DOI: 10.1002/ejoc.200900976

Highly Efficient Fluorine-Promoted Intramolecular Condensation of Benzo[*c*]phenanthrene: A New Prospective on Direct Fullerene Synthesis

Konstantin Yu. Amsharov,*[a] Mikhail A. Kabdulov,[a] and Martin Jansen[a]

Keywords: Flash pyrolysis / Cyclization / C-C coupling / Reaction mechanisms / Fullerenes

Various functional groups have been tested as alternative promoters of the intramolecular condensation of benzo[*c*]phenanthrene under flash vacuum pyrolysis conditions. Methyl and fluorine functionalization were found to be promising approaches. Unexpectedly high selectivity was observed in the cyclization of fluorinated benzo[*c*]phenanthrenes. The mechanism for the condensation reaction and the advantages of fluorine as a promoter for the rational synthesis of fullerenes are discussed.

Introduction

The discovery of fullerenes has led to appreciable interest in the synthesis of non-planar "aromatic" structures that can be regarded as fullerene fragments. Such geodesic polyarenes can be obtained by intramolecular C_{Aryl}–C_{Aryl} condensation of polycyclic aromatic hydrocarbons (PAHs), with all the carbon atoms in the required location, under flash vacuum pyrolysis (FVP) conditions.[1–5] The presence of a halogen atom in the initial precursor has been found to be essential for effective radical generation, which is the driving force for further cyclization. The same non-halogenated PAH analogues usually do not undergo intramolecular cyclization or give only trace amounts of the target products. Chlorine and bromine have been shown to be effective radical promoters for ring-closure.[1–5] This methodology was successfully employed by Scott et al. in the first rational C_{60} fullerene synthesis. Pyrolysis of the PAH precursor, containing all 60 carbon atoms at the programmed positions needed for fullerene formation and three chlorine atoms, gave C_{60} fullerene with a yield of about 0.1–1 %.[6] Despite the relatively low degree of conversion, the high selectivity makes this approach, in principle, promising for the synthesis of higher fullerenes including those that do not form under uncontrollable graphite vaporization. Recently we reported the synthesis of two PAH precursors of the higher fullerenes C_{78}:4 and C_{84}:20 and demonstrated their selective conversion to the designed fullerene cages under FVP conditions.[7,8] The yield in both cases was low due to the lack of effective radical promoters. Unfortunately, the introduction of chlorine and/or bromine atoms (the best known promoters) into the large molecules causes serious difficulties during synthesis, separation and purification. Although such complications can be partially overcome,[9] FVP of the resulting halogenated large molecules is hampered because the increase in molecular weight significantly increases the vaporization temperature of the precursor, causing its considerable decomposition during sublimation. Moreover, in the FVP experiment the reactive chlorine radicals formed can attack the target molecule and cause various side-reactions, which can completely nullify the yield of the target molecule.[10] The availability of alternative radical precursors that do not have these disadvantages seems to be a key prerequisite for successful direct fullerene synthesis. Herein we present the investigation of such alternative promoters for intramolecular condensation. Fluorine was found to be an excellent candidate for an efficient intramolecular condensation and seems to possess all the required properties of an "ideal promoter".

Results and Discussion

The conversion of benzo[*c*]phenanthrene (**5**) to benzo[*ghi*]fluoranthene (**6**) was chosen as a model reaction to investigate the new radical promoters. Benzo[*c*]phenanthrene is the smallest molecule bearing the so-called fjord region in which the new bond should be established. Moreover, the efficiency of chlorine and bromine demonstrated previously with benzo[*c*]phenanthrene systems have been proven transferable to the synthesis of various buckybowl structures.[11] Earlier studies have shown that the best position for activation is one of the carbon atoms at which the new bond should be established. In the system under consideration, these carbon atoms always belong to the fjord region. According to the condensation mechanism proposed, the radical formed attacks the adjacent carbon atom with the for-

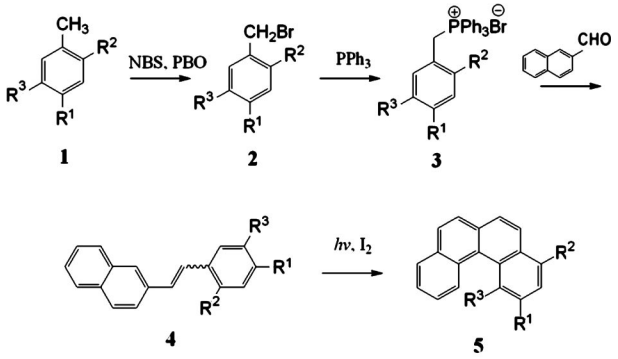
[a] Max Planck Institute for Solid-State Research,
Heisenbergstrasse 1, 70569, Stuttgart, Germany
Fax: +49-711-6891502
E-mail: k.amsharov@fkf.mpg.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.200900976.

mation of the required bond. Alternatively, the promoter can be introduced into one of the neighbouring positions. After homolytic cleavage of the corresponding C–R bond a 1,2-hydrogen shift takes place, which leads to the displacement of the radical position.[12] Although such activation is less effective, it often helps to avoid synthetic difficulties associated with the introduction of the promoter group into the sterically hampered region.

Considering the synthetic routes to fullerene-related PAHs, two approaches have been proven to be prolific. The first is based on the aldol trimerization of cyclic ketones. Although this reaction was discovered more than 100 years ago, it only recently became a powerful method for the synthesis of C_3 symmetrical PAHs as a result of the work of Scott and co-workers.[13,14] This approach works very well in many cases, but still has some limitations in the synthesis of big molecules such as the precursors of higher fullerenes. This is mostly because of the poor solubility of intermediate products.[9,14] The reaction often stops after dimerization and the target sample usually contains a considerable amount of insoluble side-products.[16] An alternative route, which avoids the solubility disadvantages, has been developed by Echavarren and co-workers. It is based on the addition of an appropriate electrophilic reagent to the truxene trianion and the subsequent Pd-catalyzed cyclization, which gives the desired product in moderate yield and high purity.[15,16] Unfortunately this method has serious disadvantages. Namely the last step, the Pd-catalyzed cyclization, excludes the option of introducing chlorine or bromine into the structure. Thus, neither of these approaches provides a way to design the required fullerene precursor molecules using chlorine or bromine as radical promoter. To solve this problem we have examined alternative radical promoters that seem to be promising whilst taking the above-mentioned synthetic approaches into consideration. Although in pristine benzo[*c*]phenanthrene **5**, both R^3 and R^1 can be used for activation, the R^1 position was chosen preferentially because of its more convenient synthetic access.

All benzo[*c*]phenanthrene derivatives **5** were synthesized by using the modified two-pot synthetic strategy[12] (Figure 1). Benzyl bromides **2** were obtained by free-radical bromination of the corresponding methylbenzenes **1** with *N*-bromosuccinimide (NBS) in the presence of dibenzoyl peroxide (PBO) in CCl_4 (or commercially available bromides were used). The corresponding benzyl bromide and triphenylphosphane were heated at reflux in toluene to form the phosphonium salt **3**, which was filtered and used in the next step without additional purification. Wittig reactions were carried out in anhydrous THF using *n*-butyllithium as the base (ethanol and potassium *tert*-butoxide were used for the synthesis of the fluoro derivatives). Chromatographic separation gave the benzo-stilbene **4** as a *cis*/*trans* isomeric mixture. No additional separation was performed because the isomers interconvert photochemically in the next step. Benzo[*c*]phenanthrenes **5** were synthesized from the benzo-stilbenes by using the Katz modification of the Mallory photocyclization reaction.[17]



Compound	R^1	R^2	R^3
a	Cl	H	H
b	CH_3	H	H
c	CF_3	H	H
d	H	H	H
e	Ph	H	H
f	F	H	H
g	H	Br	F
h	H	H	F

Figure 1. Synthetic route to benzo[*c*]phenanthrenes **5a**–**5g** (**5h** was synthesized by the debromination of **5g**).

Pyrolysis experiments were carried out in an improved FVP furnace that allowed simultaneous control of the pressure and the flow of the carrier gas in the system. A movable oven made it possible to regulate the sublimation temperature and tune the sublimation speed during the FVP experiments. A special constriction of the injector decreases the probability of contact between sample molecules and the walls of the heated quartz tube (Figure 2 and the Supporting Information).

Benzo[*c*]phenanthrene (**5d**) and 2-chlorobenzo[*c*]phenanthrene (**5a**) were selected as reference compounds. Pyrolysis of **5a** showed that effective condensation takes place under FVP conditions and the efficiency of the condensation increases with increasing temperature of pyrolysis and decreasing pressure in the system. At the same time the selectivity for benzo[*ghi*]fluoranthene (**6**) formation de-

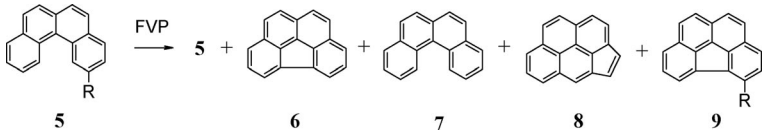


Figure 2. The main products of FVP of the benzo[*c*]phenanthrene derivatives.

creases due to the conversion of **6** to the thermodynamically more stable cyclopenta[*cd*]pyrene (**8**), in agreement with literature data.[11,18,19] Thus, the pyrolysis of **5a** at 1100 °C and a pressure of 2.5 mbar with a N_2 flow of 12 mL/min gave **8** in 50% yield, whereas **6** was formed in only 20% yield. (Here and elsewhere in the text molar percentages are given.) The optimal conditions for the condensation of **5a** to **6** were found to be T = 1000 °C, 2 mbar pressure and N_2 flow of 8 mL/min. In this case **6** was obtained in almost 80% yield, whereas unactivated benzo[*c*]phenanthrene (**5d**) gave only 3% of **6** under the same conditions. The efficiency of the alternative promoters was investigated by comparison with the efficiency of **5a** and **5d** under the conditions required for the sublimation of large fullerene precursor molecules (pressure 0.5 mbar, temperature 1100 °C). The results of the FVP experiments are summarized in Table 1.

Table 1. The effect of promoters on the condensation of benzo[*c*]-phenanthrenes **5**. Pyrolysis at 1100 °C (p = 0.1 mbar). The yields are given as a molar ratio to benzo[*ghi*]fluoranthene (**6**). Bond energy (Ph–R) according ref.[20,21]

	R[1]	Ph–R bond energy[b] [kcal/mol]	5	6	7	8	9
5a	Cl	97.1	4.56	1	0.82	1.7	0
5b	CH_3	103.5 (89.7)[b]	6.69	1	1.79	0.94	(0.6)[a]
5c	CF_3	110.5	16.27	1	0.80	1.53	(0.2)[a]
5d	H	112.9	22.5	1	–	1.1	–
5e	Ph	118	13.02	1	2.07	1.25	(0.7)[a]
5f	F	127.2	8.36	1	0.07	1.19	(0.1)[a]

[a] Concentrations were estimated on the assumption of equal sorption with benzo[*ghi*]fluoranthene. [b] The weakest bond in **5b** ($PhCH_2$–H).

As can be seen from Table 1, the efficiency of the ring-closure is in good correlation with the C–R bond dissociation energy, a measure of the effective homolytic cleavage of the corresponding C–R bond. However, the phenyl and fluorine derivatives do not fit the correlation. According to the data obtained, the methyl group can be considered as a prospective promoter. The mechanism for the cyclization of **5b** is definitely different to the "classic" mechanism. The homolytic cleavage of the $ArCH_2$–H bond to give a stable benzyl radical needs only 89.7 kcal/mol.[20] The radical formed stimulates the ring-closure without loss of the methyl group. Thus, low-temperature pyrolysis results mostly in the formation of methylbenzo[*ghi*]fluoranthene **9b**. Increasing the temperature results in the subsequent cleavage of the methyl group and formation of a benzo[*ghi*]-fluoranthene radical which finally yields **6**. Interestingly, significant transformation of **6** and **9** into the corresponding cyclopenta[*cd*]pyrenes takes place even at 1000 °C (Figure 3), although such a transformation usually needs a temperature of more than 1150 °C.[18] The formation of **7** in only trace amounts confirms that no direct C–Me bond-cleavage takes place in low-temperature FVP. In summary, the Me group promotes rather selective ring-closure, although it is not directly involved in the sterically hampered fjord region. Moreover, the subsequent cleavage of the Me group could provide the activation for the next cyclization, which makes it a rather interesting candidate for the cyclization of fullerene precursors in which a large number of new cycles should be created.

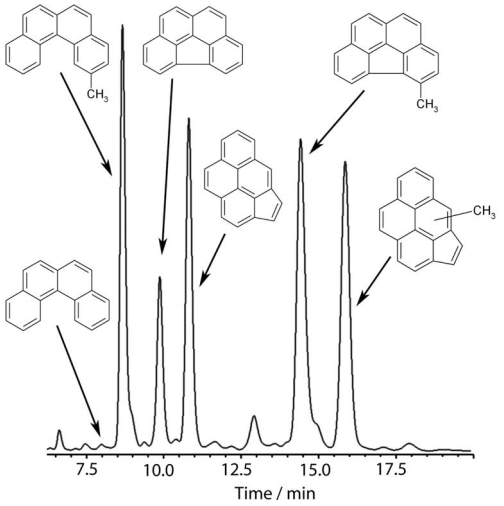


Figure 3. HPLC profile of the products of the FVP of **5b** (FVP conditions: T = 1000 °C, p = 0.1 mbar).

The deviation from the correlation between C–R bond energy and efficiency of cyclization in the case of **5e** is probably caused by the lower dissociation energy of the C–H bond in the fjord region, which stimulates ring-closure without cleavage of the phenyl group. Indeed, a significant amount of phenylbenzo[*ghi*]fluoranthene (**9e**) was registered in the pyrolysis products. Nevertheless, a rather low degree of conversion and the formation of many side-products limit the use of a Ph group as a cyclization promoter. Pyrolysis of **5c** containing a CF_3 group does not show good activation either and gave a complex mixture of the products.

Unexpectedly, fluorine was found to be highly efficient in the activation. (The results of FVP of fluorinated benzo[*c*]-phenanthrenes are summarized in Table 2.) Although some activation effect of fluorine in 1,3-difluorobenzo[*c*]phenanthrene has been described previously,[11] the activity in the case of 2-fluorobenzo[*c*]phenanthrene (**5f**) is highly unexpected. The C–F bond is considered a very stable bond in organic chemistry[22] and accordingly the proposed mechanism[12] should strongly inhibit its condensation. Because our experiments have shown high fluorine efficiency in ring-closure it is clear that the mechanism of condensation is different to that proposed for other halogens. The reason why fluorine activates the condensation reaction and also the mechanism of the process have remained widely unexplored.

The condensation of 1-fluorobenzo[*c*]phenanthrene (**5h**) gave even more exciting results. Namely, a remarkable degree of cyclization with a high selectivity, uncharacteristic for pyrolysis, was observed in the low-temperature experiment (Figure 4). Although only 10% of **5h** was converted into **6**, the selectivity of this process was found to be more

Table 2. Relative yields of the pyrolysis products (mol-%).

Compound	*T* [°C]	Yield [%]			
		5	**7**	**6**	**8**
5h	800	92.6	0	7.6	0.2
	850	89.5	0	10	0.5
	900	85.3	0	13	1.6
	1000	81.8	0	14.8	3.4
	1100	59.6	0	28.4	11.8
5f	900	100	0	0	0
	1000	96.7	0.05	1.3	1.6
	1100	79.3	0.7	9.4	11.3

than 97%. This means that unreacted **5h** can be recovered and, in principle, **5h** can be condensed to the targeted product with close to quantitative yield by repeated FVP.

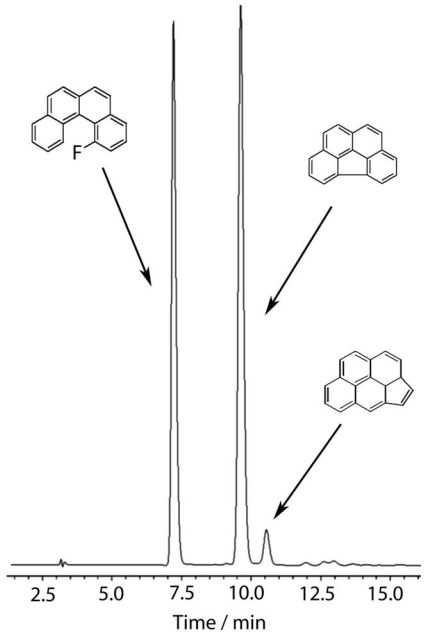


Figure 4. HPLC profile of the FVP of **5h** (FVP conditions: T = 850 °C, p = 0.1 mbar).

The potential offered by functionalization with fluorine for fullerene precursor closing is clearly promising. First, fluorine does not increase the molecular weight of the precursor drastically, which is an important prerequisite for facile sublimation. The C–F bond is stable to sublimation, which should exclude decomposition of the precursor material during vaporization. Secondly, because of its small size fluorine can be introduced into the sterically hampered fjord region of the precursor molecule rather easily. Finally, the high resistance of the C–F bond to many organic reactions provides opportunities for introducing the required number of fluorine atoms at the appropriate positions.

As stated above, the mechanism for ring-closure in the benzo[*c*]phenanthrenes is different for different functional groups. The mechanism of condensation for **5a**, **5b**, **5e**, **5f** and **5h** are summarized in Figure 5.

The mechanism for the condensation of **5a** is the same as for its brominated analogue, which has been investigated previously.[4,13] In the first step, the homolytic cleavage of the weakest bond (C–Cl) takes place. The radical **11** can be quenched by a hydrogen radical with the formation of benzo[*c*]phenanthrene (**7**) or rearrange to **12** or **14**. As has also been demonstrated previously, β-scission of the phenyl radical (82.2 kcal/mol) is less favourable than a 1,2-hydrogen shift (58.4 kcal/mol) and radical **11** converts rather selectively to radical **12**.[13] Subsequent ring-closure gives **13**, which can be quenched by a hydrogen radical with the formation of the targeted **6**. Increasing the pyrolysis temperature results in reduced selectivity for the transformation of **11** into **12**. As a result, both **12** and **14** can be formed from **11** with the same probability. Whereas **11** leads to the formation of benzo[*ghi*]fluoranthene (**6**), the intermediate **14** rearranges to carbene **16**, cyclization of which results in cyclopenta[*cd*]pyrene (**8**). As can be seen from Figure 6 the temperature-dependent **6**/**8** ratio is in a good agreement with the proposed mechanism. Thus, at low temperature the ratio of **6**/**8** in the pyrolysis products of **5a** is about 10, whereas at high temperature it approaches 1.

In the case of methylarenes the cleavage of the $ArCH_2$–H bond (89.7 kcal/mol) is favoured over Ar–CH_3 cleavage (103.5 kcal/mol). Thus, the pyrolysis of **5b** results preferentially in the formation of the benzylic radical **17** which transforms into **18** and subsequent ring-closure gives **19**. The radical **19** can rearrange to **20**, which finally yields benzo[*ghi*]fluoranthene **9b**. Although the low-temperature pyrolysis results mostly in the formation of **9b**, a remarkable amount of methylcyclopenta[*cd*]pyrene **10b** was observed in the product mixture. The most likely route to **10b** is by the rearrangement of radical **19**. Indeed, increasing the pyrolysis temperature to 1000 °C shows the formation of a considerable amount of cyclopenta[*cd*]pyrene (**8**; Figure 6). This can be a result of cleavage of the CH_3 group in **9b** and subsequent rearrangement of the benzo[*ghi*]fluoranthene radical **23** to **24**. This also confirms that the benzo[*ghi*]fluoranthene radical **19** could rather easily be transformed into the corresponding cyclopenta[*cd*]pyrene **10b**. Pyrolysis at 1100 °C is not selective and results in a complex product mixture. The formation of benzo[*c*]phenanthrene (**7**) under these conditions shows that direct Ar–CH_3 bond-cleavage takes place in **5b** as well.

The phenyl group also promotes intramolecular cyclization. According to quantum chemical calculations the presence of Ph remarkably decreases the C–H bond dissociation energy in the fjord region. Thus, the formation of **21** from **5e** needs only 106.8 kcal/mol instead of the 112.9 kcal/mol typical of homolytic C_{Ar}–H bond-cleavage. The radical intermediate **21** stimulates ring formation (**22**) and finally yields **9e**.

Because of the high stability of the C–F bond, fluorinated benzo[*c*]phenanthrene **5f** is not able to produce radical **11** by C–F bond cleavage. Our experiments have shown that rather effective elimination of the HF takes place although not through the intermediate **11** as no benzo[*c*]-phenanthrene (**7**) was found in the pyrolysis products. Of

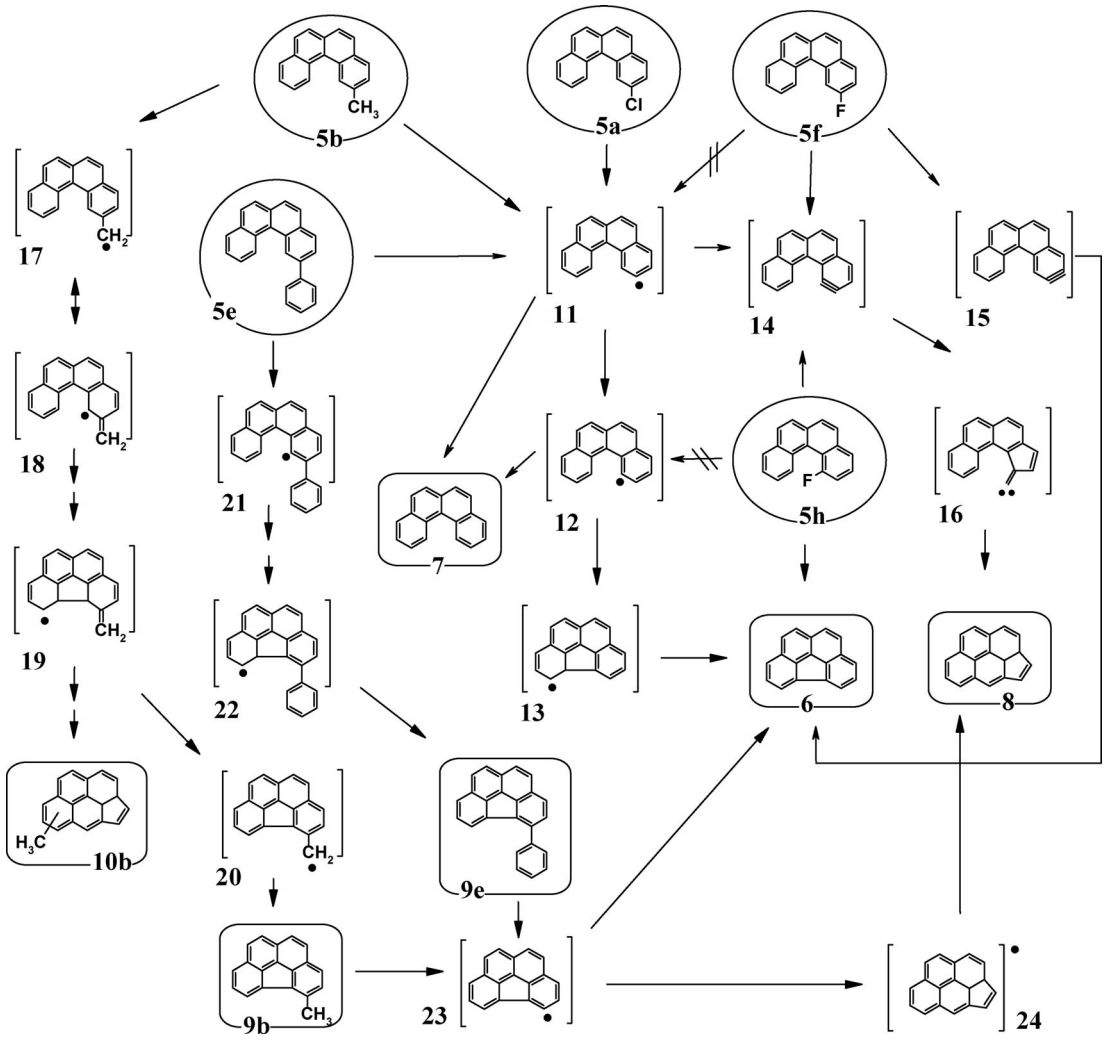


Figure 5. Proposed mechanism for the condensation of **5a**, **5b**, **5e**, **5f** and **5h** under FVP conditions.

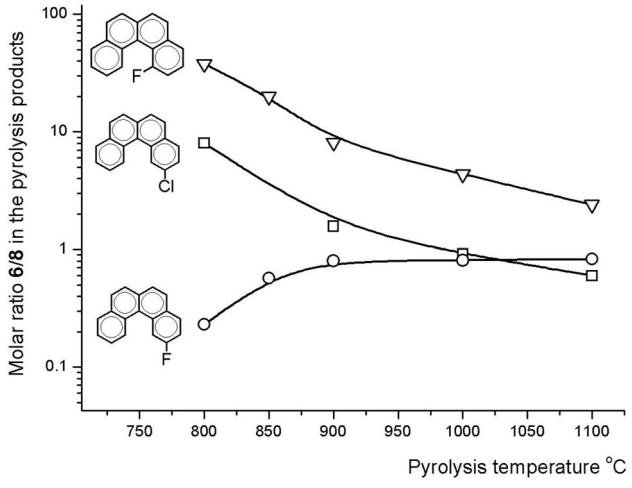


Figure 6. Influence of functional groups in benzo[*c*]phenanthrenes on the temperature-dependent ratio of **6**/**8**.

the possible ways to eliminate HF from **5f**, mechanisms via the benzynes **14** and **15** are the only possible candidates. According to quantum chemical calculations the transformation of **5f** to **14** needs 78.6 kcal/mol and 89.6 kcal/mol to form **15**. Interestingly, according to the mechanism proposed, the pyrolysis of **5f** should result in the selective formation of cyclopenta[*cd*]pyrene as the more favourable **14** leads directly to **8**. Indeed, low-temperature FVP experiments show remarkable selectivity in cyclopenta[*cd*]pyrene formation, which approaches 1 only at high temperatures (Figure 6). More interesting results were obtained by pyrolysis of **5h**. In this case intermediate **14** appears to be the only reasonable product of a concerted elimination of HF. Such a process should result in the highly selective formation of **8**. However, the opposite effect was observed experimentally. Even high-temperature pyrolysis resulted in a high preference for benzo[*ghi*]fluoranthene formation (the ratio of **6**/**8** at 1000 °C pyrolysis exceeds 4). Low-temperature pyrolysis is selective with a ratio of **6**/**8** of almost 50, which is unusually high for a pyrolysis experiment (Figure 6). Because no other side-products were detected in the product mixture, the selectivity of the condensation process is better than 97%. Such an effect can be explained by a 1,5-elimination of HF with the formation of **6** with no intermediate products. Although such an elimination step is indeed sig-

nificantly more favoured thermodynamically (6.0 kcal/mol instead of 73.7 kcal/mol for the generation of **14**), it is difficult to compare these two processes. According to the experimental data the activation barrier for the reaction of **5h** to **6** is lower than for the reaction of **5h** to **14**, but still not low enough to warrant high selectivity and high conversion simultaneously. Although it appears desirable to corroborate the mechanism for fluorine-promoted condensation suggested here by additional investigations, high selectivity and moderate conversion together with other attractive properties of fluorine makes it a very promising promoter for the condensation of PAHs to fullerenes.

Conclusions

Intramolecular condensation creating new rings is the key step in the direct synthesis of fullerenes by the folding of PAHs of an appropriate composition and constitution. By using benzo[*c*]phenanthrene as a model system we have investigated its intramolecular cyclization under FVP conditions with different promoters introduced into the pristine PAH. The methyl group and fluorine were found to be prospective promoters for intramolecular condensation under FVP conditions. The methyl group activates the cyclization without being introduced into the sterically hampered fjord region and can provide double-radical-promoted cyclization. Such a process would be particularly beneficial for fullerene synthesis in which a high number of new cycles need to be created. We observed an unexpectedly high selectivity in the intramolecular condensation promoted by fluorine by FVP. The high resistance of the C–F bond to many organic reagents and its small size and low molecular weight make it a perfect candidate for the synthesis of effective fullerene precursors. The fluorine-promoted condensation mechanism suggested seems to allow full control of the process. Thus, if the fluorine atom has only one neighbouring hydrogen atom in the precursor structure the elimination will be directed towards the desired product. Such an approach may fully solve the problem of effective activation in the direct synthesis of fullerenes by FVP. The corresponding investigations are in progress.

Experimental Section

Mass spectra were recorded with a Shimadzu AXIMA resonance spectrometer. All NMR spectra were measured at 20 °C. R_f values were determined on TLC-PET sheets coated with silica gel and a fluorescent indicator (254 nm; layer thickness 0.25 mm, medium pore diameter 60 Å; Fluka). Elemental analyses were performed with an Elementar VARIO EL elemental analyser. HPLC analyses were carried out by using a Cosmosil Buckyprep column (4.6 × 250 mm, methanol, UV detection). Chromatographic purifications were carried out with flash grade silica gel Kieselgel 60 (0.06–0.2 mm; Roth). Quantum chemical calculations were performed by the DFT method with B3LYP/6-31G using the Gaussian03 software package.[23]

Synthesis of Benzyl Bromides: The relevant methylbenzene (100 mmol) and *N*-bromosuccinimide (NBS; 100 mmol) with a catalytic amount of dibenzoyl peroxide (PBO; 5–10 mg) were dissolved in 150 mL) CCl_4 and heated at reflux until the reaction had gone to completion, as determined by TLC analysis (2–6 h). The reaction mixture was then allowed to cool, washed twice with water, dried with $MgSO_4$ and concentrated in vacuo. The crude product was purified chromatographically on silica gel using petroleum ether (PE) as the eluent.

Synthesis of Phosphonium Salts: The corresponding benzyl bromide (100 mmol) and triphenylphosphane (110 mmol) were dissolved in toluene (70 mL) and the mixture was heated at reflux with vigorous stirring for 12 h. During this time a white crystalline solid precipitated from solution. The reaction mixture was cooled to room temperature and then filtered. The solid was washed with toluene and hexane to give a total of 85–95% yield of the phosphonium salt as a white powder. The resulting salt was used in the next step without additional purification.

Synthesis of Benzo-stilbenes: The whole procedure was carried out in a round-bottomed flask under argon. The phosphonium salt (34 mmol) was dissolved in anhydrous THF (100 mL). The mixture was cooled to –78 °C and stirred while *n*-butyllithium (38 mmol) was added dropwise over 10–20 min. The orange-red solution obtained was allowed to warm to room temperature and stirred for an additional 45 min. At this point, 2-naphthaldehyde (34.1 mmol) was added as a solution in anhydrous THF. After stirring for 12 h the reaction mixture turned light-yellow. THF was removed and the resulting material was passed through a short silica gel plug using DCM as the eluent. A white solid of the title compound as a mixture of *cis*/*trans* isomers was obtained in a yield of 65–80%. The resulting stilbene was used in the next step without additional purification.

Synthesis of Benzo[*c*]phenanthrenes: The corresponding benzo-stilbene (10 mmol) as a *cis*/*trans* mixture was dissolved in cyclohexane (350 mL). The resulting solution was placed in a 500-W water-cooled quartz photochemical reactor and iodine (11 mmol) was then added. Argon was bubbled through the stirred solution for 15–20 min before an excess of propylene oxide (10 mL) was added. After irradiation for 10–30 h the colour of iodine had disappeared. The mixture was washed with aqueous $Na_2S_2O_3$ to remove residual traces of iodine, concentrated in vacuo and then purified by flash chromatography on silica gel. A mixture of light petroleum (PE) and dichloromethane (DCM; 1:1) was used as eluent. The targeted compound was obtained with 60–95% yield as a white solid.

(*E*/*Z*)-2-[2-(2-Bromo-5-fluorophenyl)ethenyl]naphthalene (4g): 2-Bromo-5-fluorobenzylphosphonium bromide (9.4 g, 17.7 mmol), *t*BuOK (1.99 g, 17.7 mmol) and 2-naphthaldehyde (2.77 g, 17.7 mmol) were dissolved in ethanol (200 mL). The mixture was heated at reflux overnight and neutralized by the addition of 1 M HCl. The product was concentrated by evaporation under reduced pressure, diluted with water and extracted with DCM. The DCM solution was dried with $MgSO_4$ and filtered through silica gel (PE/DCM, 1:1). After evaporation the title compound was obtained as a white solid (4 g, 70%).

2-Chlorobenzo[*c*]phenanthrene (5a): White solid (yield 70%). R_f = 0.38 (hexane). M.p. 61.4–61.8 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.48 (dd, J_1 = 8.57, J_2 = 2.01 Hz, 1 H), 7.52–7.68 (m, 2 H), 7.69–7.88 (m, 5 H), 7.93 (dd, J_1 = 7.87, J_2 = 1.36 Hz, 1 H), 8.96 (d, J = 8.43 Hz, 1 H), 9.03 (d, J = 1.82 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 126.12, 126.41, 126.64, 126.67, 126.94, 127.05, 127.18, 127.36, 128.14, 128.69, 129.91, 130.11, 131.15, 131.48, 131.73, 132.35, 133.52 ppm. MS (LDI-TOF): calcd. for $C_{18}H_{11}Cl$ 262.0549*m*/*z* ; found 262.06 $[M]^+$. $C_{18}H_{11}Cl_1$ (262.74): calcd. C 82.29, H 4.22; found C 81.9, H 4.2.

2-Methylbenzo[*c*]phenanthrene (5b): White solid (yield 57%). R_f = 0.31 (hexane). M.p. 75.8–76.2 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.57 (s, 3 H), 7.34 (d, J = 8.13 Hz, 1 H), 7.48–7.86 (m, 7 H), 7.93 (dd, J_1 = 6.5, J_2 = 1.42 Hz, 1 H), 8.86 (s, 1 H), 9.01 (d, J = 10.6 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 22.24, 125.65, 125.90, 125.97, 126.88, 126.95, 127.23, 127.26, 127.39, 127.65, 127.82, 128.37, 128.5, 130.42, 130.49, 131.14, 131.58, 133.45, 135.83 ppm. MS (LDI-TOF): calcd. for $C_{19}H_{14}$ $[M]^+$ 242.1096; found: 242.11. $C_{19}H_{14}$ (242.32): calcd. C 94.18, H 5.82; found C 94.1, H 5.9.

2-Trifluoromethylbenzo[*c*]phenanthrene (5c): White solid (yield 73%). R_f = 0.40 (hexane). M.p. 109.6–110.0 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.55–7.75 (m, 4 H), 7.82–7.9 (m, 3 H), 7.93–8.08 (m, 2 H), 8.92 (d, J = 8.48 Hz, 1 H), 9.33 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 121.66 (q, J = 3.38 Hz), 125.38 (q, J = 4.5 Hz), 126.41, 126.60, 126.84, 126.88, 127.42, 128.39, 128.79, 129.11, 129.33, 129.48, 129.94, 131.46, 133.7 ppm. MS (LDI-TOF): calcd. for $C_{19}H_{11}F_3$ $[M]^+$ 296.0813; found 296.10. $C_{19}H_{11}F_3$ (296.29): calcd. C 77.02, H 3.74; found C 76.1, H 4.0.

2-Phenylbenzo[*c*]phenanthrene (5e): White solid (yield 55%). R_f = 0.18 (hexane). M.p. 131.5–131.9 °C. ^{1}H and ^{13}C NMR spectra are in good agreement with the data reported previously.[24] MS (LDI-TOF): calcd. for $C_{24}H_{16}$ $[M]^+$ 304.1252; found 304.13. $C_{24}H_{16}$ (304.39): calcd. C 94.70, H 5.30; found C 94.5, H 5.2.

2-Fluorobenzo[*c*]phenanthrene (5f): White solid (yield 66%). R_f = 0.33 (hexane). M.p. 63.7–64.1 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.31 (td, J_1 = 2.42, J_2 = 8.32 Hz, 1 H), 7.49–8.09 (m, 8 H), 8.73 (dd, J_1 = 2.1, J_2 = 12.37 Hz, 1 H), 8.99 (d, J = 8.34 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 112.46 (d, J = 23.4 Hz), 115.16 (d, J = 24.23 Hz), 126.01, 126.19 (d, J = 2.42 Hz), 126.51, 126.66, 126.72, 126.77, 127.08 (d, J = 1.06 Hz), 127.11, 128.09, 128.70, 130.29, 130.6 (d, J = 9.13 Hz), 131.37 (d, J = 8.83 Hz), 131.53, 133.4, 161.45 (d, J = 244.15 Hz) ppm. MS (LDI-TOF): calcd. for $C_{18}H_{11}F$ $[M]^+$ 246.0845; found 246.04. $C_{18}H_{11}F$ (246.28): calcd. C 87.78, H 4.50; found C 86.1, H 4.5.

4-Bromo-1-fluorobenzo[*c*]phenanthrene (5g): White solid (yield 50%). R_f = 0.34 (hexane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.12–7.21 (m, 1 H), 7.49–7.59 (m, 2 H), 7.69–7.77 (m, 1 H), 7.78–7.86 (m, 2 H), 7.87–7.95 (m, 2 H), 8.08–8.28 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 112.87 (d, J = 25.74 Hz), 117.42 (d, J = 3.47 Hz), 120.3 (d, J = 13.67 Hz), 124.44 (d, J = 3.25 Hz), 125.17 (d, J = 2.94 Hz), 125.56, 125.93 (d, J = 2.19 Hz), 126.29, 127.47, 129.09, 129.22, 129.57 (d, J = 16.9 Hz), 129.83 (d, J = 3.4 Hz), 130.21 (d, J = 8.99 Hz), 131.82, 132.93, 133.35 (d, J = 4.45 Hz), 158.85 (d, J = 254.41 Hz) ppm. Crystal data: monoclinic; space group $P21/c$, a = 7.2750(8), b = 11.6037(12), c = 15.4111(16) Å, β = 91.147(2)°, V = 1300.7(2) Å^3, Z = 4, $2\theta_{max}$ = 54.26°, $-9 < h < 9$, $-14 < k < 14$, $-19 < l < 19$, λ = 0.71073 Å, T = 137(2) K, final R = 0.0369 (R_w = 0.1030).

CCDC-743279 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1-Fluorobenzo[*c*]phenanthrene (5h): 4-Bromo-1-fluorobenzo[*c*]phenanthrene (1 g, 3.1 mmol) was dissolved in anhydrous THF (50 mL). All procedures were carried out under argon. The mixture was cooled to – 78 °C and stirred while *n*-butyllithium (3.1 mmol) was added dropwise. The reaction was quenched after 3 min by the addition of cooled acetic acid (3 mL). The reaction mixture was warmed to room temperature. Afterwards H_2O was added and the product was extracted with DCM, dried with Na_2SO_4 and the solvents evaporated. The compound was purified by chromatography (silica gel, PE). White solid (yield 66%). R_f = 0.25 (hexane). M.p. 85.0–85.4 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.31 (td, J_1 = 2.42, J_2 = 8.32 Hz, 1 H), 7.49–8.09 (m, 8 H), 8.73 (dd, J_1 = 2.1, J_2 = 12.37 Hz, 1 H), 8.99 (d, J = 8.34 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 112.46 (d, J = 23.4 Hz), 115.16 (d, J = 24.23 Hz), 126.01, 126.19 (d, J = 2.42 Hz), 126.51, 126.66, 126.72, 126.77, 127.08 (d, J = 1.06 Hz), 127.11, 128.09, 128.70, 130.29, 130.6 (d, J = 9.13 Hz), 131.37 (d, J = 8.83 Hz), 131.53, 133.4, 161.45 (d, J = 244.15 Hz) ppm. MS (LDI-TOF): calcd. for $C_{18}H_{11}F$ $[M]^+$ 246.0845; found 246.06. $C_{18}H_{11}F$ (246.28): calcd. C 87.78, H 4.50; found C 87.3, H 4.4.

Supporting Information (see also the footnote on the first page of this article): NMR, UV/Vis spectra and HPLC profiles of new compounds, FVP apparatus, energies of C–H bond cleavage and energies of HF elimination from various benzo[*c*]phenanthrenes.

[1] L. T. Scott, *Angew. Chem. Int. Ed.* **2004**, *43*, 4994–5007.
[2] G. Mehta, H. S. P. Rao, *Tetrahedron Lett.* **1998**, *54*, 13325–13370.
[3] L. T. Scott, *Pure Appl. Chem.* **1996**, *68*, 291–300.
[4] V. M. Tsefrikas, L. T. Scott, *Chem. Rev.* **2006**, *106*, 4868–4884.
[5] M. J. Plater, M. Praveen, D. M. Schmidt, *Fullerene Sci. Technol.* **1997**, *5*, 781–800.
[6] L. T. Scott, M. M. Boorum, B. J. McMahon, S. Hagen, J. Mack, J. Blank, H. Wegner, A. de Meijere, *Science* **2002**, *295*, 1500–1503.
[7] K. Y. Amsharov, M. Jansen, *J. Org. Chem.* **2008**, *73*, 2931–2934.
[8] K. Y. Amsharov, M. Jansen, *Chem. Commun.* **2009**, *19*, 2691–2693.
[9] T. J. Hill, R. K. Hugher, L. T. Scott, *Tetrahedron Lett.* **2008**, *64*, 11360–11369.
[10] A. H. Abdourazak, Z. Marcinow, A. Sygula, R. Sygula, P. W. Rabideau, *J. Am. Chem. Soc.* **1995**, *117*, 6410–6411.
[11] M. J. Plater, *J. Chem. Soc. Perkin Trans. 1* **1997**, *19*, 2903–2909.
[12] M. A. Brooks, L. T. Scott, *J. Am. Chem. Soc.* **1999**, *121*, 5444–5449.
[13] A. W. Amick, L. T. Scott, *J. Org. Chem.* **2007**, *72*, 3412–3418.
[14] M. M. Boorum, L. T. Scott in *Modern Arene Chemistry* (Eds.: D. Astruc), Wiley-VCH, Weinheim, **2002**, pp. 20–31, and references cited therein.
[15] B. Gomez-Lor, O. de Frutos, A. M. Echavarren, *Chem. Commun.* **1999**, *23*, 2431–2432.
[16] A. M. Echavarren, B. Gomez-Lor, J. J. Gonzalez, O. de Frutos, *Synlett* **2003**, *5*, 585–597, and references cited therein.
[17] L. B. Liu, B. W. Yang, T. J. Katz, M. K. Poindexter, *J. Org. Chem.* **1991**, *56*, 3769–3775.
[18] M. Sarobe, L. W. Jenneskens, U. E. Wiersum, *Tetrahedron Lett.* **1996**, *37*, 1121–1122.
[19] M. J. Plater, *Tetrahedron Lett.* **1994**, *35*, 6147–6150.
[20] S. J. Blanksby, G. B. Ellison, *Acc. Chem. Res.* **2003**, *36*, 255–263.
[21] J. W. Coomber, E. Whittle, *Trans. Faraday Soc.* **1967**, *63*, 2656–2667.
[22] D. O'Hagan, *Chem. Soc. Rev.* **2008**, *37*, 308–319.
[23] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, G. Scalmani, K. N. Kudin, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, X. Li, H. P. Hratchian, J. E. Peralta, A. F. Izmaylov, E. Brothers, V. Staroverov, R. Kobayashi, J. Normand, J. C. Burant, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador,

J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacompe, W. Chen, M. W. Wong, J. A. Pople, *Gaussian03*, *Revision C.02*, Gaussian, Inc., Wallingford, CT, **2004**.

[24] L. Q. Peng, L. T. Scott, *J. Am. Chem. Soc.* **2005**, *127*, 16518–16521.

Received: August 27, 2009
Published Online: November 4, 2009

