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# Cyclisation of Stilbenes to Phenanthrenes by Flash Vacuum Pyrolysis

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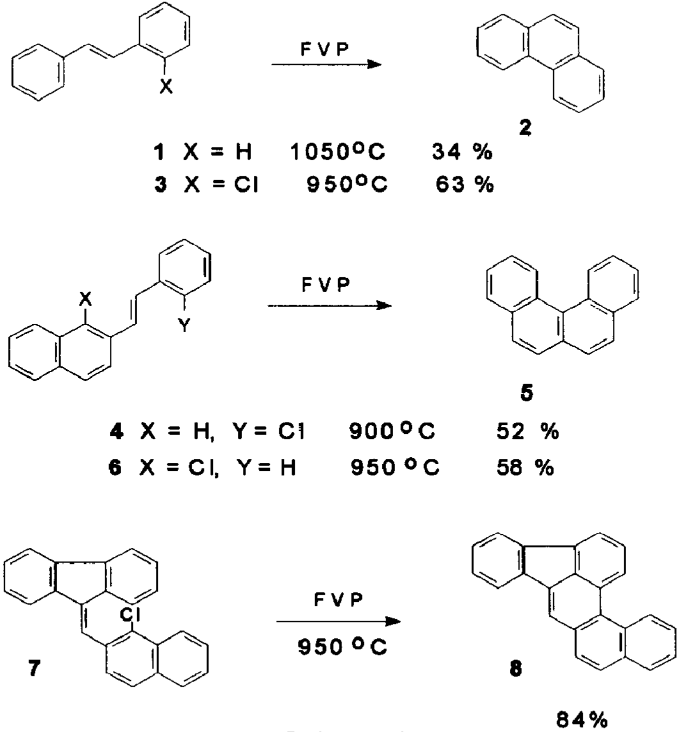
***Abstract:*** Flash Vacuum Pyrolysis of the stilbene derivatives **3**, **4**, **6** and **7** gives the corresponding phenanthrenes in reasonable yields.

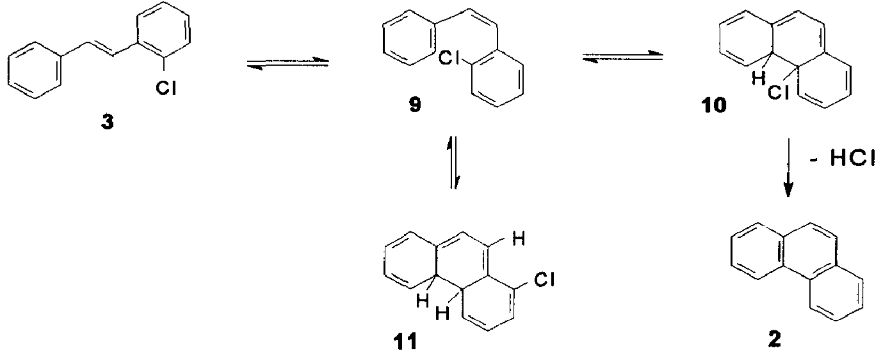
The oxidative photochemical cyclisation of stilbenes to form phenanthrenes is an important methodology used to prepare helicenes and other polycyclic aromatic hydrocarbons (PAH).[1] The reactions are typically performed on a small scale at high dilution ($10^{-3}$-$10^{-4}$ M) to prevent [2 + 2]stilbene dimerisations. In the course of our work on the synthesis of fullerene sub-structures we have shown that this preparative reaction can be accomplished by Flash Vacuum Pyrolysis (FVP)[2] which conveniently avoids the use of large volumes of solvent. Diarylethylenes are thermally stable and are easily vapourised. The parent compound trans stilbene **1** was converted to phenanthrene **2** by FVP through an unpacked quartz tube at 1050°C in 34% yield (Scheme 1).[3] However FVP of 1-chlorostilbene **3** at 950°C gave phenanthrene **2** in 63% yield.[4]



Scheme 1

The pyrolysis reactions of chlorinated precursors[5] go to completion at lower temperatures to give higher yields of products and cleaner reactions. FVP of precursors **4** and **6** gave benzo[c]phenanthrene **5** as the major product, as opposed to benz[a]anthracene, so this reaction shows the same major selectivity as the oxidative photochemical cyclisation.[1] The conversion of fluoranthene derivative **7** to compound **8** is useful because this reaction does not proceed photochemically owing to the strain of the five membered ring.

The pyrolysis mechanism probably involves a gas phase electrocyclisation followed by a rapid loss of hydrogen chloride (Scheme 2) During the pyrolysis stilbenes will rotate rapidly around the central double bond and undergo cis-trans isomerisation.[6] The formation of dihydro intermediate **11** may be disfavoured because of the steric compression between the chlorine and peri hydrogen shown. This mechanism is analogous to the solution photochemistry of halogenated stilbenes which undergo eliminative photochemical cyclisations in an alcoholic solvent in the absence of an oxidant.[7] We are currently exploring the scope of FVP to prepare larger helicenes and other twisted PAH's some of which cannot be formed by conventional photochemistry. The yields and precise threshold temperatures needed to drive the reactions to completion have not been optimised.



Scheme 2

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