

Alkynylic S_{RN}1 Reaction: Feasible or Not?

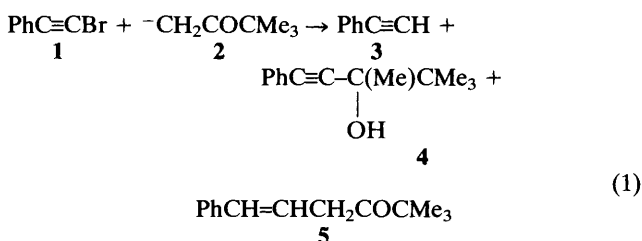
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A comparison of the relative propensity of aryl-, vinyl-, and ethynyl-halides towards a S_{RN}1 reaction is made possible by an investigation of some nucleophilic reactions with bromophenylethyne.

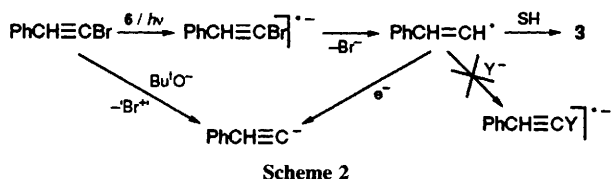
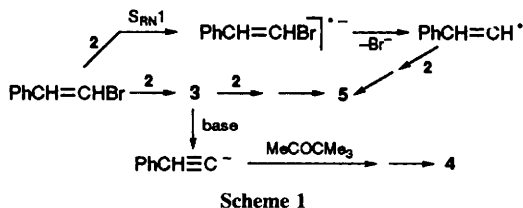
Our recent quest for a S_{RN}1-like nucleophilic reaction of vinyl halides¹ has prompted an extension of the study to the less investigated ethynyl halides. The reduction potentials of the ethynyl halides favour the S_{RN}1 pathway, as can be seen from the series PhBr, -2.9; PhCH=CHBr, -2.27; PhC≡CBr, -2.11 V (vs. SCE);² this suggests a relatively easy reduction of bromophenylethyne **1** in the S_{RN}1 initiation step.

To check this expectation, **1** was synthesised³ and treated with a threefold excess of the enolate ion of pinacolone **2** in Me₂SO under either photostimulation or iron(II) ion catalysis.⁴ In both cases, and after a short reaction time (10 min) at room temp., **1** disappeared to yield PhC≡CH (**3**, 60–80%), along with smaller amounts of **4** (10–20%) and **5** (6–10%) [eqn. (1)].



In the analogous reaction with **2**, β-bromostyrene has already been reported to give **3** by an α,β-elimination (Scheme 1);¹ subsequent addition of the conjugate base of phenylacetylene to the ketone and protonation gives **4**, while addition of **2** to **3** and protonation affords **5**. However, the latter compound is also formed by the competing S_{RN}1 reaction.¹

It is therefore conceivable that, following formation of **3** from **1** [eqn. (1)], partial conversion of it into **4** and **5** can occur, according to Scheme 1. Analogous reactions [see eqn. (1)] of **1** with either (EtO)₂PO⁻ or PhCOCH₂⁻ **6** as nucleophiles under iron(II) catalysis or photostimulation gave instead only **3**, in quantitative yield.



A better appreciation of the origin of **3** comes from other reactions carried out on **1** with **6**, instead of **2**. Partial incorporation (15%) of deuterium in **3** occurred when the reaction was conducted in (CD₃)₂SO while a moderate increase (30%) of incorporation was obtained in the presence of small amounts of a radical scavenger. It appears therefore that photostimulated or iron(II) induced ET from the nucleophile Y⁻ to **1** (a step inhibited by the scavenger) does occur to produce **1**^{-•}, which fragments to PhC≡C^{-•}; abstraction of hydrogen (or deuterium) from the solvent leads to **3** in a ECC process. However, interception and reduction of PhC≡C^{-•} by further ET may afford PhC≡C^{-•}, which protonates to **3** in a ECEC process. In addition, a blank reaction with Bu⁻O⁻ alone, which is the base used in slight excess to generate the anions (Y⁻), shows that **1** can suffer efficient Br⁺-abstraction to produce PhC≡C^{-•}, which protonates to give **3** (ca. 75% in 10 min); this ionic pathway, which is unaffected by the electron-scavenger, is not available to the enolate ion, or at least not with comparable efficiency (Scheme 2).

In no cases was the S_{RN}1 substitution product (*i.e.* PhC≡CY) observed from **1**. This finding is in sharp contrast to the fact that an aryl halide such as PhBr gives only S_{RN}1 substitution and no reduction of the halogen.⁵ Consistently, also vinyl halides other than β-bromostyrene, *i.e.* structurally unable to any competing α,β-elimination and ensuing pathways thereafter (Scheme 1), did give unambiguous S_{RN}1 substitution as the major pathway, accompanied by minor amounts of hydrodehalogenation.^{1b} In comparison to this behaviour of the aryl and vinyl halides, the X⁺-abstraction step by the base, as also the 'two-electron' reduction occurring with the ethynyl halide, both processes affording the carbanion PhC≡C^{-•}, can reflect the relative stability (pK_a) of the conjugate base of the parent hydrocarbons Ph⁻ and PhCH=CH⁻ (*ca.* 42–44),⁶ PhC≡C^{-•} (28.7).⁷

In conclusion, the initial ET-induced dehalogenation of **1** is followed by further reduction of the alkynylic radical intermediate to PhC≡C^{-•}, the latter deriving also from a competing X⁺-removal step due to the slight excess of the base (Bu⁻O⁻).

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