140.7 and 139.0 (C^{Ph}_{ipso}C=), 128.2, 129.6, 128.2 and 127.1 (C_{Ar}), 105.2 (=CBr) ppm. HRMS: calcd for $C_{14}H_{11}{}^{81}Br$ 260.0021; found 260.0011.

General Procedure for Irradiation Reactions: Under a stream of argon, the substrate (0.2 mmol) was added to a solution of the parent acid of the anion (0.7 mmol) and sublimed *t*BuOK (0.8 mmol) in 5 mL of Me_2SO. The mixture was stirred at room temperature under argon, while being irradiated with 16 "350-nm" lamps. In some cases the electron scavenger *p*-dinitrobenzene was added (ca. one third of the molar amount of the substrate). After an appropriate time, typically 20−60 min, the irradiation was stopped, 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 followed. The GC yields of the products were determined by calibration of the response factors of pure samples of the compounds vs. the standard, and are averages of at least two injections (typical error: ±4%).

Synthesis of Products: Compounds **21**, **22** and 1,1-bis(*p*-anisyl)-ethene,[24] and compound **27** and phenylacetylene[2b] were available from previous studies.

Products 12, 13 and 14. a: A solution of pinacolone (220 μL; 1.96 mmol), sublimed *t*BuOK (0.91 g, 8.1 mmol) and **10** (0.27 g, 1.37 mmol) in Me_2SO (22 mL) was irradiated in the Rayonet reactor for 30 min. Workup with diethyl ether gave 0.18 g of a residue, which was chromatographed on silica gel first with petroleum ether (40−70 °C) and a second time with a 20:1 petroleum ether (40−70 °C)/$CHCl_3$ mixture to afford 20 mg of **12**. ^{1}H NMR: δ = 7.4−7.3 (m, 5 H, Ph), 5.29 and 5.08 (d, J_{gem} = 1.3 Hz, 2 H, $=CH_2$), 2.73 (m, 2 H, CH_2CO), 2.62 (m, 2 H, $=CCH_2$), 1.09 (s, 9 H, CMe_3) ppm. ^{13}C NMR: δ = 215.2 (C=O), 147.6 (Ph*C*=), 140.7 (C^{Ph}_{ipso}C=), 128.4, 127.6 and 126.1 (C_{Ar}), 112.7 (=CH_2), 44.2 (*C*Me_3), 35.5 (=C*C*H_2), 29.6 (*C*H_2CO), 26.4 (CH_3) ppm. MS: *m*/*z* = 216 [M$^+$]. HRMS: calcd. for $C_{15}H_{20}O$ 216.1509, found 216.1501. In earlier chromatographic fractions we had detected **11** and identified it by comparison with the MS data and retention time of a pure sample. Further elution of the same column gave 90 mg of **13**. ^{1}H NMR: δ = 7.4−7.2 (m, 10 H, Ph), 5.59 (d, 1 H, =CH), 5.53 and 5.29 (2 d, J_{gem} = 1.6 Hz, 2 H, =CH_2), 4.05 (m, 1 H, =CHC*H*CO), 3.05 and 2.75 (2 dd, 2 H, =CC*H*$_2$CHCO), 1.82 (br. s, 3 H, =CCH_3), 1.05 (s, 9 H, CMe_3) ppm. ^{13}C NMR: δ = 215.9 (C=O), 145.6 and 143.2 (Ph*C*=), 140.5 and 136.5 (C^{Ph}_{ipso}C=), 128.4, 128.2, 127.6 and 127.1 (C_{Ar}), 126.3 (CH=), 115.3 (=CH_2), 45.9 (=CH*C*HCO), 44.6 (*C*Me_3), 39.0 (=C*C*H_2), 26.1 (CH_3), 16.4 (*C*H_3C=) ppm. MS: *m*/*z* = 332 [M$^+$]. HRMS: calcd. for $C_{24}H_{28}O$ 332.2133; found 332.2126. **b:** Treatment of **10** (32 mg, 0.16 mmol) and sublimed *t*BuOK (30 mg, 0.27 mmol) in Me_2SO (3 mL) was run without photostimulation at room temperature for 45 min. Workup as in **(a)**, followed by chromatography with a 20:1 petroleum ether (40−70 °C)/$CHCl_3$ mixture, gave 14 mg of **14**. ^{1}H NMR: δ = 7.3−7.2 (m, 5 H, Ph), 5.29 and 5.08 (d, J_{gem} = 1.3 Hz, 2 H, =CH_2), 4.27 (m, 2 H, CH_2O), 1.26 (s, 9 H, CMe_3) ppm. MS: *m*/*z* = 190 [M$^+$]. HRMS: calcd. for $C_{13}H_{18}O$ 190.1353; found 190.1344.

Product 19: A solution of pinacolone (305 μL, 2.71 mmol), sublimed *t*BuOK (0.34 g, 3.03 mmol) and **18** (245 mg, 0.57 mmol) in Me_2SO (13 mL) was irradiated in the Rayonet reactor for 60 min. Workup with diethyl ether gave 0.34 g of a residue, which was chromatographed on silica gel initially with a petroleum ether (40−70 °C)/toluene (1:1) mixture, and then with pure toluene, to give 67 mg of pure **19** (26%) as a solid, m.p. 128−130 °C: ^{1}H NMR: δ = 7.0−6.6 (m, 12 H, Ph), 3.65 (s, 9 H, CH_3O), 3.55 (s, 2 H, CH_2CO), 0.97 (s, 9 H, CMe_3) ppm. ^{13}C NMR: δ = 214.2 (C=O), 137.1, 133.2, 132.3, 128.4, 127.2, 126.6, 125.1 and 123.4 (C_{Ar}), 45.3 (*C*Me_3), 40.4 (CH_3O), 36.3 (*C*H_2CO), 26.6 (CH_3) ppm. MS: *m*/*z* = 444 [M$^+$]. HRMS: calcd. for $C_{29}H_{32}O_4$ 444.2292; found 444.2267.

Product 26: A solution of PhSH (290 μL, 2.8 mmol), sublimed *t*BuOK (0.32 g, 2.8 mmol) and **3** (114 mg, 0.34 mmol) in Me_2SO (30 mL) was irradiated in the Rayonet reactor for 60 min. Workup with diethyl ether gave 78 mg of a residue, which was chromatographed on silica gel with a petroleum ether (40−70 °C)/$CHCl_3$ (5:1) mixture to give 38 mg of **26** (31%) as an oil. ^{1}H NMR: δ = 7.3−7.0 (m, 20 H, Ph) ppm. ^{13}C NMR: δ = 146.5, 143.8, 142.4, 139.1, 135.7, 134.2, 131.6, 129.8, 128.4, 127.2, 126.2, 125.3 ppm. MS: *m*/*z* = 364 [M$^+$]. HRMS: calcd. for $C_{26}H_{20}{}^{32}S$ 364.1281; found 364.1268.

Product 28: A solution of PhSH (795 μL, 7.7 mmol), sublimed *t*BuOK (0.88 g, 7.8 mmol) and **15** (229 mg, 0.88 mmol) in Me_2SO (30 mL) was irradiated in the Rayonet reactor for 80 min. Workup with diethyl ether gave 260 mg of a residue, which was chromatographed on silica gel, initially with petroleum ether (40−70 °C) and then with a petroleum ether (40−70 °C)/$CHCl_3$ (4:1) mixture, to give 145 mg of **28** (57%) as an oil: ^{1}H NMR: δ = 7.5−7.2 (m, 15 H, Ph), 6.85 (s, 1 H, =CH) ppm. ^{13}C NMR: δ = 142.7, 141.2, 139.4, 136.7, 131.6, 129.9, 128.6, 127.4, 124.6 ppm. MS: *m*/*z* = 288 [M$^+$]. HRMS: calcd. for $C_{20}H_{16}{}^{32}S$ 288.0969; found 288.0954. In earlier chromatographic fractions we had detected **17** and identified it by comparison with MS data and retention time of a pure sample.

Product 29: A solution of $PhCH_2SH$ (360 μL, 3.0 mmol), sublimed *t*BuOK (0.47 g, 4.2 mmol) and **15** (319 mg, 1.9 mmol) in Me_2SO (30 mL) was irradiated in the Rayonet reactor for 80 min. Workup with diethyl ether gave 390 mg of a residue, which was chromatographed on silica gel, initially with petroleum ether (40−70 °C) and then with a petroleum ether (40−70 °C)/$CHCl_3$ (4:1) mixture, to give 44 mg of **29** (12%) (*m*/*z* = 378 [M$^+$]) as an oil; it was partially contaminated with **30** (*m*/*z* = 288 [M$^+$]) that was eluted from the column subsequently. Both compounds were identified by their MS data. In earlier chromatographic fractions we had detected **27** and **31**, and identified them by comparison with MS data and retention time of pure samples.

Product 32: A solution of $PhCH_2SH$ (1.2 mL, 10.2 mmol), sublimed *t*BuOK (1.66 g, 14.8 mmol) and **15** (300 μL, 1.9 mmol) in Me_2SO (22 mL) was irradiated in the Rayonet reactor for 90 min. Workup with diethyl ether gave 770 mg of a residue, which was chromatographed on silica gel with petroleum ether (40−70 °C) to give 200 mg of **32** (35%) as an oil. ^{1}H NMR: δ = 7.3−7.0 (m, 15 H, Ph), 6.48 (s, 1 H, =CH), 3.83 (s, 2 H, CH_2S) ppm. ^{13}C NMR: δ = 142.5, 140.6, 139.2, 138.4, 130.6, 129.5, 128.4, 127.1, 125.4, 39.4 ppm. MS: *m*/*z* = 302 [M$^+$]. HRMS: calcd. for $C_{21}H_{18}{}^{32}S$ 302.1125; found 302.1116. Treatment of **15** (23 mg, 89 μmol) with Bu_3SnH (29 mL, 0.11 mmol) and AIBN (5 mg, 30 μmol) in Me_2SO (3 mL) at 60 °C for 3.5 h gave only 1,1-diphenylethene (**17**), by H abstraction from the intermediate 2,2-diphenylvinyl radical, and no traces of diphenylacetylene (**16**). Treatment of **15** (31 mg, 0.12 mmol) with sublimed *t*BuOK (32 mg, 0.29 mmol) in Me_2SO (3 mL), in the presence of cyclopentene (40 μL, 0.45 mmol) as a carbene scavenger, at room temperature for 40 min, followed by conventional workup with diethyl ether, gave evidence (GC-MS) of

the formation of diphenylacetylene (**16**), with residual **15**, but no other product that could reasonably derive from the addition of an intermediate carbene onto the olefin was detected. The reaction was repeated in neat cyclohexene (2 mL) as the solvent, with **15** (18 mg, 69 μmol) and *t*BuOK (11 mg, 98 μmol), in the presence of benzyltriethylammonium chloride (2 mg) as a phase-transfer agent, but no addition product of the postulated carbene could be detected.

Product 33: A solution of PhSH (0.75 mL, 7.3 mmol), sublimed *t*BuOK (1.04 g, 9.3 mmol) and (*E*)-**2** (160 μL, 1.2 mmol) in Me_2SO (20 mL) was irradiated in the Rayonet reactor for 30 min. Workup with diethyl ether gave 800 mg of a residue, which was chromatographed first on silica gel with toluene and a second time with hexane, to give 36 mg of **33** (14%) as an (*E*)/(*Z*) (4:1 by NMR) mixture: ^{1}H NMR: δ = 7.5−7.2 (m, 10 H, Ph), 6.95 and 6.80 [dd, *J* = 15.4 Hz, 2 H, CH=CH (*E*) isomer], 6.65 and 6.55 [dd, *J* = 10.7 Hz, 2 H, CH=CH (*Z*) isomer] ppm. ^{13}C NMR: δ = 136.6, 135.1, 132.3, 130.2, 129.4, 128.2, 127.3, 124.5 ppm. MS: *m*/*z* = 212 [M^+]. HRMS: calcd. for $C_{14}H_{12}{}^{32}S$ 212.0657; found 212.0638. This substitution reaction was inhibited by *p*-dinitrobenzene. Under strictly comparable conditions, treatment of **2** with PhO^- (or $tBuO^-$) gave only phenylacetylene (plus unchanged **2**).

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