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Synthesis of Benzo[ghi]fluoranthenes from 1-Halobenzo[c]phenanthrenes by Flash Vacuum Pyrolysis

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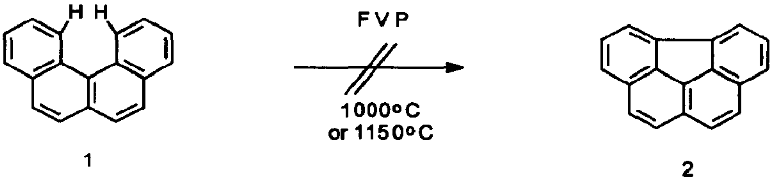
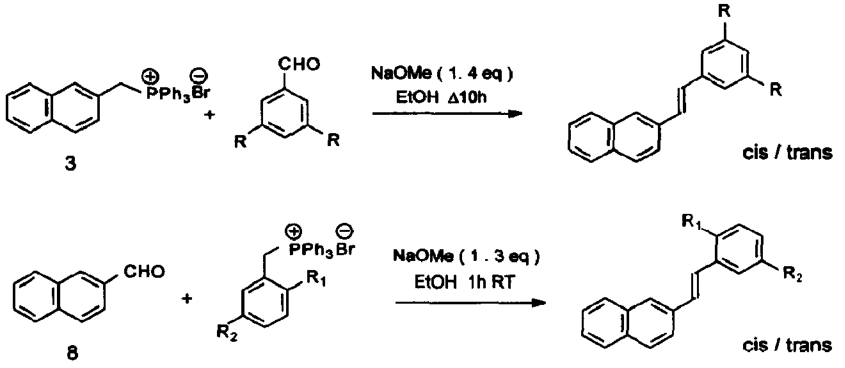
Abstract: 1-Chlorobenzo[c]phenanthrene **23** was prepared via the oxidative photochemical cyclisation of suitably halogenated stilbenes and was cyclised to benzo[ghi]fluoranthene **2** by flash vacuum pyrolysis.

Flash Vacuum Pyrolysis (FVP) promises to be an important method for the synthesis of sub-structures of C_{60} which might ultimately be assembled into C_{60} and C_{60} encapsulation compounds.[1] High temperature gas phase pyrolyses with a short contact time in the hot zone provides polycyclic aromatic hydrocarbon substrates with a large activation energy which is needed to effect endothermic cyclisation reactions forming a strained polycyclic carbon framework. Four types of gas phase cyclisation reactions are summarised: (1) An electrocyclisation followed by a loss or migration of hydrogen or loss of hydrogen halide[2] (2) Cyclisation of a benzylic radical,[3] benzylic carbene[4] or vinylic carbene.[5] (3) Cyclisation of an aryl radical.[6] (4) Intramolecular coupling of two benzylic,[7] benzylic and aryl or two aryl radicals.[8]

We have studied the transformation of benzo[c]phenanthrene **1** to benzo[ghi]fluoranthene **2** (Scheme 1).[9] This reaction is an important model study for larger systems such as the synthesis of the C_{60} half-unit tri-indenotriphenylene[10] or hemifullerene from tribenzotriphenylene.[11] The reaction does not proceed by photolysis in solution or by FVP. The aryl hydrogens shown are not sufficiently weakened by steric compression to break during pyrolysis to generate an aryl radical which might cyclise. 1-Chlorobenzo[c]phenanthrene **23** was prepared which has a sterically compressed chlorine substituent which might break generating an aryl radical on pyrolysis.[12] Appropriate stilbenes were prepared as mixtures of cis/trans isomers by a Wittig condensation between a phosphonium salt (1.2-1.3 eq) and an aldehyde in dry ethanol with sodium methoxide as base (Scheme 2).[13] Each cis/trans mixture of stilbenes was



Scheme 1

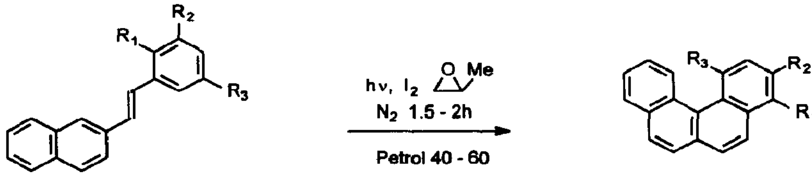


Scheme 2

Aldehyde	R	Stilbene (C/T)
4	Cl	5 85%
6	F	7 81%

Salt	R_1	R_2	Stilbene (C/T)
9	Cl	Cl	10 87%
11	Br	Cl	12 77%
13	F	Cl	14 93%
15	F	F	16 78%

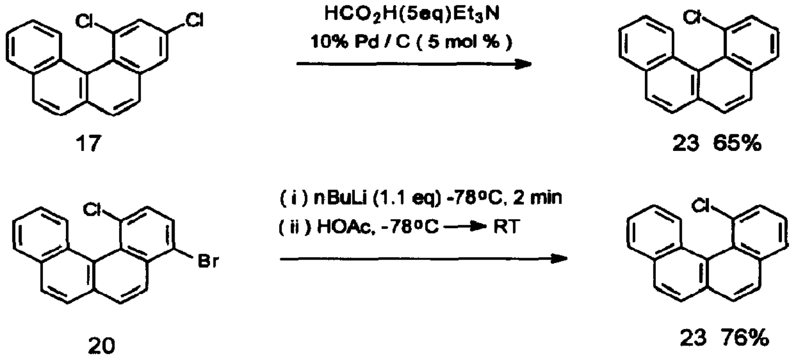
photocyclised[14] to the halogenated benzo[c]phenanthrenes (Scheme 3). The carbocyclic framework of the none fluorinated derivatives was proved by complete dehalogenation to benzo[c]-phenanthrene **1** using Pd/C, formic acid and triethylamine.[15] With TLC reaction monitoring the outer less hindered chlorine



Scheme 3

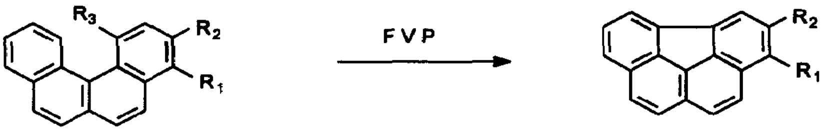
Stilbene (C/T)	R_1	R_2	R_3	Product
5	H	Cl	Cl	17 73%
7	H	F	F	18 76%
10	Cl	H	Cl	19 83%
12	Br	H	Cl	20 80%
14	F	H	Cl	21 81%
16	F	H	F	22 71%

on compound **17** could be selectively reduced to give compound **23** in 65% yield (Scheme 4). The best synthesis of precursor **23**[16] involved debromination of compound **20** by metal halogen exchange with nBuLi



Scheme 4

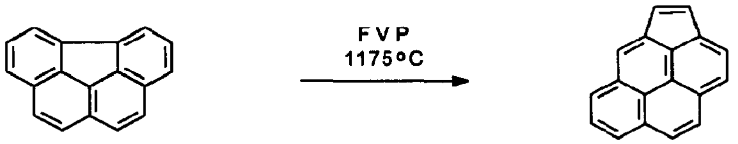
followed by quenching with acetic acid. FVP of the 1-chloro substituted precursors through an unpacked quartz tube gave the corresponding benzo[ghi]fluoranthenes (Scheme 5). The mechanism might involve an electrocyclisation followed by a loss of hydrogen chloride or an aryl radical cyclisation. No benzo[c]phenanthrene **1** was formed which suggests that if an aryl radical forms it cyclises rapidly and does not survive for long enough to react with a source of hydrogen. Hydrogen will be produced during the pyrolysis because some material is carbonised forming a thin lining of carbon on the quartz tube. The fluorinated precursor **22** also follows the desired reaction pathway on pyrolysis.



Scheme 5

Compound	R_1	R_2	R_3	Temp	Product
23	H	H	Cl	1030°C	2 53%
19	Cl	H	Cl	1000°C	24 38%
21	F	H	Cl	1030°C	25 46%
22	F	H	F	1150°C	25 23% + 22 32%

At high temperatures compound **2** isomerises to cyclopenta[cd]pyrene **26** which was identified by comparison of its spectral properties to authentic material.[17] This rearrangement involves the interconversion of a five and six membered ring and is analogous to the Stone-Wales paracyclene rearrangement proposed as a mechanistic pathway by which fullerene isomerises might interconvert.[18]



2

26 12% + 2 35%

Scheme 6

The successful pyrolysis of the fluorinated precursor **22** is significant because larger polycyclics capable of undergoing multiple ring couplings may be easier to prepare owing to the smaller size of the fluorine group. These studies are in progress.

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