A New Insight into the $S_{RN}1$ Vinylic Substitution

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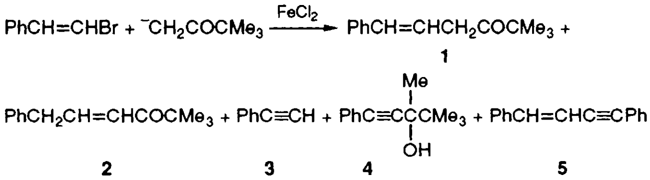
Evidence is gathered on vinylic nucleophilic substitutions that suggests the occurrence of an ionic elimination–addition route along with the originally proposed $S_{RN}1$ route.

A 1976 paper[1] reported that unactivated vinyl halides, in analogy to the aryl halides,[2] react with nucleophiles by the $S_{RN}1$ route under stimulation by photons or electrons. As an example, β-bromostyrene reacted in liquid NH_3 with the enolate ion from acetone, $^-CH_2COMe$, under photostimulation, giving mainly the direct substitution product, $PhCH{=}CHCH_2COMe$, together with its tautomer $PhCH_2CH{=}CHCOMe$.[1]

We wanted to check if the already described[3] stimulation procedure of the aromatic $S_{RN}1$ reaction by iron(II) ions was also able to induce a vinylic nucleophilic substitution; we chose β-bromostyrene as the substrate, in reaction with the

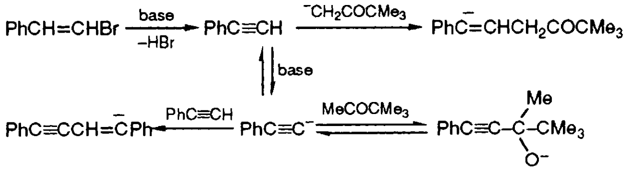


Scheme 1 *Yields* (%) (*a*) after 10 min: **1** 21, **2** 7, **3** 27, **4** 42; (*b*) after 3 h: **1** 45, **2** 14, **3** 18, **4** 9

enolate ion from pinacolone, $^{-}CH_2COCMe_3$, with $FeCl_2$ as the catalyst in Me_2SO. The products obtained are given in Scheme 1: their peculiarity has partially set aside our original interest towards the initiation technique, in favour of a reinterpretation of the mechanistic picture.

Sampling the reacting mixture after 10 min revealed that β-bromostyrene had disappeared, the tertiary alcohol **4** being the major component of the mixture; after 3 h, however, the yield of alcohol had decreased, while the yield of the two isomeric substitution products **1** and **2** had risen. β-Chlorostyrene behaved in the same way. A similar picture was obtained also in NH_3 under photostimulation. It is to be stressed that **4** and the direct substitution product **1** are structural isomers and have very similar GC retention times, even on a capillary column. It is possible that the early investigators[1] failed to recognize **4** because they had not sampled the reaction at early stages but only after 5 h and, what is more, used a packed GC column with a consequent lower resolution capacity.

We found that the presence of the electron scavenger $4\text{-}NO_2\text{-}C_6H_4NO_2$ severely reduced (but not suppressed) the amount of the two substitution products, while **4** remained largely unaffected. On the basis of this evidence, we suspect the occurrence of an ionic β-elimination–addition mechanism of substitution (Scheme 2) along with the $S_{RN}1$ route. The formation of **4** would readily occur from the addition of the conjugate base of the elimination product PhC≡CH, a key intermediate, to the ketone carbonyl; this addition step is likely to be reversible and, gradually, will allow the build up of the substitution products by addition of the enolate ion to PhC≡CH, in a route which is an alternative to the $S_{RN}1$ route and is unaffected by the electron-scavenger.



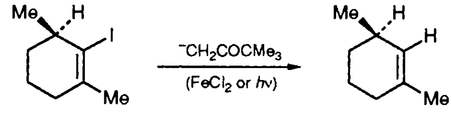
Scheme 2

The relevance of a β-elimination–addition route is supported by a 'blank' reaction on PhC≡CH (Scheme 3): a product distribution comparable with that obtained from β-bromostyrene was found.

$$\mathrm{PhC{\equiv}CH} \xrightarrow{^{-}\mathrm{CH_2COCMe_3}} \mathbf{1}+\mathbf{2}+\mathbf{4}+\mathbf{5}$$

Scheme 3 Yields (%) (*a*) after 10 min: **1** 5, **2** 2, **4** 63; (*b*) after 3 h: **1** 52, **2** 8, **4** 8

We sought to suppress the elimination–addition pathway by using **6** as the vinylic substrate, which is structurally unable to react by a β-elimination route. Strangely enough, no substitution product was obtained from it with $^{-}CH_2COCMe_3$, but only hydrodeiodination occurred and, once more, this was irrespective of the initiation technique ($FeCl_2$ or *h*ν). This seems to contrast with a former indication[1] of an $S_{RN}1$ nucleophilic substitution taking place on 1-iodocyclopentene by $^{-}CH_2COMe$, and suggests that the vinylic $S_{RN}1$ route is perhaps more complex than the early investigators[1] suspected.



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