

Homo-elimination of HF—An Efficient Approach for Intramolecular Aryl–Aryl Coupling

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The discovery of fullerenes has given rise to appreciable interest in the field of synthesis of non-planar “aromatic” structures, especially in the context of the direct synthesis of fullerenes.^[1–7] The strategy generally followed starts with the synthesis of a planar polycyclic aromatic hydrocarbon (PAH) that already contains the carbon framework required for the formation of the target molecule. Such “unrolled” molecules can be “rolled up” to form fullerenes under flash vacuum pyrolysis (FVP) conditions.^[8–12] The high temperatures applied at FVP result in intramolecular condensation of the precursor and provide the energy necessary to build up the strained fullerene molecule. The presence of halogen atoms, such as chlorine or bromine, in the initial precursor has been found to be essential for effective radical generation, which is the driving force for further aryl–aryl coupling. Although this approach has proven to be quite prolific for the synthesis of many small non-planar PAHs,^[1–5] selective and high yielding direct synthesis of fullerenes still remains a challenge for organic chemistry. The principal possibility of selective fullerene cage formation through FVP has been demonstrated by the examples of C₆₀,^[1–5] C₇₈^[6] and C₈₄.^[7] However, the rates of conversion to the target molecules have remained disappointingly low. C₆₀ has been obtained with 0.1–1 % yield,^[3–5] whereas higher fullerenes were only detected by mass spectrometry.^[6,7] The low yields in converting precursors to the respective fullerene result from a lack of efficient promoters of intramolecular condensation. The frequently employed bromine or chlorine functionalisations reach their limits in the case of large molecules due to decomposition of such halogenated precursors during sublimation. The molar masses will generally be high, since the large number of new C–C bonds that need to be formed in

the fullerene precursor necessitates the introduction of a considerable number of promoter groups. Moreover, the radical nature of the condensation significantly affects the selectivity of the process.

In the search for more efficient promoters of ring closure we have turned our attention to the possibility of using fluorine for this purpose. Recently, we reported on the efficient intramolecular ring closure in fluorinated benzo[*c*]phenanthrenes by HF elimination.^[13] Herein, we present experimental and computational evidence that HF elimination is a synchronous process leading directly to the target molecule without any intermediates, and therefore, producing no side products. We confirm that HF elimination is a homo-elimination process. The data obtained provide new prospects for rational fullerene synthesis by using fluorine as an activating group, which seems to possess all the required properties of an “ideal” promoter of ring closure.

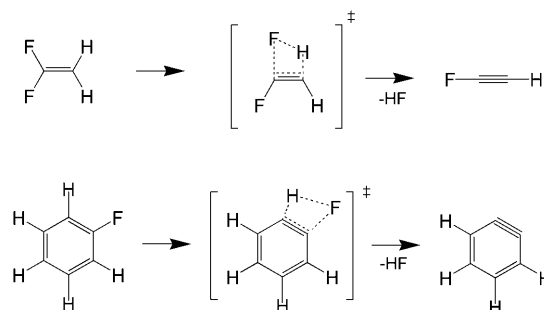
To systematically study the effect of fluorine functionalisation on the selectivity of thermally activated aryl–aryl coupling, we have synthesised 1-fluorobenzo[*c*]phenanthrene (**1**) and 2-fluorobenzo[*c*]phenanthrene (**2**), and have subjected them to FVP. The products obtained give clear evidence for selective 1,5 ring closure in the case of **1**.^[13] Such fluorine activity in intramolecular condensation is unexpected, since the C–F bond is considered to be one of the most stable bonds in organic chemistry.^[14] In contrast to other halogens, the high stability of the C–F bond makes it impossible to produce a radical by homolytic bond cleavage. The mechanism of the fluorine activation observed in this study is obviously different and includes synchronous HF elimination.

HF elimination is a well known decomposition process in the photolysis of fluoroethylenes.^[15–20] Although the photofragmentation would be expected to proceed from an excited electronic state, it has been shown that dissociation most likely occurs through the ground state.^[15,20] This is supported by the fact that thermal fragmentation of fluoroethylenes shows a similar result, and the main decomposition process is the unimolecular 1,2-HF elimination.^[21] Theoretical studies have revealed that 1,2-HF elimination is the main decomposition channel, which passes through a four- or three-

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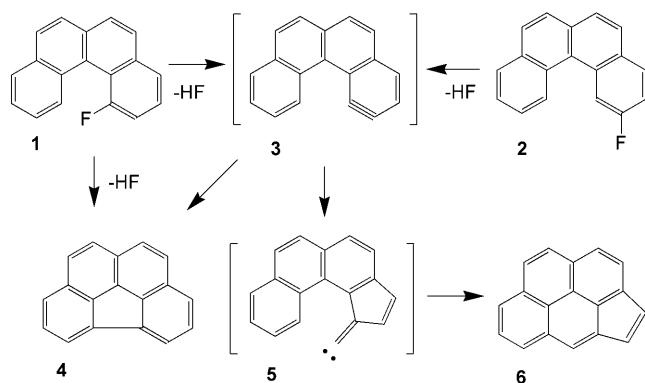
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centred transition state. The activation barrier for HF elimination in fluoroethylenes has been calculated to be as low as 74 kcal mol^{-1} .^[22] A similar elimination process has been identified as the main channel of fluorobenzene decomposition. The activation barrier in the latter case is higher and amounts to 92 kcal mol^{-1} (Scheme 1).^[23]



Scheme 1. 1,2-HF elimination through a four-centred transition state—the main channel of difluoroethene and fluorobenzene decomposition.

Considering the pyrolysis of **1** and **2**, the formation of benzyne **3** as an intermediate through 1,2-HF elimination appears to be most probable (Scheme 2). The highly reac-

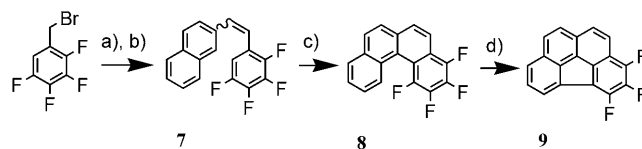


Scheme 2. Decomposition of 1- and 2-fluorobenzo[c]phenanthrenes under FVP conditions through HF elimination.

tive intermediate **3** could relax by ring closure and result in the target benzo[ghi]fluoranthene (**4**). According to this mechanism both **1** and **2** should provide comparable activity in intramolecular condensation. The FVP experiments show however, that **1** is remarkably more active than **2**. For instance, the pyrolysis at 1000°C results in 15% of **4** in the case of **1**, whereas pyrolysis of **2** at the same conditions gave only 1% of the product. Moreover, pyrolysis of **2** preferably results in the formation of cyclopenta[cd]pyrene (**6**), whereas **1** almost exclusively leads to the desired **4**. Such a large difference in the reactivity of **1** and **2** indicates that **3** is not a relevant intermediate in the condensation path from **1** to **4**. The effective cyclisation of **1** can only be understood as a 1,5 elimination of HF from the fjord region of the 1-fluoro-

benzo[c]phenanthrene molecule, which leads directly to the target molecule without any intermediates. This process is supposed to be energetically more favourable than the competing 1,2 elimination.

To corroborate the presented hypothesis, and to prove the principal possibility of 1,5-HF elimination experimentally, 1,2,3,4-tetrafluorobenzo[c]phenanthrene (**8**) has been synthesised and subjected to FVP under the same conditions. The synthetic route to compound **8** is summarised in Scheme 3. None of the fluorine atoms in **8** has immediate



Scheme 3. The synthetic route to 1,2,3,4-tetrafluorobenzo[c]phenanthrene **8** and its condensation to trifluorobenzo[ghi]fluoranthene **9**. a) PPh_3 , toluene, 97% b) 2-naphthaldehyde, KOtBu , EtOH , 87% c) $h\nu$, I_2 , propylene oxide, cyclohexane, 43% d) FVP, 1100°C , 60%.

hydrogen neighbours, and therefore **8** is not able to eliminate HF through conventional 1,2 elimination. Thus, the formation of benzo[ghi]fluoranthene would unambiguously confirm that direct 1,5-HF elimination had occurred. Indeed, FVP of **8** at 900°C resulted in highly selective benzo[c]phenanthrene formation. In particular, no cyclopenta[cd]pyrene derivatives were found in the pyrolysis products, additionally confirming the proposed mechanism. Since all other channels of HF elimination are blocked in **8**, increasing the pyrolysis temperature up to 1100°C does not affect the selectivity substantially. This has made it possible to achieve a remarkably selective and efficient condensation of **8** to **9** under FVP conditions with up to 60% yield. Almost no side products were detected in the pyrolysis product (see the Supporting Information). This means that unreacted **8** can be recovered, and in principle condensed to the target product with close to quantitative yield by repeated FVP.

Quantum chemical calculations show that 1,5 elimination in the 1-fluorobenzo[c]phenanthrene molecule is possible through the four-centred transition state. The transition state and its optimum geometrical parameters are presented in Figure 1. The activation energy for this process was found to be only $80.2 \text{ kcal mol}^{-1}$. The 1,5-HF elimination is, thus, substantially favoured over the 1,2 elimination (92 kcal mol^{-1}), which is in excellent agreement with our experimental data.

Interestingly, none of the carbon atoms involved changes its hybridisation during the reaction, which is atypical for an elimination process. The formal increase in unsaturation, a necessary prerequisite of any elimination process, is realised through the formation of a new ring in the system. The π system of benzo[c]phenanthrene is not involved in the condensation process and the elimination process can thus be considered as a four-centred homo-elimination. To estimate

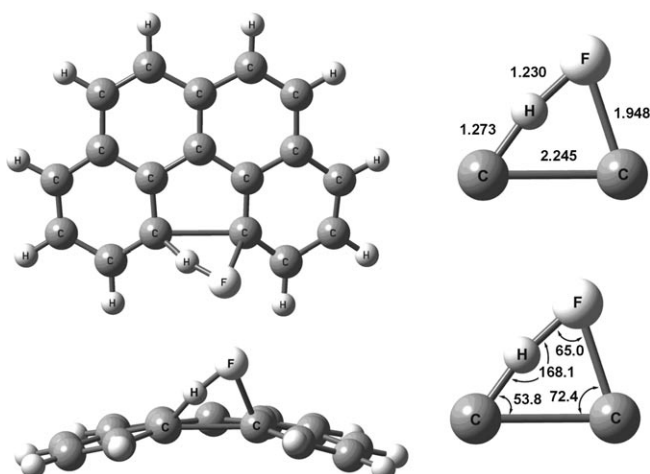


Figure 1. Transition-state geometry for HF homo-elimination predicted with the DFT B3LYP/6-311G(d,p) method. On the right, only those bonds broken or formed during the reaction are shown. Bond lengths are given in Å, angles in degrees. The geometry of the benzo[c]phenanthrene moiety in the transition state is characterised by sufficient deviation from planarity. The four-centred transition state is highly distorted from square geometry, and the H atom is placed virtually on the C–F axis.

the influence of the π system on the condensation process, the model reaction between benzene and fluorobenzene to form biphenyl has been investigated theoretically. Indeed, a low energetic path to biphenyl with a similarly low activation energy barrier of $84.2 \text{ kcal mol}^{-1}$ was also found for this system. This confirms our conclusion that HF elimination in the system considered is actually a homo reaction. Ordinarily, such a process cannot possibly occur due to entropy reasons, but it becomes viable in the case of benzo[c]phenanthrene, in which the benzene rings are already oriented in an appropriate way in space. In other words, $\text{C}_{\text{sp}^2}\text{--H}$ and $\text{C}_{\text{sp}^2}\text{--F}$ groups can interact directly through space, whereas the rest of the molecule is not involved in the process, but is just interconnecting the reacting atoms. This interaction finally results in formation of a new $\text{C}_{\text{sp}^2}\text{--C}_{\text{sp}^2}$ bond and elimination of HF.

The geometries of the transition states for benzene–fluorobenzene condensation and for the cyclisation in **1** were found to be similar, except for a higher deviation from planarity in the case of the biphenyl system. The angular orientation of benzene rings with a 113° angle was found to be optimal for homo HF elimination (see the Supporting Information). Such an orientation of benzene rings in benzo[c]phenanthrene requires partial perturbation of the aromatic system, but according to our calculations the deviation from planarity does not contribute significantly to the energy. As an important consequence, the cyclisation occurs through a transition state with an already curved π system, which is required for geodesic PAHs and fullerenes. Regarding the condensation of fullerene precursors in which the “benzene rings” are already oriented in an appropriate angular manner, such a bent geometry seems to be suitable for condensation and the activation barrier for HF elimination is expected to be low.

In summary, the HF homo-elimination has proven to be an efficient approach for intramolecular aryl–aryl coupling, for example, in closing five membered rings in PAHs. The through-space fluorine activation mechanism has been identified experimentally and confirmed by quantum chemical calculations. The activation energies found are qualitatively in good accordance with FVP experimental data. Taking into consideration that fluorine can promote the desired ring closure only if hydrogen is placed in a neighbouring position in space in the precursor structure, it seems to be possible to fully control the direction of the condensation. According to our results highly efficient intramolecular condensations of appropriately functionalised PAH to non-planar PAHs by homo-HF elimination can be achieved. Use of fluorine as an activating group solves the problem of selectivity in FVP and should provide an effective conversion of the respective planar PAH precursors to the desired fullerene cage.

Experimental Section

The synthesis of 1- and 2-fluorobenzo[c]phenanthrenes and FVP details were reported elsewhere.^[13] The full synthesis routes for new compounds **7**, **8** and **9** are given in the Supporting Information. DFT was employed to characterise the ground electronic potential energy surface for the HF elimination reactions. The DFT calculations were carried out with the B3LYP hybrid functional and the 6-311G(d,p) standard basis set,^[26] which previously had been applied successfully for the investigation of HF elimination in fluorobenzene.^[23] Frequency calculations were then performed to characterise stationary points as minima or saddle points and to evaluate zero point vibrational energies. The transition states were found by following the minimum energy path from the reactant to the expected product. The activation energies are given including zero point energy corrections. All the calculations were carried out by using the GAUSSIAN 03 program package.^[27]

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