Sandmeyer reactions. Part 4.[1] An investigation into the cyclisation modes of Pschorr phenanthrene synthesis

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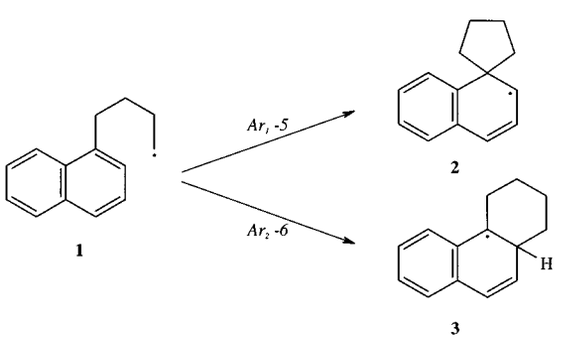
Comparison of the cyclisation regiochemistries in the heterolysis and the copper-catalysed homolysis of methyl (*E*)-3-(2-diazoniophenyl)-2-(3-halophenyl)propenoate tetrafluoroborates indicates that the homolytic pathway involves direct closure of the six-membered ring and not a five-membered ring closure followed by ring expansion. From competition experiments in which homolytic cyclisation of the corresponding non-halogenated compound was run against hydrogen abstraction from hypophosphorous acid, a cyclisation rate constant $k_C = (3.0 \pm 0.5) \times 10^9$ s^{-1} at ambient temperature was estimated which, when used in conjunction with a literature value for the homolytic phenylation of benzene, allows evaluation of a statistically corrected effective molarity of 2×10^4 mol dm^{-3} for homolytic Pschorr phenanthrene closure. Regioselectivity considerations imply that, by contrast, heterolytic Pschorr phenanthrene closure exhibits unit effective molarity. A mechanistic rationale is presented to explain these patterns of behaviour.

Understanding of the stereoelectronic requirements of cyclisation reactions has advanced greatly since the seminal papers of Baldwin[2–5] and Beckwith[6–8] which relate to heterolytic and homolytic processes, respectively. The argument common to both of these contributions is that when reactants of whatever kind come together in a kinetically controlled process, there is a preferred trajectory of approach which enables the most effective overlap of the principal orbitals involved, so minimising the energy of the rate-determining transition state. Thus, nucleophilic attack upon a carbonyl group, which requires overlap of the nucleophile's lone-pair orbital with the C=O π* orbital, puts the nucleophile on a trajectory of approach above (or below) the trigonal plane of the carbon atom such that the nucleophilic atom X lies in the plane containing the C=O bond which is orthogonal to the trigonal plane, and XCO subtends an angle of *ca.* 110° over the reaction path.[2] Baldwin[3] envisaged the refinement that when the carbonyl group was part of a composite function such as an amide, having contributions from canonical forms: $–C(=O)NH_2$ and $–C(=NH_2^+)O^-$, the nucleophile's approach trajectory would be deflected from the orthogonal plane containing C–O towards that containing C–N to an extent determined by the relative canonical weightings of C=N and C=O in the amide. For additions to trigonal carbon which lead to cyclisation, the existence of preferred trajectories results in constraints upon ring closure. Thus, for the closure of rings comprising first row atoms, *e.g.* homolytic cyclisations where the principal orbital interaction requires the SOMO of the radical centre to overlap the π* LUMO at the attacked alkenic carbon, the stereoelectronic requirements impose a strong *exo*-regioselectivity on the ring closure.

The work of Menger[9–11] qualifies this approach. He has argued that for real reactions in solution, the concept of a single transition state occurring at a saddle-*point* on a potential energy surface is inappropriate. Rather, a reaction might occur *via* numerous transition states of comparable energies, each being characterised by multiple bending modes of low restoring force, and which thus occupy numerous points on a potential energy surface having a 'flattened-saddle' shape. Each of these states is associated with a different trajectory of approach and with different extents of bond making and breaking. The weighted sums of the properties of these several states are what are perceived to be those of *the* transition state for the reaction. The consequence of this view is that reactants may approach one another *via* a *cone of trajectories* defining a *reaction funnel*, the cross-section of which, at any distance between the reacting centres, represents the *reaction window* at that distance. Furthermore, early transition states are associated with wide reaction windows and, within the reaction window, the precise direction of approach of one reaction centre to the other may be less important for the probability of reaction than the time the two centres remain within a critical separation (the spatio-temporal hypothesis).

When a homolytic cyclisation involves radical attack upon an aromatic carbon, only reaction at the *ipso* position gives wholly *exo*-ring closure, the delocalised Kekulé double bonds of the ring imposing roughly equal *exo*/*endo* character to closure at the *ortho* position. The 4-(1-naphthyl)butyl radical **1** is known to undergo competitive Ar_1-5 and Ar_2-6 cyclisations to **2** and **3** respectively (Scheme 1), the former being reversible unless the



1 **2** **3**

Scheme 1

conditions are oxidative when rapid oxidation of **2** gives a corresponding *spiro*-carbocation which undergoes ring expansion.[12] It was inferred that closure of the 5-membered ring is the more rapid cyclisation process.

Although bimolecular addition of aryl radicals to aromatic systems has been kinetically well documented,[13–15] intramolecular processes involving such addition have been much

less studied despite their association with long-established synthetic procedures, *i.e.* Pschorr cyclisations. We have already calibrated the cyclisation of 2-benzoylphenyl radical[16] which involves closure of a 5-membered ring and have used this as a radical clock for estimating rate constants for ligand transfer steps in Sandmeyer hydroxylation and chlorination reactions.[1] We now report an investigation into the cyclisation mode of a Pschorr phenanthrene synthesis in which a 6-membered ring is closed. The customary synthetic procedure uses copper powder as catalyst indicating that the process is homolytic.[17]

The investigations of mechanism carried out on the reaction 40–50 years ago distinguished between homolytic and heterolytic pathways but there was apparently no explicit consideration as to whether only 6-membered ring closure occurs or whether 5-membered ring closure is in any way involved. Hey and Mulley[18] noted that phenanthrene ring closure typically gives higher yields than similar cyclisations producing fluorenes, fluorenones and carbazoles *via* 5-membered ring closure and, consequently, was less prone to by-product formation. This was explained in terms of the attainable relative proximities, in the precursors, of the two atoms which become linked in the cyclisation process. An assumption of more efficient 6-membered ring closure was thus implicit. However, homolytic Pschorr cyclisation of **4** to the phenanthridone **5**, which ostensibly involves a 6-membered ring closure comparable with phenanthrene synthesis, gave **6** as major product in addition to **5**.[19] The conservation of the *para* substitution pattern in the rearranged aryl group of **6** proves Ar_1-5 closure to a *spiro* intermediate which could occur on the reaction path to **5** (Scheme 2).

Given these long-established facts and the more recent work into the stereoelectronic subtleties of ring closure, it became of interest to investigate the cyclisation mode of the Pschorr phenanthrene synthesis.

Results

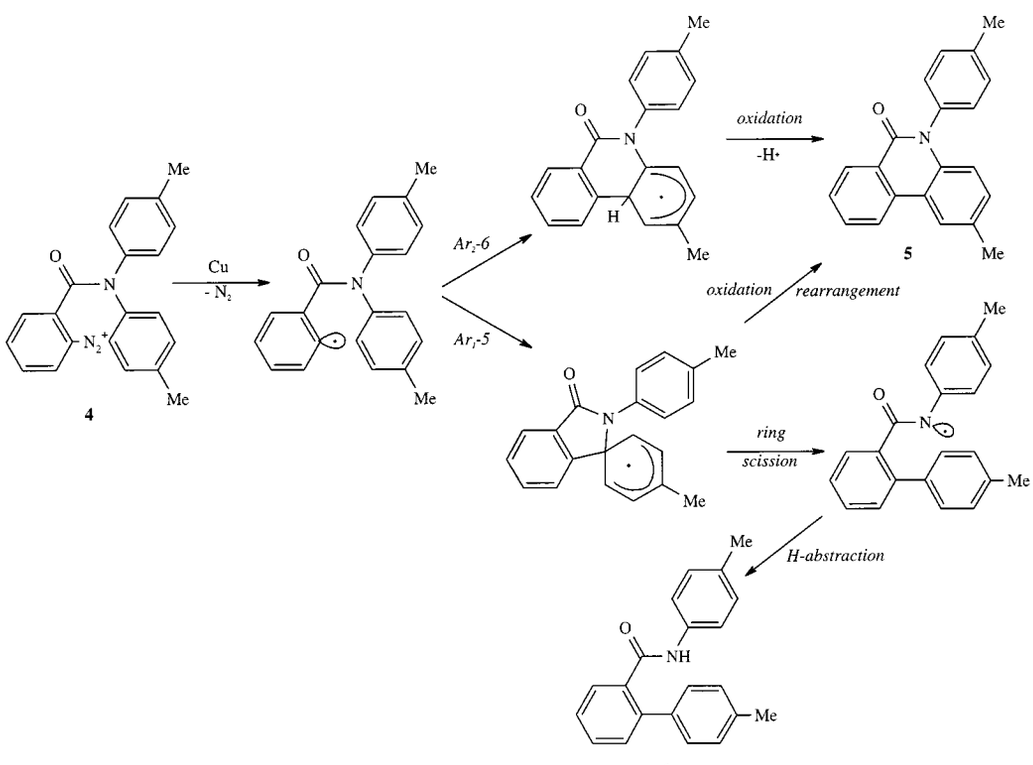
(i) The approach

Irrespective of whether Pschorr cyclisation of a stilbene-2-diazonium ion to a phenanthrene is homolytic or heterolytic, whenever the aromatic ring attacked by the radical or cation is unsymmetrically substituted, mixed isomeric products result (a consequence which limits the synthetic utility of the reaction). Our approach has been to compare the regioselectivity of the cyclisation of unsymmetrically halogenated stilbenediazonium precursors in the homolytic and heterolytic reaction variants (Scheme 3), the rationale being as follows.

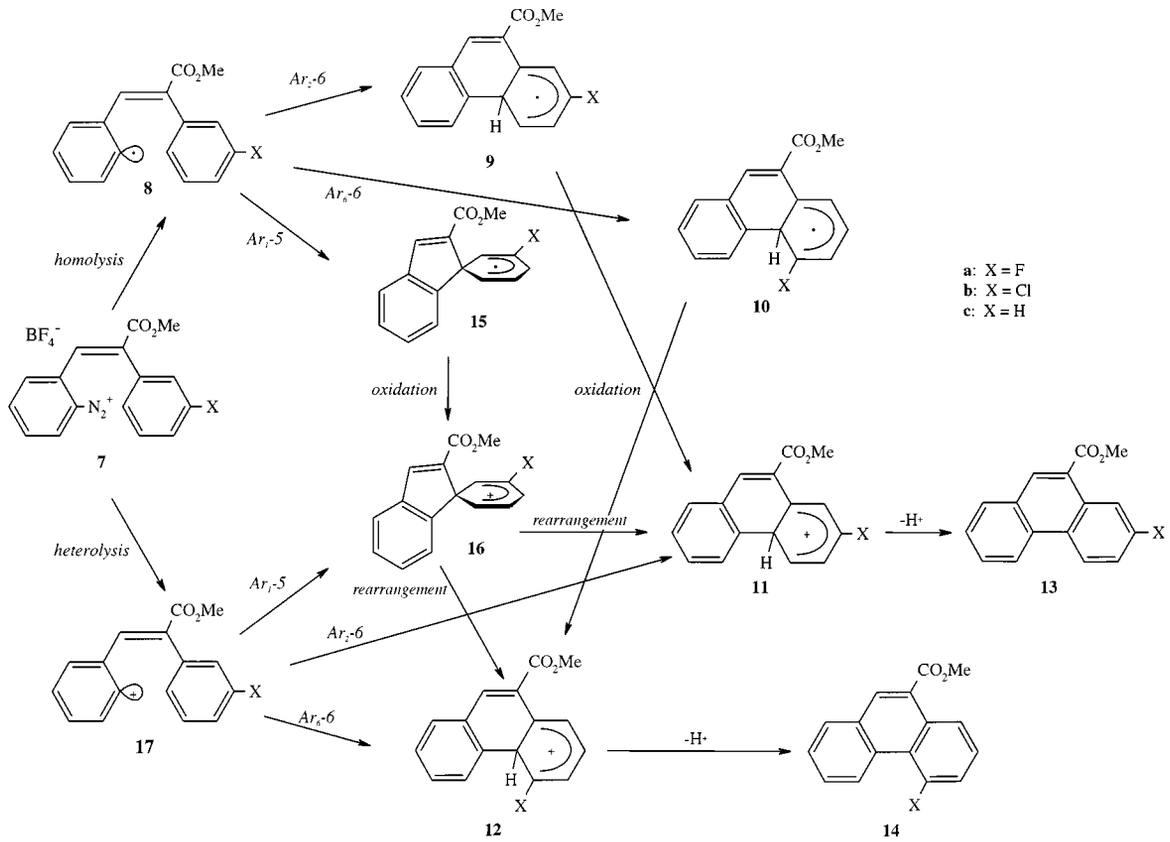
Both homolytic and heterolytic phenanthrene formation can, in principle, occur in two ways: the direct Ar_2-6 and Ar_6-6 routes and the indirect Ar_1-5 route. If the homolytic reaction involves direct cyclisation of **8** to **9** and **10** the final product ratio **13**:**14** is expected to be determined by the rates of cyclisation: ring closure is not expected to be reversible in view of the difference in stability between σ-aryl and π-cyclohexadienyl radicals and the fact that the rapid oxidation of the latter can be assured by having an excess of oxidant present.[20] On the other hand, if the homolytic route were to involve only the indirect Ar_1-5 mode, the product ratio would be determined, *after* similar oxidation of **15** to **16**, by the regioselectivity of ring expansion of the latter to **11** and **12** which is expected to be influenced by the electronic character of the substituent, leading to an isomer distribution resembling that from either the direct or indirect heterolytic modes. Cyclisation by concurrent Ar_1-5 and $Ar_{2(6)}$-6 routes would give a mixture of products where the regioselectivity would be determined by the relative contributions of the two routes. Fluorine was chosen as a substituent, X, on account of its powerful electronic effects and its minimal steric effect; it also has nuclear spin which aids unambiguous identification of the isomeric products. Parallel experiments using chlorine as the substituent were also carried out.

(ii) Synthesis of reactants

(*E*)-2-(3-Fluorophenyl)-3-(2-nitrophenyl)propenoic acid was prepared by Perkin condensation of 2-nitrobenzaldehyde with (3-fluorophenyl)ethanoic acid and esterified with methanol (esters were expected to be more amenable than carboxylic acids to GC analysis of the subsequent reaction products). Reduction of the nitro group with ammoniacal $FeSO_4$ gave the



Scheme 2



Scheme 3

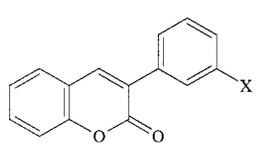
corresponding amine which was diazotised and the diazonium tetrafluoroborate **7a**, isolated (Scheme 3). A similar reaction sequence furnished the analogous chloro compound **7b**.

(iii) Pschorr cyclisations

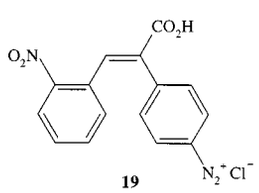
For homolytic Pschorr cyclisations at ambient temperature (293 K), the diazonium tetrafluoroborates **7** were dissolved in an aqueous solution of $Cu(NO_3)_2$ (0.1 mol dm^{-3}) and reaction was initiated by addition of a small quantity of ascorbic acid which produces Cu^{I} *in situ*. Evolution of dinitrogen was immediate. For heterolytic cyclisations, the diazonium salts **7** were dissolved in water at room temperature, raised to 353 K for twenty minutes and finally cooled. In both cases the products were extracted into ethyl ethanoate and analysed by GC.

(iv) Product composition

Homolysis of **7a** gave a product comprising two components which were recognised by GC-MS as the expected isomeric methyl fluorophenanthrene-10-carboxylates, **13a** and **14a**. Heterolysis of the same compound gave a product which also contained **13a** and **14a** as major components together with a third major component of longer retention time, and two minor components. The third major component exhibited $m/z = 240$ consistent with the formulation $C_{15}H_9FO_2$. Hey and Mulley[18] reported the isolation of 3-phenylcoumarin, **18a**, from a heterolytic Pschorr synthesis of phenanthrene-9-carboxylic acid; notwithstanding the use of the appropriate (*E*)-stilbenediazonium ion as precursor, partial isomerisation of the initial alkene had occurred during the heterolysis. Comparison of the mass spectral fragmentation pattern of our product $C_{15}H_9FO_2$ with that of 3-phenylcoumarin ($C_{15}H_{10}O_2$)[21] confirmed the identity of the unknown third major component of the heterolysis product to be 3-(3-fluorophenyl)coumarin, **18b**. Hey and Osbond[22] cited (*E*) to (*Z*) isomerisation of the alkene function during Sandmeyer chlorination of **19**. Conceivably, the 2-nitro group in **19** and the 2-diazonium function in **7a** assist alkene



18 **a**: X = H
b: X = F
c: X = Cl



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hydration and so enable bond rotation. The minor products in the heterolysis of **7a** are more easily accounted for: one, for which $m/z = 274$, corresponding to $C_{16}H_{12}F_2O_2$, is the product of minor heterolytic fluorodediazoniation *via* the tetrafluoroborate counter ion of **7a** (Schiemann reaction); the other has $m/z = 272$ ($C_{16}H_{13}FO_3$) and is interpreted as the phenolic hydrolysis product of **7a**.

Heterolysis of methyl (*E*)-2-(3-chlorophenyl)-3-(2-diazoniophenyl)propenoate tetrafluoroborate, **7b**, gave products corresponding to each of those described for the heterolysis of the fluoro analogue together with an additional trace product, isomeric with the phenol and with a very similar mass spectral fragmentation pattern. This could be the hydrolysis product arising after isomerisation of the initial alkene.

None of the products from either the homolysis or the heterolysis of each substrate **7** indicated the occurrence of any side reaction which could compromise the phenanthrene product-ratio as an index characteristic of the particular reaction condition.

(v) Identification of isomeric phenanthrenes

It was apparent from the GC analysis that the particular methyl fluorophenanthrenecarboxylate isomer, which is the major isomer from the homolytic Pschorr cyclisation of **7a**, is the minor isomer from its heterolytic cyclisation. Which isomer is which was determined from ^{19}F NMR spectra: **14a** was expected to be the isomer which exhibited one *ortho* proton coupling in its ^{19}F

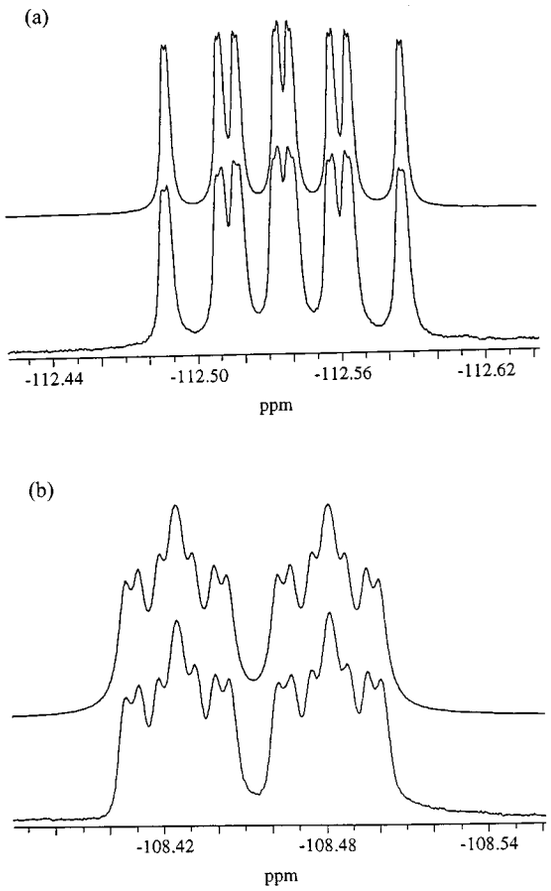


Fig. 1 Experimental (lower) and simulated (upper) ^{19}F NMR spectra (470.8 Hz) of (a) methyl 2-fluorophenanthrene-10-carboxylate, **13a**, (b) methyl 4-fluorophenanthrene-10-carboxylate, **14a**.

NMR signal whereas **13a** was expected to exhibit two such couplings. The isomer mixture from homolysis gave two ^{19}F NMR signals which were multiplets centred at *ca.* δ −108.5 and δ −112.5, relative to CCl_3F; these gave relative integrated intensities of (1.21 ± 0.06) : 1.00, respectively. Both multiplets were analysed in terms of four doublet splittings and satisfactorily simulated (Fig. 1a and b). The couplings shown by the signal of the major isomer at δ −108.5 were 14.3, 5.1, 3.2 and 1.3 Hz, respectively; those shown by the minor isomer at δ −112.5 were 11.8, 7.5, 5.7 and 0.5 Hz, respectively. For each isomer, three of these splittings no doubt arise from the three protons of the fluorinated ring and the fourth is most probably due to H(5). Three-bond (*ortho*) couplings of hydrogen to F are expected to exceed 6 Hz, four-bond (*meta*) couplings to be in the range 5–6 Hz and five-bond (*para*) couplings to be up to 2 Hz.[23] The major isomer from the homolysis is thus identified as methyl 4-fluorophenanthrene-10-carboxylate, **14a** and the minor isomer is the 2-fluoro isomer. The converse is true for the phenanthrenes from heterolyses.

There was a similar alternation between the major and minor isomers from homolysis and heterolysis of methyl (*E*)-2-(3-chlorophenyl)-3-(2-diazoniophenyl)propenoate tetrafluoroborate, **7b**. On grounds of electronic analogy with the fluorine case, the major isomer from homolysis was expected to be methyl 4-chlorophenanthrene-10-carboxylate, **14b**. This was confirmed by experiments in which nuclear Overhauser enhancements in the proton spectra of the isomeric mixture were examined. The ^1H NMR spectrum of the mixture of products from homolysis of **7b**, recorded at 500 MHz, showed the presence of two methyl singlets at δ 4.03 and 4.04 of relative integrated intensity 1.54 : 1. There were two additional singlets in the same ratio at δ 8.39 and 8.52 which were assigned to the H(9) protons in the two isomers;[24] irradiation at the frequency of each of these signals in turn caused enhancement of the corresponding methyl signal thus confirming the assignment. The minor isomer also exhibited a signal at δ 9.00 showing only one small doublet splitting of 2.2 Hz. This signal is ascribed to H(1) in **13b** as it is the only ring-proton in either isomer [other than the already identified H(9) protons] which does not have an adjacent *ortho* proton and hence does not also show a larger splitting. The assignment was confirmed by the observation that irradiation at the frequency of the doublet also caused enhancement of the methyl resonance at δ 4.04. The signal from H(1) in the major isomer occurred as a doublet of doublets (J_{HH} 8.4 and 1.3 Hz) centred at δ 8.78, irradiation of which resulted in the enhancement of the methyl resonance at δ 4.03. The observations thus confirm that **14b** is the major isomer from the homolysis of **7b** and **13b** is the minor.

Table 1 Mean molar ratios of methyl 2- and 4-halophenanthrene-10-carboxylates from Pschorr cyclisations of **8a** and **8b**

		4-Fluoro : 2-Fluoro	4-Chloro : 2-Chloro
Homolysis	GC	(1.09 ± 0.01) : 1.00	(1.44 ± 0.08) : 1.00
	NMR	(1.21 ± 0.06)[a] : 1.00	(1.54 ± 0.08)[b] : 1.00
Heterolysis	GC	1.00 : (1.35 ± 0.02)	1.00 : (1.12 ± 0.05)

[a] By integration of ^{19}F NMR signals. [b] By integration of ^1H NMR signals from ester Me groups and H(9) protons.

(vi) Relative proportions of isomeric phenanthrenes

The mean molar ratios of the methyl halophenanthrene-carboxylates produced in both homolytic and heterolytic variants of Pschorr cyclisation of **7** are given in Table 1. The values for the fluorinated phenanthrenes are based on duplicate or triplicate GC analyses of the products of five homolytic and six heterolytic cyclisations. Those for the chlorinated phenanthrenes are based on analyses in triplicate of the products of two homolyses and two heterolyses. The quoted uncertainties correspond to 95% confidence levels. For the GC analysis, isomeric phenanthrenes were assumed to have equal response factors. The corresponding molar ratios obtained by integration of NMR signals are given for comparison; here an uncertainty of 5% is indicated. Although NMR gives a marginally higher estimate of the homolytic product ratio than GC, the differences are not regarded as significant. It is apparent that each cyclisation mechanism shows a regioselectivity which is characteristic and significantly different from that shown by the other.

(vii) An absolute rate constant for homolytic Pschorr cyclisation

The *prima facie* evidence is that Pschorr phenanthrene ring closure occurs very rapidly: Hey and Mulley[18] noted the typically high yields (*ca.* 90%) which imply that alternative reactions of the intermediate radical do not compete effectively; Ruggli and Staub[25] reported the yield of phenanthrene from the cyclisation of *cis*-2-aminostilbene (by diazotisation in ethanol using amyl nitrite and subsequent decomposition in the presence of Cu powder) to be, surprisingly, *increased* in the presence of sodium hypophosphite. Hypophosphite and alcohol are commonly used as hydrogen donors for the reduction of aryl radicals.[26] Whatever their rôle in improving the phenanthrene yield, their reduction of the intermediate aryl radical evidently does not compete very effectively with its cyclisation.

We have previously estimated a value of (9.0 ± 1.0) × 10^7 dm^3 mol^{-1} s^{-1} at 293 K for the rate constant for the abstraction of hydrogen from hypophosphorous acid [phosphinic acid, $H_2P(O)OH$] by 2-benzoylphenyl radical and evidence was also presented that the *ortho* benzoyl substituent does not significantly sterically hinder hydrogen abstraction reactions.[16] On the assumption that **8c** reacts at the same rate as 2-benzoylphenyl radical and is similarly unencumbered by its *ortho* side-chain,

Table 2 Competition between reduction and cyclisation of **8c**: ratio of products as a function of the concentration of added hypophosphorous acid

$[H_3PO_2]$/mol dm^{-3}	$R^{H,C}$
0.0	0.000
2.0	0.059
3.0	0.097
4.0	0.129
6.0	0.179
8.0	0.214

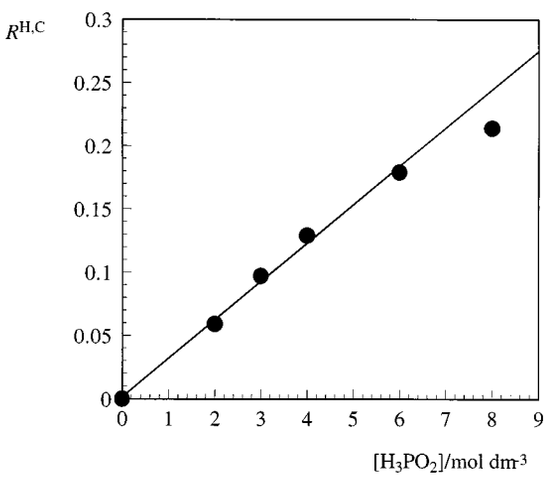
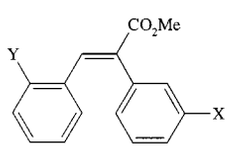


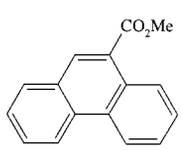
Fig. 2 Competition between reduction and cyclisation of **8c**: product ratio as a function of the concentration of added hypophosphorous acid.

competition between H-abstraction from hypophosphorous acid and Pschorr cyclisation should provide a means of estimating the rate constant for the cyclisation.

A series of decompositions was carried out in which the diazonium salt **7c** was first dissolved in aqueous solutions 0.1 mol dm^{-3} in $Cu(NO_3)_2$ and of variable concentration in $H_2P(O)OH$, and then homolysis was initiated by addition of a small amount of ascorbic acid. When evolution of nitrogen subsided the products, methyl 2,3-diphenylpropenoate **20a** and



20 **a**: X = Y = H
b: X = H, Y = I
c: X = F, Y = H



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methyl phenanthrene-9-carboxylate **21**, were extracted into ethyl ethanoate and their molar ratio quantified by GC, the chromatograph being calibrated by the use of authentic materials. The results are given in Table 2 and plotted in Fig. 2. It is evident from these data that the reduction of the intermediate radical is minor relative to its cyclisation even at the highest concentration of hypophosphorous acid used, consistent with Ruggli and Staub's result.[25]

The reduction/cyclisation product ratio, $R^{H,C}$ = **[20a]**/**[21]**, is an essentially linear function of hypophosphorous acid concentration between 0 and 6 mol dm^{-3} though this linearity is lost at higher concentration when the solution becomes noticeably more viscous. Routine kinetic analysis shows that $R^{H,C}$ is given by eqn. (1), where k^H is the rate constant for hydrogen transfer

$$R^{H,C} = (k^H/k^C)[H_2P(O)OH] \quad (1)$$

and k^C is that for cyclisation. Equating the gradient of the

Table 3 Competition between iodination and cyclisation of **8c**: ratio of products as a function of the concentration of added tri-iodide

$[I_3^-]$/mol dm^{-3}	$R^{I,C}$
0.000	0.000
0.005	0.019
0.099	0.028
0.149	0.048
0.199	0.080
0.248	0.088

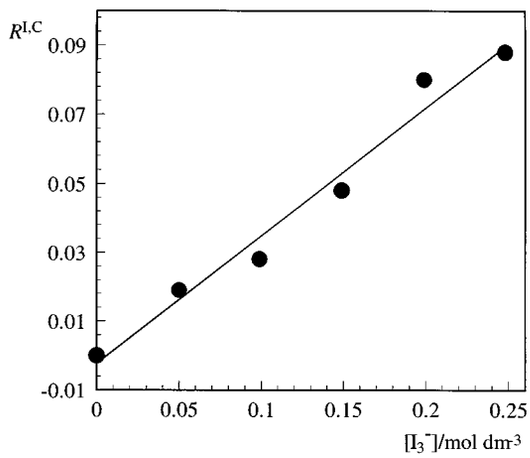


Fig. 3 Competition between iodination and cyclisation of **8c**: product ratio as a function of the concentration of added tri-iodide ion.

linear section of the graph [(0.030 ± 0.004) dm^3 mol^{-1}] to (k^H/k^C) and substituting k^H = (9.0 ± 1.0) × 10^7 dm^3 mol^{-1} s^{-1} gives k^C = (3.0 ± 0.5) × 10^9 s^{-1} as the cyclisation rate constant; the uncertainties in these figures represent the 95% confidence levels.

In view of the indirect method of evaluation of this rate constant, it was felt desirable to obtain a confirmatory comparison. Abeywickrema and Beckwith[27] have provided Arrhenius activation parameters for the cyclisation of 2-(but-3-enyloxy)phenyl radical in benzene which allow the calculation of a cyclisation rate constant at 293 K of (2.5 ± 0.4) × 10^8 s^{-1}. These authors have also used this cyclisation as a radical clock for estimating a rate constant of 'about 5.0 × 10^9 dm^3 mol^{-1} s^{-1}' for the transfer of iodine from I_3^- and/or I_2 to the same radical in acetone at 293 K;[28] data given in their paper can be used to obtain the more precise figure of (4.2 ± 1.8) × 10^9 dm^3 mol^{-1} s^{-1} for the iodine transfer rate constant. We have carried out experiments where **7c** was homolysed at 293 K in acetone solutions which were 0.40 mol dm^{-3} in sodium iodide and of various, lesser concentrations in iodine. The molar ratio of iodinated stilbene to phenanthrene produced $R^{I,C}$ = **[20b]**/**[21]** (measured by GC calibrated with authentic materials) is a linear function of the iodine concentration and hence of tri-iodide concentration (since $[I^-] \gg [I_2]$ and the triiodide formation constant in acetone is 2 × 10^8 dm^3 mol^{-1}),[29] according to eqn. (2) where k^I is the iodine transfer rate constant and k^C is

$$R^{I,C} = (k^I/k^C)[I_3^-] \quad (2)$$

again the cyclisation rate constant (Table 3 and Fig. 3). Equating the gradient of the plot [(0.332 ± 0.084) dm^3 mol^{-1}] with (k^I/k^C) and adopting k^I = (4.2 ± 1.8) × 10^9 dm^3 mol^{-1} s^{-1} enables evaluation of k^C as (1.2 ± 0.5) × 10^{10} s^{-1}.

We thus have two estimates for the rate of phenanthrene formation from **8c**: (3.0 ± 0.5) × 10^9 s^{-1} in water and (1.2 ± 0.5) × 10^{10} s^{-1} in acetone. The agreement is fair considering the indirect methods by which both have been derived. We adopt the former in view of the solvent difference and the extent of

interpolation in evaluating the latter. Both values confirm that the rate constant for homolytic phenanthrene closure is very large.

(viii) Conformational mobility

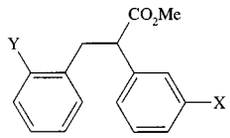
In view of the large rate constant for cyclisation which has been estimated, the possibility arises that the isomeric product ratio might be conformationally affected. The literature contains contradictions in respect of the conformational properties of *cis*-stilbenes. For example, Trætterberg and Frantsen [30] reported a gas-phase electron diffraction study of the molecular structure of *cis*-stilbene itself at 438 K. They concluded that it has a propeller-like conformation of C_2 symmetry in which the aryl rings are rotated about 40° out of coplanarity with the alkene bond. The magnitudes found for the vibrational amplitudes of non-bonded carbon atoms were construed to be consistent only with a rigid conformation and not with a structure in which the phenyl groups are able to rotate. In contrast, the majority of spectroscopic and theoretical results, while agreeing with a C–Ph twist angle of similar magnitude, imply low barriers to phenyl ring rotation; *e.g.* work aimed at explaining the variation with stereostructure of the shape of the long wavelength UV absorption band in stilbenes concluded that the barrier to torsion of the phenyl groups in the ground state of *cis*-stilbene is 26 kJ mol^{-1} (6.2 kcal mol^{-1}) [31] which translates, *via* the Eyring equation, into a torsion rate of 1.4×10^8 s^{-1} at 293 K. Also consistent with a rapid rotation of the phenyl rings at ambient temperature is the observation that the long wavelength UV absorption of *cis*-stilbene shows a bathochromic shift when the temperature is lowered from ambient to 77 K: depletion of the populations of the upper torsional vibrational levels of the ground state results in a shift to a lower value of the C–Ph twist angle of maximum probability, with a consequent increase in conjugation and concomitant reduction in electronic excitation energy.[32,33] The number of signals in the ^{13}C NMR spectra of *cis*-stilbenes indicates that, at the usual temperature of measurement, the pairs of *ortho* and *meta* atoms in each ring are equivalent, indicative of a rapid exchange of environments.[34]

We have examined the temperature dependence of the ^{1}H spectrum at 400.13 MHz and the ^{19}F spectrum at 470.8 MHz of methyl 2-(3-fluorophenyl)-3-(phenyl)propenoate, **20c**, in toluene-d_8 solution. The ^{1}H spectrum was observed in the temperature interval 198–298 K and the ^{19}F spectrum in the interval 206–350 K. Although the chemical shifts are temperature dependent, indicative perhaps of ring current effects arising from varying torsional rates, there is no evidence of any line broadening with decrease in temperature which could be ascribed to an approach to the lower limit of the fast exchange regime for torsion of the fluorinated ring.

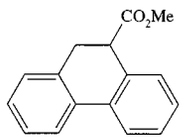
(ix) A search for evidence of Ar_1-5 cyclisation

In the homolytic Pschorr phenanthrene ring closures described above, it is unlikely that direct evidence of any Ar_1-5 cyclisation would be observed. The prevailing condition of excess Cu^{2+} would ensure the oxidation of the *spiro*-cyclohexadienyl radicals **15** to **16**, which would be followed by rearrangement of the carbocation to give the same products as $Ar_{2(6)}$-6 cyclisation (Scheme 3).[35–37] In an endeavour to detect whether the cyclising radical **8c** might be capable of Ar_1-5 cyclisation, we treated methyl (*E*)-3-(2-iodophenyl)-2-(phenyl)propenoate **20b** with tributyltin hydride in benzene solution at reflux, initiating the reaction with azoisobutyronitrile. Under these essentially reductive conditions, it was hoped that any of the *spiro*-cyclohexadienyl radical **15c** might either be reduced or dimerised.[38]

After standard procedures to remove tin compounds, analysis of the reaction mixture by GC-MS showed unreacted **20b** and the cyclised (and oxidised) product, methyl phenanthrene-9-carboxylate **21**, as the major components. The minor components included the (*Z*)-isomer of the reactant, the (*E*)- and



22 **a**: X = Y = H
b: X = H, Y = I



23

(*Z*)-isomers of **20a**, the alkene-reduction products **22a** and **22b**, and methyl 9,10-dihydrophenanthrene-9-carboxylate **23**. [Some hydrodeiodination of the reactant was expected and a blank experiment using **20a** showed alkene isomerisation and reduction also to be a consequence of the reaction conditions.] There was sufficient discrepancy between the mass spectrum found for the material we identify as methyl 9,10-dihydrophenanthrene-9-carboxylate **23** and the literature precedent [39] for this compound that—in order to be sure of our assignment—we synthesised the authentic material by reduction of **21** using lithium in liquid ammonia.[40,41] The ^{1}H NMR exhibited by **23** was in agreement with precedent [40] and a ^{13}C NMR spectrum entirely consistent with its structure was obtained. It gave a GC retention time and mass spectrum identical with that of the component from tin hydride reduction which we identify as methyl 9,10-dihydrophenanthrene-9-carboxylate.

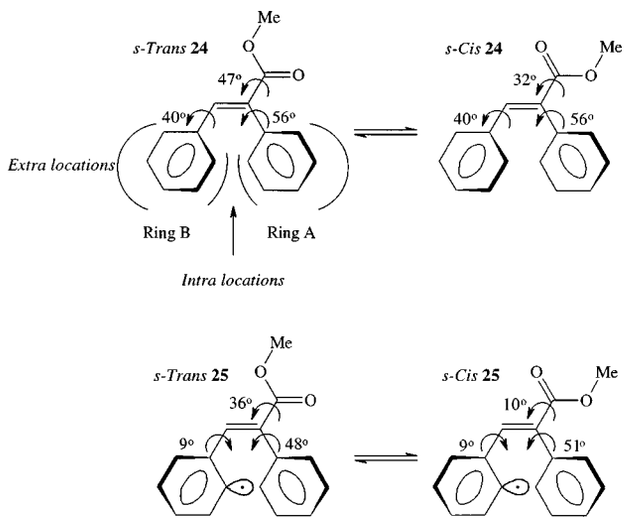
The (*E*)- and (*Z*)-isomers of **20a** and **23** were the only products detected having *m*/*z* 238. There was thus no evidence of any isomeric component which might be a reduction product of the *spiro*-cyclohexadienyl radical **15c**. The only species exhibiting *m*/*z ca.* 474 [expected for a dimer of **15c**] was the isotopomeric fragment ion $[C_{24}H_{33}O_2{}^{120}Sn]^+$ arising from a very minor product (<0.5%). There was thus no positive evidence found for the involvement of the *spiro*-cyclohexadienyl radical **15c** during the reactions in refluxing benzene of the stilbene radical **8c**. In view of this, we consider it to be unlikely that radicals **15a** or **15b** have any rôle in phenanthrene formation in aqueous solution.

(x) Semi-empirical molecular orbital calculations

We have carried out AM1 molecular orbital calculations [42,43] for various relevant species (UHF for radicals) in order to obtain insight into their conformational and electronic properties.

a) Conformational properties. In agreement with others we find for *cis*-stilbene a minimum energy structure in which the phenyl rings are conrotated 40° from coplanarity with the alkene.[44] Monohalogenation of one of the rings in the 3-position with either F or Cl has negligible consequence for these rotation angles. When *cis*-stilbene is functionalised on the alkene by a CO_2Me group, the rotation from coplanarity of ring B [see **24**] remains at 40° but that of ring A increases to 56° irrespective of the conformation of the ester group. For the *s-trans* enoate conformation, the ester group was rotated 47° from coplanarity with the alkene while for the *s-cis* enoate conformation the rotation was 32°.

Conversion of a *cis*-stilbene into an aryl radical by removal of a hydrogen atom from an *ortho* position of one ring has a consequence for the conformation when the hydrogen is removed from an *intra* location [see **24**]: then the rotation of the radical ring decreases. For *cis*-stilbene itself, the radical ring moves into coplanarity with the alkene while the intact ring adopts a twist angle of 38°. [If the hydrogen is removed from an *ortho* position in an *extra* location, both rings retain the 40° twist of the parent hydrocarbon consistent with this angle of twist being determined by the balance of conjugation with steric repulsion between *intra*, *ortho* hydrogens.] Similarly, when the *intra*, *ortho* hydrogen is removed from ring B of **24**, the radical ring adopts more nearly coplanar preferred conformations [see **25**].



The various conformational energy minima which occur during rotation of ring A or the ester group in **25** are essentially isoenergetic. Rotation through 180° of ring A in **25** requires the surmounting of two disparate energy barriers which are of similar sizes for both conformations of the enoate function: in each case, the lower barrier of *ca.* 10 kJ mol^{-1} occurs when the π-systems of ring A and the alkene are orthogonal and conjugation is lost; the higher barrier of *ca.* 22 kJ mol^{-1} occurs as ring A passes through coplanarity with the alkene and sweeps past ring B. The barriers to rotation of the ester function in **25** are about 10 kJ mol^{-1}. As a consequence of this low value, the twist of the ester group is sensitive both to the formal conformation of the enoate and the rotational state of ring A. In the *s-cis* enoate conformation, the ester group varies from being almost coplanar with the alkene in the conformational minima of the A ring to being almost orthogonal at its higher conformational maximum. For the *s-trans* enoate conformation, the twist of the ester group is more marked in the conformational minima of ring A and less marked at its higher maximum than is the case in the *s-cis* enoate.

Substitution of **25** in the 3-position of ring A by fluorine has little consequence for the barriers to rotation of the substituted ring. However, substitution by chlorine increases the lower barrier marginally to *ca.* 12.5 kJ mol^{-1} and the higher barrier more significantly to *ca.* 30 kJ mol^{-1}. The higher barrier heights of 22 and 30 kJ mol^{-1} calculated for **25** and its 3-chlorinated derivative translate, *via* the Eyring equation, into respective torsion rates of 7.3×10^8 and 2.7×10^7 s^{-1} at 293 K. These rates imply that in **25** and its halogenated derivatives torsion of ring A is a slower process than homolytic Pschorr cyclisation. This is not important, however, for the regioselectivity of cyclisation of the halogenated derivatives since this does not depend on which face of ring A is attacked but upon which ring-position and the relevant positions are accessible on either face.

The *lower* barrier encountered during rotation of ring A is associated with a libration of the ring which exchanges the 3-substituent between *intra* and *extra* locations; a barrier of 12.5 kJ mol^{-1} as in the chloro-radical corresponds to an exchange rate of 5×10^{10} s^{-1} at 293 K, so this oscillation is at least an order of magnitude faster than the homolytic Pschorr cyclisation rate. The oscillation also exchanges the ring positions on ring A which are attacked on cyclisation between locations each alternately 3.9 and 2.5 Å from the radical centre on ring B. The conformational minima between which the oscillation occurs are almost isoenergetic, thus each ring position which is attacked during cyclisation is exposed to the radical centre for equal times at equal distances and we deduce that libration of ring A is not significant in determining the Pschorr product ratio which must therefore be electronically controlled.

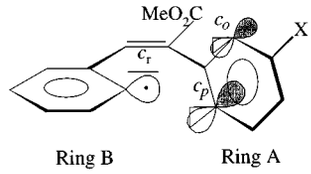


Fig. 4 Structure of radicals **8a** and **8b** in which ring A is orthogonal to the alkene and ring B, and in which the radical centre is equidistant from the attacked atoms.

b) Electronic properties. In order to understand how the regioselectivity of the homolytic Pschorr cyclisation process is governed, we have adopted a simple frontier orbital-type approach, the reasoning being that, in view of the high reactivity demonstrated for the cyclisation, it is likely that transition states will be reactant-like (early). We have carried out AM1 UHF calculations for **8a** and **8b** where ring B, with its radical centre located *intra*, is held coplanar with the alkene and ring A is held orthogonal to the alkene plane. The ester group was allowed to optimise in the *s-trans* conformation. The purpose of the calculations was to obtain the amplitudes of the π-orbitals of ring A and their energies relative to that of the radical orbital. Since the orthogonality of ring A decouples its π-system from that of the rest of the molecule, the conformation of the ester moiety was secondary. This structure, which resembles in geometry and energy that at the pinnacle of the low librational barrier discussed above, equalises the distances between the radical centre and the two atoms which are attacked in the Pschorr ring closure (see Fig. 4). In Table 4 are summarised the energies of the seven molecular orbitals comprising the isolated π-system of ring A together with the components of their amplitudes (c_o and c_p) that are parallel to the alkene bond at those atoms *ortho* and *para* to the substituent halogen which are attacked on cyclisation. Also included in Table 4 are the energy and amplitude (c_r) parallel to the alkene bond of the SOMO at the radical centre.† It is noteworthy that the SOMO lies at lower energy than the upper two occupied molecular orbitals of ring A in both radicals. This is not a consequence of the rigid structure imposed on the radicals in these calculations. The same situation arises for structures which are free to optimise their geometries.

We also carried out calculations for chlorobenzene, fluorobenzene and the phenyl radical. In the latter case, the in-plane singly-occupied orbital and the upper pair of occupied π-orbitals had closely similar energies, −10.2441, −10.1590 and −9.9908 eV, respectively.

Discussion

(i) The effective molarity of homolytic phenanthrene ring closure

The second order rate constant for the addition of phenyl radical to benzene (in Freon 113) which has been measured[15] to be $(4.5 \pm 0.3) \times 10^5$ dm^3 mol^{-1} s^{-1} at 298 K and the rate constant of $(3.0 \pm 0.5) \times 10^9$ s^{-1} estimated in (vii) above for the cyclisation of **8c**, when statistically corrected to account for the relative numbers of equivalent reaction sites, together allow an effective molarity for phenanthrene ring closure of $[3 \times (3.0 \pm 0.5) \times 10^9]/(4.5 \pm 0.3) \times 10^5$ *i.e.* $(2.0 \pm 0.4) \times 10^4$ mol dm^{-3}, to be calculated. (Here the solvent difference and a 5 °C temperature difference are ignored.) This figure may be compared with the values of up to 5×10^5 mol dm^{-3} which have been estimated for homolytic additions to alkenes.[45]

It follows from the Eyring equation that the effective molarity, M_E, found by a comparison of first and second order rate

† In a UHF calculation all orbitals are singly occupied; by SOMO in this context is meant that orbital in the α-spin set which is not paired with an occupied orbital of comparable symmetry and energy in the β-spin orbitals.

Table 4 AM1 energies of the ring A π-orbitals and the SOMO, and the components of their amplitudes which are parallel to the alkene in **8a** and **8b** oriented as in Fig. 4

	8a			**8b**		
Ring A	Energy/eV	c_o	c_p	Energy/eV	c_o	c_p
π(1)	−16.059	−0.16113	−0.06065	−14.155	0.20237	0.12277
π(2)	−12.956	−0.26504	−0.35642	−12.319	0.10990	0.26672
π(3)	−9.891	−0.50180	0.05863	−9.781	0.38324	−0.05250
π(4)	−9.532	0.22767	−0.49622	−9.474	0.15006	−0.35261
π(5)	0.177	−0.19296	−0.23430	0.252	−0.10901	−0.40384
π(6)	0.389	−0.33711	0.30015	0.416	0.49887	−0.33174
π(7)	2.648	−0.28566	−0.30492	2.688	−0.32705	−0.35504
SOMO		c_r			c_r	
	−10.598	0.68789		−10.576	0.69888	

Table 5 Comparison with observed values of the regioselectivities of homolytic phenanthrene cyclisation calculated from bimolecular partial rate factors

	Bimolecular regioselectivity[a] *i.e.* f_o/f_p	$\delta\Delta G^{\ddagger}_{bimolec} = RT \ln m(f_o/f_p)$/ J mol^{-1}	$\delta\Delta G^{\ddagger}_{unimolec}$/ J mol^{-1}	Unimolecular regioselectivity **14/13**	
Substituent				Calculated	Observed
F	2.0/1.1 = 1.82	1484	591 ± 22	1.27 ± 0.01	1.09 ± 0.01
Cl	2.5/1.5 = 1.67	1270	505 ± 19	1.23 ± 0.01	1.44 ± 0.08

[a] Values from ref. 37.

constants is related to the difference in free energies of activation for the two compared processes by eqn. (3). An effective

$$\ln (M_E/\text{mol dm}^{-3}) = \delta\Delta G^{\ddagger}/RT \quad (3)$$

molarity of (2.0 ± 0.4) × 10^4 mol dm^{-3} thus corresponds to a difference in free energy of activation of (24.5 ± 0.5) kJ mol^{-1} at 298 K. Using the Eyring equation, the free energy of activation for the phenylation of benzene may be calculated from the rate constant[15] to be (40.7 ± 0.2) kJ mol^{-1} at 298 K; hence the observed effective molarity is equivalent to a 40% reduction in the activation free energy barrier on going from the bimolecular to the unimolecular reaction mode.

Partial rate factors for the homolytic phenylation of the positions *ortho* and *para* to the substituent in fluorobenzene and chlorobenzene have been determined for oxidising conditions at 80 °C (Table 5).[37] The ratios of these figures correspond to statistically corrected *ortho*/*para* product ratios of 1.82 and 1.67 for the phenylation of fluorobenzene and chlorobenzene, respectively. If it is assumed that the cyclisations of **8a** and **8b** occur with the same effective molarity as the cyclisation of **8c**, the differences in activation free energy which determine the cyclisation product ratios will be 40% of the differences which determine the bimolecular product ratios and, as a consequence, the intramolecular regioselectivity is expected to be less than the intermolecular regioselectivity. In Table 5 cyclisation product ratios calculated on this basis are compared with those observed.

The intramolecular ratios, both calculated and observed, are indeed smaller than the intermolecular ratios but the above reasoning leads to the expectation that the *ortho*/*para* ratio which is larger for F than Cl in the bimolecular reaction should remain the larger in the cyclisation; this is not the case. Nor does the calculation give a good prediction of either of the individual values: the cyclisation of **8a** is calculated to occur with a greater regioselectivity than is observed experimentally whereas the converse is true for **8b**.

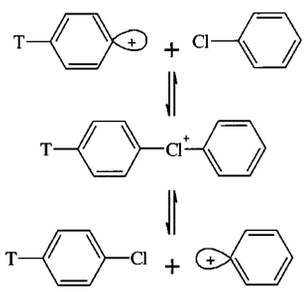
Halogenation increases the reactivity of an aromatic ring to homolytic substitution: competition experiments at 80 °C indicate that, relative to benzene itself, the reactivities in phenylation of fluorobenzene and chlorobenzene are 1.23 and 1.43, respectively.[37] An absolute rate constant for the homolytic phenylation of fluorobenzene is not available but the ratio of absolute rate constants determined for the homolytic phenylation of chlorobenzene [(1.18 ± 0.13) × 10^6 dm^3 mol^{-1} s^{-1}] and benzene [(4.5 ± 0.3) × 10^5 dm^3 mol^{-1} s^{-1}] in Freon 113 at the lower temperature of 25 °C[15] indicates a relative reactivity for chlorobenzene of 2.6 ± 0.3 under these conditions. If the inter- and intramolecular reactions were activated to similar extents by a substitution, the effective molarity of phenanthrene formation would be expected to remain independent of ring substitution. The inter- and intramolecular transition states would be separated by an essentially constant free energy difference as the absolute free energies of transition states changed under substitution. The consequence is that the more strongly activating substituent should cause the greater loss of regioselectivity in the intramolecular mode when compared with the intermolecular mode. Again the facts do not agree: Cl is the more activating halogen but it shows the lesser loss of regioselectivity between the inter- and intramolecular reaction modes and we are forced to conclude that the effective molarity of a phenanthrene cyclisation must depend upon the particular substituent in the ring undergoing homolytic attack. Although the effective molarities for the closure of different substituted stilbenes to phenanthrenes must derive, in part, from essentially constant losses in translational and conformational entropy, nevertheless, there must also be enthalpic differences which affect the magnitudes of the observed regioselectivities of closure. Steric hindrance can be disregarded in the present instance as homolytic phenanthrene ring-closure occurs with greater selectivity for the position *ortho* to the larger halogen.

(ii) The effective molarity of heterolytic phenanthrene ring closure

In the absence of absolute rate constants for both intermolecular electrophilic phenylations and heterolytic phenanthrene cyclisation reactions, the direct calculation of an effective molarity for the latter is not possible. Even a comparison of the regioselectivities of the two types of reaction is difficult for want of reliable values. The most recent isomeric phenylation ratios[46] and derived partial rate factors for the electrophilic phenylation of neat fluorobenzene and chlorobenzene have used radiogenically produced Ph^+ where 4-[^{3}H]-

phenyl cations were produced by radioactive decay of 1,4-ditritiobenzene.

The statistically corrected *para*/*ortho* ratios were 1.4 and 0.84 for fluorobenzene and chlorobenzene, respectively. However, in addition to attack by Ph^+ at the ring carbon positions, it was shown that substrates incorporated the radioactive label *via* reversible reaction *at the substituent*. This exchange accounts for 5% and 22%, respectively, of the total radioactivity of the recovered aromatic products in fluorobenzene and chlorobenzene (Scheme 4).



Scheme 4

The possibility of reversible capture of the phenyl cation by the halogen could result in an enhancement of the reactivity of the *ortho* positions over their notional intrinsic reactivity as dissociation of a diphenylchloronium ion could deliver the electrophile preferentially to the adjacent *ortho* positions. Such a process may be less likely in dilute solution of the halobenzene in a polar solvent. Statistically corrected *para*/*ortho* ratios of 0.75 and 1.15 have been reported[47] for the phenylation of chlorobenzene in acetonitrile and dimethyl sulfoxide, respectively, the source of Ph^+ or other phenylating entity [see (v) below] being heterolysis of benzenediazonium ion at 40 °C. Evidently, the behaviour in MeCN resembles that in the neat substrate where electrophile capture by the halogen substituent may be important, whereas in DMSO a greater relative reactivity of the *para* position is apparent, consistent with less (or no) capture of the electrophile by Cl.

Comparison of the *para*/*ortho* ratio for the intermolecular phenylation of neat fluorobenzene (where electrophile capture by the halogen is minor),[46] *i.e.* 1.4, with that for cyclisation of **17a** in aqueous solution, *i.e.* 1.35, shows no significant difference in selectivity and, likewise, comparison of the regioselectivity of phenylation of chlorobenzene in DMSO,[47] *i.e.* 1.15, with that of cyclisation of **17b** in aqueous solution, *i.e.* 1.12, also shows no significant difference. On the assumption that these comparisons are valid, and following the argument in the previous section that a reaction which exhibits an effective molarity should show a reduction in regioselectivity between its bimolecular and unimolecular modes, it appears that heterolytic phenanthrene ring closure has an effective molarity which is not detectably different from unity.

Taken together our results indicate that whether or not the closure of a stilbene reactive intermediate to a phenanthrene manifests an effective molarity is governed by the nature of the cyclising intermediate, whether it be cation or radical. Only the homolytic closure exhibits an appreciable effective molarity and here its magnitude is dependent on the nature of substituents.

(iii) Regioselectivities of homolytic arylation reactions

Referring to Fig. 4, the regioselectivity of ring closure will be determined by the relative strength of the interactions beween the radical centre and the two ring atoms attacked. This can be estimated by application of a second order perturbational expression[48] to calculate stabilisations ε for the interaction of the singly occupied orbital with the π-orbitals of ring A at each attacked atom. Thus the stabilisation, ε_o resulting from interaction at the cyclisation position *ortho* to the substituent is given by eqn. (4), where c_r and c_o are orbital amplitudes as

$$\varepsilon_o = -(c_r\gamma)^2 \sum_{n=1}^{7} \frac{c_{o,n}^2}{|E_n - E_r|} \qquad (4)$$

indicated for Fig. 4 and given in Table 4, γ is an appropriate bond integral for the formation of the new C–C bond and $|E_n - E_r|$ is the magnitude of the energy difference between the *n*th π-orbital of ring A and the singly occupied orbital.

An analogous expression holds for the stabilisation resulting from interaction at the ring position *para* to the substituent. In each case the sum is taken over all seven π-orbitals of ring A as radical stabilisation may result from interaction with both filled and empty orbitals. In fact, the contribution from interactions with unfilled orbitals is minor, particularly for **8a**. The calculated *ortho*/*para* ratio ($\varepsilon_o/\varepsilon_p$) for each radical is thus given by eqn. (5).

$$\varepsilon_o/\varepsilon_p = \left[\sum_{n=1}^{7} \frac{c_{o,n}^2}{|E_n - E_r|}\right] \Big/ \left[\sum_{n=1}^{7} \frac{c_{p,n}^2}{|E_n - E_r|}\right] \qquad (5)$$

For both radicals, the main contribution to stabilisation arises from interaction of the radical with filled orbitals π(3) for the *ortho* site and π(4) for the *para* site. The values obtained for **8a** and **8b** were 1.47 and 1.32, respectively. These compare with the observed values of 1.09 and 1.44, respectively (*cf.* Table 1). Eqn. (5) may also be applied to calculate regioselectivities for the additions of phenyl radical to fluorobenzene and chlorobenzene. The ratios found were 2.49 and 2.08, respectively, which compare with observed values of 1.82 and 1.67 (*cf.* Table 5).

This simple approach thus succeeds in reproducing the lower regioselectivity observed in the homolytic phenylation of chlorobenzene relative to fluorobenzene, and the diminution in regioselectivity when both rings are arylated intramolecularly in Pschorr cyclisations; however, like the previous argument from effective molarity considerations, it fails to account for the lower regioselectivity observed for the Pschorr cyclisation to give fluorophenanthrenes relative to that giving chlorophenanthrenes. The fact of attachment of the halogenated rings to the alkene in **8** reduces their symmetry relative to the corresponding halobenzenes with a consequential effect on the nodal properties of their π-orbitals. This, together with the difference between the two halogens, affects the amplitudes of the halogenated ring π-orbitals at the sites of radical attack and hence the prediction made by eqn. (5). Evidently, the simple approach *via* eqn. (5) is inadequate to reflect the subtler substituent-dependent changes which occur as the orbitals of the reactant radicals evolve into those of the transition states for cyclisation.

(iv) The origin of the effective molarity in homolytic phenanthrene ring closure

For a homolytic aromatic phenylation reaction, the in-plane sp^2 singly-occupied orbital of the phenyl radical must achieve σ-overlap with the molecular π-orbitals of the attacked molecule at one of its ring atoms. Such σ-overlap is most effective when the phenyl radical approaches the attacked site near perpendicularly but some oblique approaches may achieve sufficient overlap for bonding to commence and a cone of trajectories, as envisaged by Menger,[9–11] will arise. It might be expected for a highly reactive entity such as the phenyl radical that the cone of trajectories would be wide, the extent of new bonding in an early transition state not being strongly developed. However, the phenyl radical has its own π-system and the energies of the upper filled π-orbitals are very similar to that of the singly-occupied orbital [see Results (x)b] so, as its approach to an aromatic molecule becomes increasingly oblique, the repulsion between the π-systems will increase as the effectiveness of the required overlap declines. In the extreme case of a face-to-face encounter the radical and molecule will

experience only repulsion. We suggest that the increasing repulsion between the π-systems for increasingly oblique approaches of the phenyl radical to the system under attack serves to narrow the cone of trajectories at each reaction centre and hence limit the fraction of collisions that are productive. By contrast, in the homolytic Pschorr cyclisation to produce a phenanthrene, the rigid alkene framework holds the attacking radical moiety and the attacked ring in orientations which maximise the probability of productive overlap and minimise π–π repulsions; the cyclisation rate is consequently very fast. The effective molarity of homolytic phenanthrene ring closure thus has its origin in an attenuation of the rate of the bimolecular comparator reaction, relative to that of cyclisation, which arises from π–π repulsions in collisions of the radical with its substrate which are too oblique.

(v) Heterolytic phenanthrene closure

Scaiano and Kim-Thuan[49] estimated the lifetime of the phenyl cation in water to be less than 500 ps; in other words, its rate of hydrolysis exceeds 2×10^9 s^{-1}. Later work by Zollinger and coworkers[50,51] showed that, on thermolysis of diazonium ions in water, the phenyl cation *per se* is, in fact, by-passed as an intermediate, solvolysis occurring *via* reaction of the tight [Ph^+–N_2] ion–molecule pair. So presumably it is this paired intermediate to which the high rate of hydrolysis actually applies. Presumably also, a similarly paired species is the intramolecular electrophile in the heterolytic Pschorr cyclisation; were it not, the formation of phenolic products on heterolysis of **7a** and **7b** in water would not be minor in comparison to that of phenanthrenes [see Results (iv)]. We estimate the molar ratio of combined phenanthrenes to the corresponding stilbene-derived phenol to be about 30 : 1 which, in view of the above-mentioned hydrolysis rate, implies a cyclisation rate of *ca.* 6×10^{10} s^{-1}. Lorand[52] has adduced evidence that the trapping of phenyl cation by anions (Br^-, Cl^- and NCS^-) occurs at the diffusion controlled limit and that its rate of reaction with N_2 is close to the limit. It does not seem unreasonable that aromatic rings which are more nucleophilic than molecular nitrogen should also react at rates near the diffusion controlled limit. If this is so, then both inter- and intramolecular heterolytic arylation reactions occur with rate constants of magnitudes of the order of 10^{10} and the inferred effective molarity for the intramolecular case of about unity is explained. The finding of *para*/*ortho* product ratios >1 for both intramolecular and intermolecular processes, however, indicates that site-discrimination persists even at such high reactivities. This is most marked for fluorinated rings. Conceivably, the high electronegativity of fluorine induces sufficient permanent dipolar character on the substrate ring as to confer a Coulombic bias in favour of reaction at the *para* position relative to the *ortho* in diffusional or librational encounter with the cationic electrophile.

Conclusions

Methyl (*E*)-3-(2-diazoniophenyl)-2-(3-halophenyl)propenoate tetrafluoroborates **7a** and **7b** undergo homolysis and heterolysis to produce isomeric phenanthrenes with regioselectivities which are characteristic of the mechanism.

For the homolytic mechanism, no evidence could be found for prior closure of a five-membered ring but a cyclisation rate constant of $(3.0 \pm 0.5) \times 10^9$ s^{-1} at 293 K was estimated for the direct closure of a six-membered ring. This value, when compared with literature precedent for the homolytic phenylation of benzene, indicates that the homolytic ring closure of phenanthrenes is characterised by an effective molarity of about 2×10^4 mol dm^{-3}, though varying with substitution. The origin of this effective molarity lies in a relative attenuation of the bimolecular comparator reaction arising from π–π repulsions between the aryl radical and the attacked ring. In the unimolecular reaction such repulsions are minimised by the rigid framework of the molecule holding the reactive moieties in appropriate orientation. The pattern of homolytic relative reactivities is explained in terms of a simple second-order perturbational treatment which fails only in its account of the relative magnitude of the substituent effect on the cyclisation.

Analysis of patterns of regioselectivity between unimolecular and bimolecular modes indicates that heterolytic phenanthrene ring closure has an effective molarity of approximately unity. This is explained by both reaction modes proceeding with very high rates though site selectivity which may stem from the dipolar nature of the attacked ring still persists.

Experimental

(i) Materials

2,3-Diphenylpropenoic acid (α-phenylcinnamic acid) was a commercial material (Aldrich) used as supplied; other 2,3-diarylpropenoic acids were prepared by condensation of appropriately substituted benzaldehydes with appropriately substituted phenylethanoic acids according to the method of DeTar[53] or a variant employing potassium carbonate as base in place of triethylamine. All propenoic acids were esterified by refluxing in methanol acidified with sulfuric acid. Methyl 2-aryl-3-(2-nitrophenyl)propenoate esters which were precursors of diazonium ions were reduced by means of ammoniacal iron(II) sulfate in aqueous ethanol according to the procedure of Ruggli and Staub[25] and the resultant amines were isolated as their hydrochlorides. These amine hydrochlorides were diazotised in aqueous hydrochloric acid using sodium nitrite and the diazonium tetrafluoroborates were precipitated by addition to excess of sodium tetrafluoroborate solution.[54] The following reaction sequence is typical.

(*E*)-2-(3-Fluorophenyl)-3-(2-nitrophenyl)propenoic acid. 2-Nitrobenzaldehyde (4.7 g), 3-fluorophenylethanoic acid (7.0 g), ethanoic anhydride (17.0 g) and triethylamine (2.7 g) were reacted according to DeTar's procedure[53] for the unfluorinated analogue, producing *(E)-2-(3-fluorophenyl)-3-(2-nitrophenyl)-propenoic acid*, 5.7 g (64%), mp 179–180 °C (Found: M^+, 287.0591. $C_{15}H_{10}FNO_4$ requires *M* 287.0594); *m*/*z* 287 (3%, M^+), 242 (16), 214 (18), 194 (19), 183 (35), 123 (100), 119 (60), 95 (35) and 92 (55); ν_{max}(Nujol)/cm^{-1} 1698 (C=O), 1518 and 1337 (NO_2), 1265 (C–O); δ_H(270 MHz, $CDCl_3$) 6.91–7.03 (m, 4 H), 7.19–7.27 (m, 1 H), 7.41 (quint. d, *J* 7.5, 1.7, 2 H), 8.15 (dd, *J* 8.0, 1.8, 1 H) and 8.31 (s, 1 H); δ_C(67.9 MHz, $CDCl_3$) 115.2 (d, $^2J_{CF}$ 20), 117.4 (d, $^2J_{CF}$ 22), 124.7, 126.1 (d, $^4J_{CF}$ 2.7), 129.4, 129.7 (d, $^3J_{CF}$ 8.2), 131.2, 131.7, 132.8, 133.3, 135.7 (d, $^3J_{CF}$ 8.2), 140.6, 162.3 (d, $^1J_{CF}$ 246) and 171.6.

Methyl (*E*)-2-(3-fluorophenyl)-3-(2-nitrophenyl)propenoate. The above acid (5.4 g) was refluxed for 16 h in methanol (20 cm^3) containing H_2SO_4 (4.5 g). The excess of methanol was then evaporated and iced water added; the organic product was extracted into ether and the extract washed with a saturated solution of Na_2CO_3 and with water. After drying, removal of the ether gave *methyl (E)-2-(3-fluorophenyl)-3-(2-nitrophenyl)-propenoate*, 5.4 g (95%), mp 57–59 °C (aqueous MeOH) (Found: M^+, 301.0762. $C_{16}H_{12}FNO_4$ requires *M* 301.0750); *m*/*z* 301 (1.5%, M^+), 270 (2.5), 256 (15), 242 (30), 214 (15), 194 (15), 183 (25), 123 (100), 119 (45), 95 (25) and 92 (40); ν_{max}(Nujol)/cm^{-1} 1712 (C=O), 1523 and 1337 (NO_2), 1256 (C–O); δ_H(270 MHz, $CDCl_3$) 3.94 (s, 3 H), 6.93–7.05 (m, 4 H), 7.21–7.29 (m, 1 H), 7.43 (quint. d, *J* 7.5, 1.7, 2 H), 8.15 (dd, *J* 7.5, 1.7, 1 H) and 8.2 (s, 1 H); δ_C(67.9 MHz, $CDCl_3$) 52.6, 115.0 (d, $^2J_{CF}$ 20), 117.2 (d, $^2J_{CF}$ 23), 124.6, 126.0 (d, $^4J_{CF}$ 2.7), 129.1, 129.6 (d, $^3J_{CF}$ 8.2), 131.4, 131.7, 133.1, 133.4, 136.3 (d, $^3J_{CF}$ 8.2), 138.3, 148.0, 162.3 (d, $^1J_{CF}$ 246) and 166.7.

Methyl (*E*)-3-(2-ammoniophenyl)-2-(3-fluorophenyl)propenoate chloride. Methyl (*E*)-2-(3-fluorophenyl)-3-(2-nitrophenyl)-propenoate (5.2 g) was reduced to the corresponding amine using ammoniacal $FeSO_4$ in aqueous ethanol according to the procedure of Ruggli and Staub[25] for 2-nitrostilbene. The volume of solvent was reduced and ether was added to the residue; after filtration to remove inorganic products, the amine-containing ether phase was separated and concentrated. Addition of concentrated HCl precipitated *methyl (E)-3-(2-ammoniophenyl)-2-(3-fluorophenyl)propenoate chloride* (2.0 g, 38%), mp 164–166 °C (MeOH–conc. HCl, 1:2) [Found: M^+ (amine), 271.1012. $C_{16}H_{14}FNO_2$ requires 271.1009]; *m/z* 271 (45%, M^+), 240 (90), 238 (25), 222 (20), 212 (100), 211 (80), 183 (30), 165 (15), 117 (15) and 90 (15); ν_{max}(Nujol)/cm^{-1} 3000 and 2500 (NH_3^+), 1682 (C=O), 1276 (C–O); δ_H[270 MHz, $(CD_3)_2SO$] 3.83 (s, 3 H), 4.6 (br, NH_3^+), 6.74 (d, *J* 7.8, 1 H), 6.99 (t, *J* 7.5, 1 H), 7.1–7.2 (m, 3 H), 7.3–7.5 (m, 3 H) and 8.10 (s, 1 H); δ_C[67.9 MHz, $(CD_3)_2SO$] 53.3, 115.6 (d, $^2J_{CF}$ 20), 117.9 (d, $^2J_{CF}$ 22), 123.1, 126.0, 127.3, 128.2, 130.9, 131.0 (d, $^3J_{CF}$ 9.6), 131.4, 134.6, 135.7, 137.1, 138.3 (d, $^3J_{CF}$ 8.2), 162.6 (d, $^1J_{CF}$ 243) and 167.5.

Methyl (*E*)-3-(2-diazoniophenyl)-2-(3-fluorophenyl)propenoate tetrafluoroborate, 7a. Methyl (*E*)-3-(2-ammoniophenyl)-2-(3-fluorophenyl)propenoate chloride (1.6 g) was suspended in a solution of HCl (12 cm^3, 2 mol dm^{-3}), heated for 10 min at 50 °C, then cooled to 0 °C and diazotised by dropwise addition of a solution of $NaNO_2$ (0.5 g) in 3 cm^3 water. After filtration, the solution was added to $NaBF_4$ (1.6 g) in water (4 cm^3) and after stirring 2 h the *methyl (E)-3-(2-diazoniophenyl)-2-(3-fluorophenyl)propenoate tetrafluoroborate* (1.2 g, 61%) was isolated and purified by repeated precipitation from acetone with ether, mp 88–90 °C (decomp.) [Found: M^+ (FAB), 283.0882. $C_{16}H_{12}FN_2O_2$ requires 283.0883]; *m/z* 283 (60% M^+), 223 (100) and 196 (25); ν_{max}(Nujol)/cm^{-1} 2277 (N≡N$^+$), 1722 (C=O), 1279 (C–O), 1070br (BF_4^-); δ_H[270 MHz, $(CD_3)_2SO$] 3.85 (s, 3 H), 7.05–7.25 (m, 3 H), 7.25–7.5 (m, 2 H), 7.75–8.0 (m, 2 H), 8.06 (s, 1 H) and 8.58 (dd, *J* 8.2, 1.2, 1 H).

Directly comparable procedures were used to prepare the following:

(*E*)-2-(3-Chlorophenyl)-3-(2-nitrophenyl)propenoic acid. (49%) mp 158–160 °C (aqueous MeOH), lit.[55] 160–162 °C (Found: M^+, 303.0311. $C_{15}H_{10}NO_4{}^{35}Cl$ requires 303.0320); *m/z* 305 (1.5%, M^+), 303 (5%, M^+), 286 (5), 274 (2), 258 (20), 242 (17), 240 (10), 230 (23), 213 (11), 199 (7), 195 (8), 176 (35), 165 (40), 139 (100), 119 (99); ν_{max}(Nujol)/cm^{-1} 1690 (C=O), 1528 and 1341 (NO_2), 1289 (C–O); δ_H(270 MHz, $CDCl_3$) 6.97–7.06 (m, 2 H), 7.16–7.30 (m, 3 H), 7.38–7.50 (m, 2 H), 8.17 (d, *J* 7.8, 1.7, 1 H) and 8.35 (s, 1 H); δ_C(67.9 MHz, $CDCl_3$) 124.0, 124.8, 128.4, 128.6, 129.5, 130.3, 131.1, 131.7, 133.2, 134.1, 135.3, 138.9, 140.7, 148.1 and 171.2.

Methyl (*E*)-2-(3-chlorophenyl)-3-(2-nitrophenyl)propenoate. (71%) mp 65–66 °C (aqueous MeOH) (Found: M^+, 317.0467. $C_{16}H_{12}{}^{35}ClNO_4$ requires 317.0455); *m/z* 319 (0.3%, M^+), 317 (1.0%, M^+), 290 (0.5), 288 (2), 286 (2), 274 (5), 272 (15), 260 (8), 258 (25), 232 (5), 230 (15), 176 (28), 165 (25), 141 (33), 139 (100) and 119 (65); ν_{max}(Nujol)/cm^{-1} 1711 (C=O), 1520 and 1337 (NO_2), 1244 (C–O); δ_H(270 MHz, $CDCl_3$) 3.94 (s, 3 H), 6.97–7.06 (m, 2 H), 7.18–7.32 (m, 3 H), 7.38–7.50 (m, 2 H), 8.15–8.19 (m, 1 H) and 8.2 (s, 1 H); δ_C(67.9 MHz, $CDCl_3$) 52.7, 124.7, 128.2, 128.5, 129.2, 129.3, 130.2, 131.3, 131.8, 133.2, 133.4, 134.0, 136.0, 138.4, 148.1 and 166.7.

Methyl (*E*)-3-(2-ammoniophenyl)-2-(3-chlorophenyl)propenoate chloride. (44%) mp 146–148 °C (MeOH–conc. HCl, 1:2) [Found: M^+ (amine), 287.0719. $C_{16}H_{14}{}^{35}ClNO_2$ requires 287.0713]; *m/z* 289 (15%, M^+), 287 (45%, M^+), 258 (30), 256 (100), 230 (25), 229 (30), 228 (80), 227 (65), 193 (50), 165 (40) and 117 (18); ν_{max}(Nujol)/cm^{-1} 2900 and 2600 (NH_3^+), 1717 (C=O), 1268 (C–O); δ_H[270 MHz, $(CD_3)_2SO$] 3.74 (s, 3 H), 3.5–5.5 (br, NH_3^+), 6.56 (d, *J* 7.5, 1 H), 6.6–6.8 (m, 1 H), 7.1–7.2 (m, 3 H), 7.3–7.35 (m, 3 H) and 7.92 (s, 1 H); δ_C[67.9 MHz, $(CD_3)_2SO$] 49.5, 115.8, 120.4, 123.7, 128.2, 128.9, 129.3, 129.4, 130.7, 131.1, 132.0, 133.8, 138.8 (2 C), 134.0 and 162.1.

Methyl (*E*)-3-(2-diazoniophenyl)-2-(3-chlorophenyl)propenoate tetrafluoroborate, 7b. (30%) mp 94–96 °C (decomp.) (Found: M^+ (FAB), 299.0585. $C_{16}H_{12}{}^{35}ClN_2O_2$ requires 299.0587); *m/z* 301 (30%, M^+), 299 (90%, M^+), 241 (35), 239 (100) and 192 (40); ν_{max}(Nujol)/cm^{-1} 2273 (N≡N$^+$), 1722 (C=O), 1277 (C–O), 1072br (BF_4^-); δ_H(270 MHz, D_2O) 3.94 (s, 3 H), 7.23 (d, *J* 7.6, 1 H), 7.35–7.48 (m, 2 H), 7.49–7.53 (m, 2 H), 7.85 (appt. t, 1 H), 8.04 (appt. t, 1 H), 8.09 (s, 1 H) and 8.56 (dd, *J* 8.3, 1.1, 1 H).

(*E*)-3-(2-Nitrophenyl)-2-phenylpropenoic acid. (68%) mp 194–196 °C (ethanol), lit.[53] 197.8–198.3 °C. *m/z* 269 (2%, M^+), 241 (1), 224 (15), 208 (10), 196 (32), 176 (20), 152 (16), 119 (68) and 105 (100); ν_{max}(Nujol)/cm^{-1} 1684 (C=O), 1519 and 1339 (NO_2), 1277 (C–O); δ_H(270 MHz, $CDCl_3$) 6.94 (dd, *J* 7.3, 1.6, 1 H), 7.10–7.20 (m, 2 H), 7.20–7.27 (m, 3 H), 7.27–7.41 (m, 2 H), 8.09 (dd, *J* 8.0, 1.6, 1 H) and 8.24 (s, 1 H); δ_C(67.9 MHz, $CDCl_3$) 124.6, 128.2(3C), 129.1, 130.3(2C), 131.6, 131.9, 133.1, 133.6, 134.0, 139.6, 148.1 and 172.2.

Methyl (*E*)-3-(2-nitrophenyl)-2-phenylpropenoate. (61%) mp 73–74 °C, lit.[56] 75–76 °C (Found: M^+, 283.0848. $C_{16}H_{13}NO_4$ requires 283.0845); *m/z* 283 (1%, M^+), 252 (1.5), 238 (15), 224 (25), 196 (25), 176 (20), 165 (30), 119 (55) and 105 (100); ν_{max}(Nujol)/cm^{-1} 1713 (C=O), 1520 and 1350 (NO_2), 1258 (C–O); δ_H(270 MHz, $CDCl_3$) 3.78 (s, 3 H), 6.82–6.85 (m, 1 H), 7.00–7.10 (m, 2 H), 7.10–7.20 (m, 3 H), 7.99 (dd, *J* 7.9, 1.6, 1 H) and 8.02 (s, 1 H); δ_C(67.9 MHz, $CDCl_3$) 52.6, 124.5, 128.0, 128.1(2C), 128.8, 130.2(2C), 131.9, 132.0, 132.9, 134.2, 134.9, 137.3, 148.2 and 176.3.

Methyl (*E*)-3-(2-ammoniophenyl)-2-phenylpropenoate chloride. (65%) mp 177–180 °C (MeOH–conc. HCl, 1:2) [Found: M^+ (amine), 253.1109. $C_{16}H_{15}NO_2$ requires 253.1103]; *m/z* 253 [55%, M^+ (amine)], 222 (85), 220 (35), 204 (15), 194 (100), 193 (75) and 165 (25); ν_{max}(Nujol)/cm^{-1} 3000 and 2500 (NH_3^+), 1717 (C=O), 1259 (C–O); δ_H[270 MHz, $(CD_3)_2SO$–D_2O] 3.71 (s, 3 H), 6.71 (d, *J* 7.4, 1 H), 6.88–6.98 (m, 1 H), 7.05–7.13 (m, 2 H), 7.20–7.30 (m, 5 H), 7.82 (s, 1 H); δ_C[270 MHz, $(CD_3)_2SO$–D_2O] 54.4, 124.3, 128.6, 129.8, 130.0, 130.1(2C), 131.5(2C), 132.0, 132.5, 133.1, 135.6, 135.8, 137.7 and 169.8.

Methyl (*E*)-3-(2-diazoniophenyl)-2-phenylpropenoate tetrafluoroborate, 7c. (60%) mp 87–88 °C (decomp.) (Found: M^+ (FAB), 265.0972. $C_{16}H_{13}N_2O_2$ requires 265.0977); *m/z* 265 (65%, M^+), 236 (20), 222 (5), 205 (100), 193 (10) and 178 (45); ν_{max}(Nujol)/cm^{-1} 2275 (N_2^+), 1727 (C=O), 1268 (C–O) and 1072br (BF_4^-); δ_H[270 MHz, $(CD_3)_2SO$–D_2O] 3.88 (s, 3 H), 7.27 (d, *J* 7.5, 1 H), 7.30–7.5 (m, 5 H), 7.85 (t, *J* 7.8, 1 H), 7.98 (t, *J* 7.8, 1 H), 8.09 (s, 1 H) and 8.75 (d, *J* 8.0, 1 H).

Methyl (*E*)-2,3-diphenylpropenoate, 20a. (72%) mp 74–75 °C, lit.[57] 76–77 °C; *m/z* 238 (100%, M^+), 207 (10), 205 (10), 179 (85), 178 (80), 152 (15), 121 (85); ν_{max}(Nujol)/cm^{-1} 1704 (C=O), 1252 (C–O); δ_H(270 MHz, $CDCl_3$) 3.78 (s, 3 H), 7.00–7.06 (m, 2 H), 7.10–7.25 (m, 5 H), 7.32–7.40 (m, 3 H) and 7.86 (s, 1 H); δ_C(67.9 MHz, $CDCl_3$) 52.4, 127.8, 128.2(2C), 128.6(2C), 129.0, 129.7(2C), 130.6(2C), 132.4, 134.6, 135.8, 140.5 and 168.3, in excellent agreement with precedent.[57,58]

Methyl phenanthrene-9-carboxylate, 21. Methyl (*E*)-3-(2-diazoniophenyl)-2-phenylpropenoate (50 mg) was dissolved in 50 cm^3 of an aqueous solution of $Cu(NO_3)_2$ (0.1 mol dm^{-3}). Addition of 1 cm^3 of a 0.1 mol dm^{-3} aqueous solution of

ascorbic acid initiated homolysis. The solution was stirred for 10 minutes then extracted with ethyl ethanoate (25 cm^3); after evaporation of the extract, the product (32 mg, 96%) was recrystallised from methanol to give *methyl phenanthrene-9-carboxylate*, mp 115–117 °C, lit.[59] 118–119 °C; *m/z* 236 (100%, M^+), 205 (75), 177 (55), 176 (38) and 149 (10); ν_{max}(Nujol)/cm^{-1} 1711 (C=O), 1253 (C–O); δ_H(270 MHz, $CDCl_3$) 4.05 (s, 3 H), 7.60–7.80 (m, 4 H), 7.96 (dd, *J* 7.7, 1.0, 1 H), 8.48 (s, 1 H), 8.65–8.75 (m, 2 H) and 8.90–8.95 (m, 1 H); δ_C(67.9 MHz, $CDCl_3$) 52.3, 122.6, 122.8, 126.1, 126.6, 126.9, 127.0, 127.4, 128.9, 129.0, 129.9, 130.0, 130.6, 132.1, 132.4 and 168.0.

Methyl 9,10-dihydrophenanthrene-9-carboxylate, 23. Methyl phenanthrene-9-carboxylate (313 mg) was reduced by an excess of lithium metal in liquid ammonia (80 cm^3) following the procedure of Harvey and co-workers.[40,41] After work-up and chromatography of the crude product on a silica column, eluting with light petroleum (bp 40–60 °C)–ethyl ethanoate (50 : 1) gave *methyl 9,10-dihydrophenanthrene-9-carboxylate* (60 mg, 19%) as a pale yellow oil; *m/z* 238 (24%, M^+), 179 (100), 178 (47), 177 (7), 176 (11), 152 (8), 151 (6) and 89 (6); ν_{max}(film)/cm^{-1} 1735 (C=O), 1210 (C–O); δ_H(270 MHz, $CDCl_3$) 3.09 (dd, *J* 15.3, 5.8, 1 H), 3.31 (dd, *J* 15.3, 5.8, 1 H), 3.59 (s, 3 H), 3.87 (t, *J* 5.8, 1 H), 7.20–2.40 (m, 6 H), 7.73 (d, *J* 7.5, 1 H) and 7.65 (d, *J* 7.5, 1 H); δ_C(67.9 MHz, $CDCl_3$) 31.7, 44.6, 52.0, 123.6, 124.0, 127.3, 127.6, 127.8, 128.1, 128.4, 128.6, 133.6, 133.7, 134.1, 134.4 and 173.4.

The precedent for the mass spectrum of this compound [lit.[39] 238 (15), 179 (95), 178 (100) and 165 (40)] indicated different relative intensities within the base peak ion-cluster and also the presence of a significant fragment with *m/z* 165. It was the discrepancy between this precedent and the mass spectrum of material from the tin hydride reduction of **20b** which prompted our synthesis. The mass spectrum (EI, 70 eV) of authentically synthesised, gas-chromatographically homogeneous methyl 9,10-dihydrophenanthrene-9-carboxylate exhibited no significant fragment with *m/z* 165. (This fragment corresponds to $[C_{13}H_9]^+$ and others have commented[60,61] on the variability in stability of ions of this composition and hence on the variable intensity of the peak at *m/z* 165 in the spectra which manifest it.)

(*E*)-2-(3-Fluorophenyl)-3-phenylpropenoic acid. (48%) mp 189–191 °C; *m/z* 242 (100%, M^+), 223 (10), 197 (72), 196 (60), 183 (5), 177 (15), 176 (25), 136 (35), 107 (30); ν_{max}(Nujol)/cm^{-1} 1675 (C=O), 1263 (C–O); δ_H(270 MHz, $CDCl_3$) 7.00–7.20 (m, 5 H), 7.20–7.31 (m, 3 H), 7.34–7.43 (m, 1 H) and 8.01 (s, 1 H); δ_C(67.9 MHz, $CDCl_3$) 115.0 (d, $^2J_{CF}$ 20.5), 116.9 (d, $^2J_{CF}$ 21.9), 125.6 (d, $^4J_{CF}$ 2.7), 128.3(2C), 129.7, 130.2 (d, $^3J_{CF}$ 8.2), 130.7(2C), 132.5, 137.5 (d, $^3J_{CF}$ 6.8), 142.9, 162.8 (d, $^1J_{CF}$ 246) and 172.3.

Methyl (*E*)-2-(3-fluorophenyl)-2-phenylpropenoate, 20c. (47%), mp 53–55 °C (aqueous MeOH) (Found: M^+, 256.0903. $C_{16}H_{13}FO_2$ requires 256.0900); *m/z* 256 (100%, M^+), 225 (10), 197 (78), 196 (70), 177 (10) and 121 (90); ν_{max}(Nujol)/cm^{-1} 1724 (C=O) and 1254 (C–O); δ_H(270 MHz, $CDCl_3$) 3.80 (s, 3 H), 6.82–7.53 (m, 9 H) and 7.87 (s, 1 H); δ_C(67.9 MHz, $CDCl_3$) 52.5, 114.8 (d, $^2J_{CF}$ 20.5), 116.8 (d, $^2J_{CF}$ 21.9), 125.6, 128.3(2C), 128.5, 129.3, 130.1 (d, $^3J_{CF}$ 8.2), 130.5(2C), 131.0, 134.1, 137.9 (d, $^3J_{CF}$ 8.2), 141.2, 162.8 (d, $^1J_{CF}$ 246) and 167.7; δ_F(470.6 MHz, PhMe, 300 K) −112.7 (ddd, $^3J_{FH}$ 9.5, $^3J_{FH}$ 8.7 and $^4J_{FH}$ 5.9).

2-Iodobenzaldehyde, being commercially unavailable, was prepared from 2-bromobenzaldehyde by halogen exchange as follows.

2-(2-Bromophenyl)-1,3-dioxolane. Bromobenzaldehyde (18.5 g, 0.1 mol), ethane-1,2-diol (7.15 g, 0.11 mol) and toluenesulfonic acid (1.9 g, 0.01 mol) were refluxed in a Dean–Stark apparatus for 5 h during which 1.8 cm^3 of water was collected.[62] The reaction mixture was thrice washed with 0.3 mol dm^{-3} KOH (100 cm^3), then with water and dried over $MgSO_4$. The crude product (22.0 g, 96%) was distilled to give *2-(2-bromophenyl)-1,3-dioxolane* bp 148–152 °C/14 mmHg, lit.[62] 144–145 °C/12 mmHg (19.0 g, 83%); δ_H(270 MHz, $CDCl_3$) 3.92–4.10 (m, 4 H), 6.06 (s, 1 H), 7.14 (td, *J* 7.6, 1.7, 1 H), 7.27 (td, *J* 7.5, 1.0, 1 H) and 7.49–7.59 (m, 2 H); δ_C(67.9 MHz, $CDCl_3$) 65.3, 102.4, 122.8, 127.3, 127.8, 130.5, 132.8 and 136.6.

2-(2-Iodophenyl)-1,3-dioxolane. 2-(2-Bromophenyl)-1,3-dioxolane (19 g) in THF (20 cm^3) was converted into the Grignard reagent by the method of Wannagat and Schrader.[63] The resultant solution was added dropwise over 2 h to a stirred solution of iodine (23.4 g) in THF (35 cm^3). After stirring a further 30 minutes, the solution was shaken with an aqueous solution of sodium thiosulfate (5%) and then extracted with diethyl ether (150 cm^3 × 4). After drying ($MgSO_4$) and removal of solvent, the crude product was distilled to give *2-(2-iodophenyl)-1,3-dioxolane* (16.6 g, 72%) bp 84 °C/0.8 mmHg, lit.[64] 110–112 °C/0.1 mmHg; *m/z* 276 (45%, M^+), 275 (100), 231 (25), 204 (10), 149 (25), 105 (15), 89 (25); δ_H(270 MHz, $CDCl_3$) 4.13 (m, 4 H), 5.93 (s, 1 H), 7.07 (appt. t, 1 H), 7.38 (appt. t, 1 H), 7.56 (dd, *J* 7.8, 1.7, 1 H) and 7.85 (d, *J* 7.8, 1 H); δ_C(67.9 MHz, $CDCl_3$) 65.7, 95.5, 102.2, 127.1, 128.3, 128.9, 137.4 and 144.7. The mass spectral and ^{1}H NMR data agree well with precedent.[64]

2-Iodobenzaldehyde. A mixture of 2-(2-iodophenyl)-1,3-dioxolane (9 g), THF and 5% aqueous HCl (50 cm^3) was stirred for 20 h at ambient temperature.[65] The solution was reduced in volume *in vacuo* then extracted with ether. After drying ($MgSO_4$), the solvent was removed from the extract and the residue crystallised to give *2-iodobenzaldehyde* (6.4 g, 83%) mp 35.5–36.5 °C, lit.[66] 37 °C; *m/z* 232 (100%, M^+), 203 (10), 127 (5), 105 (60); ν_{max}(Nujol)/cm^{-1} 1688 and 1703 (C=O); δ_H(270 MHz, $CDCl_3$) 7.26–7.32 (m, 1 H), 7.47 (t, *J* 7.5, 1 H), 7.88 (dd, *J* 7.8, 1.7, 1 H), 7.95 (dd, *J* 7.8, 1.0, 1 H) and 10.05 (s, 1 H); δ_C(67.9 MHz, $CDCl_3$) 100.7, 128.7, 130.2, 135.1, 135.5, 140.6 and 195.8.

The 2-iodobenzaldehyde was used to prepare: *(E)-3-(2-iodophenyl)-2-phenylpropenoic acid* (31%) mp 174–176 °C, lit.[67] 179–180 °C; *m/z* (CI, NH_3) 368 (45%, $M + NH_4^+$), 351 (15%, $M + H^+$), 333 (5), 240 (30), 223 (100), 205 (25), 194 (20), 178 (55); ν_{max}(Nujol)/cm^{-1} 1684 (C=O), 1258 (C–O); δ_H(270 MHz, $CDCl_3$) 6.73 (dd, *J* 7.8, 1.8, 1 H), 6.88 (td, *J* 7.5, 1.8, 1 H), 6.99 (td, *J* 7.6, 1.0, 1 H), 7.10–7.20 (m, 2 H), 7.25–7.30 (m, 3 H), 7.85 (dd, *J* 7.8, 1.3, 1 H) and 7.97 (s, 1 H); δ_C(67.9 MHz, $CDCl_3$) 100.8, 127.6, 128.0, 128.2(2C), 130.0, 130.2(2C), 130.9, 133.4, 133.9, 138.7, 139.1, 145.9 and 172.7. *Methyl (E)-3-(2-iodophenyl)-2-phenylpropenoate*, **20b**, (99%) mp 94–96 °C, lit.[67] 98–100 °C. *m/z* 364 (2%, M^+), 333 (1), 305 (1), 237 (100), 222 (10), 205 (7), 194 (15), 178 (30); ν_{max}(Nujol)/cm^{-1} 1704 (C=O), 1246 (C–O); δ_H(270 MHz, $CDCl_3$) 3.78 (s, 3 H), 6.62 (dd, *J* 7.6, 1.8, 1 H), 6.79 (td, *J* 7.5, 1.8, 1 H), 6.91 (td, *J* 7.5, 1.3, 1 H), 7.03–7.08 (m, 2 H), 7.16–7.21 (m, 3 H), 7.75 (s, 1 H) and 7.77 (dd, *J* 8.0, 1.5, 1 H); δ_C(67.9 MHz, $CDCl_3$) 52.5, 100.6, 127.5, 127.8, 128.1(2C), 129.6, 130.1(2C), 130.8, 134.2, 134.5, 139.0, 139.2, 143.9 and 167.8.

(ii) Regioselectivity of Pschorr cyclisations

The procedure for the homolytic cyclisations of **7a** and **7b** was as detailed above for the preparation of methyl phenanthrene-9-carboxylate, **21**. Isomeric product ratios were determined by GC analysis of the ethyl ethanoate extracts under the following conditions: the chromatograph was a Pye Unicam PU4500 instrument served by an HP 3395 integrator; column, Carbowax capillary (30 m); carrier gas, He; temperature, 250 °C. The pairs of isomeric phenanthrenes were assumed to exhibit equal chromatographic response factors, *i.e.* molar ratios of products

Table 6 Compounds eluted in addition to the expected phenanthrenes in the heterolytic cyclisations of **7a** and **7b**

Product no. (%)[a]	Retention time/s	Identification
From **7a**		
1(2.0)	210	Methyl 2-(3-fluorophenyl)-3-(2-fluorophenyl)propenoate, *m/z* 274 (M^+, 85%), 243 (10), 215 (68), 214 (60), 194 (25) and 139 (100); *cf.* MS of **20a** and **20c**.
2(2.3)	530	Methyl 2-(3-fluorophenyl)-3-(2-hydroxyphenyl)propenoate, *m/z* 272 (11%, M^+), 254 (10), 240 (15), 223 (20), 213 (21), 212 (22), 219 (16), 196 (45), 183 (100) and 165 (60).
3(27.1)	650	Methyl 4-fluorophenanthrene-10-carboxylate, **14a**.[b]
4(37.8)	780	Methyl 2-fluorophenanthrene-10-carboxylate, **13a**.[b]
5(30.8)	920	3-(3-Fluorophenyl)coumarin, **18b**, *m/z* 240 (100%, M^+), 212 (87), 183 (83) and 157 (15); *cf.* MS of 3-phenylcoumarin.[21]
From **7b**		
1(4.1)	300	Methyl 2-(3-chlorophenyl)-3-(2-fluorophenyl)propenoate, *m/z* 292 (27%, M^+), 290 (66%, M^+), 259 (10), 231 (37), 196 (50), 176 (15) and 139 (100).
2(1.6)	790	Methyl 2-(3-chlorophenyl)-3-(2-hydroxyphenyl)propenoate (*E* or *Z*), *m/z* 290 (2.5%, M^+), 288 (8.5, M^+), 270 (2), 253 (40), 228 (10), 221 (25), 194 (35), 193 (55), 176 (20) and 165 (100).
3(1.9)	900	Methyl 2-(3-chlorophenyl)-3-(2-hydroxyphenyl)propenoate (*E* or *Z*), *m/z* 290 (1%, M^+), 288 (5%, M^+), 270 (2.5), 252 (22), 228 (30), 221 (55), 194 (60), 193 (48), 176 (18) and 165 (100).
4(31.1)	1210	Methyl 4-chlorophenanthrene-10-carboxylate, **14b**.[b]
5(34.8)	1450	Methyl 2-chlorophenanthrene-10-carboxylate, **13b**.[b]
6(26.9)	1765	3-(3-Chlorophenyl)coumarin, **18c**, *m/z* 258 (31%, M^+), 256 (100%, M^+), 228 (75), 199 (7), 165 (55); *cf.* MS of 3-phenylcoumarin.[21]

[a] As a percentage of total product, estimated from GC peak areas. [b] See Experimental, section (ii).

were taken to be equivalent to ratios of their integrated chromatographic peak areas.

The major methyl fluorophenanthrene-10-carboxylate, **14a** [identified as reported in Results (v)], eluted after 10.8 min, and the minor, **13a**, after 13.0 min. The mass spectra of the two isomers were essentially identical: *m/z* 254 (100%, M^+), 223 (85), 195 (68), 194 (35), 175 (12), 169 (7) and 168 (7). When allowance is made for the mass of F, the fragmentation pattern is essentially the same as that observed for the unsubstituted ester **21**.

The major methyl chlorophenanthrene-10-carboxylate, **14b** [identified as reported in Results (v)], eluted after 20.2 min, and the minor, **13b**, after 24.2 min. Again the MS were identical: *m/z* 272 (34%, M^+), 270 (100%, M^+), 239 (73), 211 (40), 176 (65), 150 (8) and 88 (28) and indicated a principal fragmentation pattern in common with **13a**, **14a** and **21**. The nuclear Overhauser enhancements observed on the mixture of **13b** and **14b** allowed the following tentative assignment of ^{1}H NMR spectra: **13b**, δ_H(500 MHz, $CDCl_3$) 4.04 (s, Me), 7.60–7.68 (m, H7), 7.70–7.78 (m, H3 and H6), 7.94 (dd, *J* 7.7, 1.6, H8), 8.52 (s, H9), 8.58 (d, *J* 9.1, H4 or H5), 8.60 (d, *J* 9.3, H4 or H5) and 9.00 (d, *J* 2.2, H1); **14b**, δ_H(500 MHz, $CDCl_3$) 4.03 (s, Me), 7.53 (dd, *J* 7.7, 7.6, H2), 7.60–7.68 (m, H7), 7.70–7.78 (m, H3 and H6), 7.94 (dd, *J* 7.7, 1.6, H8), 8.39 (s, H9), 8.78 (dd, *J* 8.4, 1.3, H1) and 9.83 (d, *J* 8.2).

For heterolytic cyclisations, **7a** or **7b** (50 mg) was dissolved in water (50 cm^3) by stirring for 10 minutes at ambient temperature then the temperature was raised to 80 °C for 20 min. After cooling, the products were extracted into ethyl ethanoate and analysed by GC as described above. Compounds in addition to the expected phenanthrenes eluted are listed in Table 6.

(iii) Rates of cyclisation

Calibration *via* hydrogen abstraction from hypophosphorous acid in aqueous solution. Commercial hypophosphorous acid (BDH, 49–53%) was diluted and standardised by titration with sodium hydroxide solution (1.0 mol dm^{-3}). Mixed solutions were prepared which were 0.1 mol dm^{-3} with respect to $Cu(NO_3)_2$ and of concentrations between 2 and 8 mol dm^{-3} with respect to H_3PO_2 (Table 2). To 10 cm^3 aliquots of these solutions was added methyl (*E*)-3-(2-diazoniophenyl)-2-phenylpropenoate tetrafluoroborate, **7c** (10 mg) and, after stirring for ten minutes to ensure dissolution, homolysis was initiated by addition of a solution of ascorbic acid (0.2 cm^3, 0.5 mol dm^{-3}). Following fifteen minutes further stirring, the organic products were extracted into ethyl ethanoate (5 cm^3) and the extract analysed by GC, the chromatograph being calibrated using authentic samples of methyl (*E*)-2,3-diphenylpropenoate **20a** and methyl phenanthrene-9-carboxylate **21** and operated isothermally at 250 °C using the Carbowax capillary column previously described. From the gradient of the linear segment of the plot of **[20a]/[21]** *versus* $[H_3PO_2]$ (Fig. 2) (*i.e.* 0.030 ± 0.004 dm^3 mol^{-1}), a cyclisation rate of (3.0 ± 0.5) × 10^9 s^{-1} was estimated on the assumption that the radical **8c** abstracts hydrogen from H_3PO_2 at the same rate as was found for the 2-benzoylphenyl radical.[16]

Calibration *via* iodine abstraction from tri-iodide ion in propanone. Methyl (*E*)-3-(2-diazoniophenyl)-2-phenylpropenoate tetrafluoroborate, **7c** (20 mg) dissolved in propanone (5 cm^3) was added as quickly as possible to 25 cm^3 of vigorously stirred solutions containing NaI (0.48 mol dm^{-3}) and various lesser concentrations of iodine (Table 3). Evolution of dinitrogen was immediate. After stirring for fifteen minutes, the excess of iodine was removed by addition of sodium thiosulfate solution (5% w/v) and the solutions were evaporated under reduced pressure to remove propanone. The residual aqueous solutions were extracted twice with diethyl ether (20 cm^3) and the extracts combined and concentrated for GC analysis which was performed on a SE54 capillary column (30 m) where the temperature was first held for 2 minutes at 150 °C then ramped at 6 °C min^{-1} to 240 °C. The chromatograph was calibrated using authentic samples of methyl (*E*)-3-(2-iodophenyl)-2-phenylpropenoate **20b** and **21**.

The formation constant of I_3^- in propanone being large,[29] it can be assumed that, for the conditions employed, the concentration of I_3^- is equal to the analytical concentration of I_2 in the reaction mixtures. From the gradient of the plot of **[20b]/[21]** *versus* $[I_3^-]$ (Fig. 3) (*i.e.* 0.370 ± 0.084 dm^3 mol^{-1}) and a value for the iodine transfer rate constant at 20 °C of (4.2 ± 1.8) × 10^9 dm^3 mol^{-1} s^{-1} interpolated from the data of Abeywickrema and Beckwith,[27,28] a cyclisation rate of (1.2 ± 0.5) × 10^{10} s^{-1} is estimated for **8c**.

(iv) *ipso*-Cyclisation

Evidence for the possibility of *ipso*-cyclisation of **8c** to form **15c** was sought in the form of reduction or dimerisation products of the latter when produced in reducing conditions. To methyl (*E*)-3-(2-iodophenyl)-2-phenylpropenoate **20b** (250 mg) and azoisobutyronitrile (10 mg) in benzene (10 cm^3), refluxing

Table 7 Significant product eluted after cyclisation of **8c** in reducing conditions

Substance no. (%)[a]	Retention time/s	Identification
1 (5.4)	1046	Methyl 2,3-diphenylpropanoate **22a**; *m/z* 240 (M^+, 12%), 181 (15), 180 (7), 121 (8), 118 (12), 103 (8) and 91 (100); lit.[68] *m/z* 240 (17), 181 (17), 180 (7), 121 (8), 118 (10) and 91 (100).
2 (3.4)	1196	Methyl (*E*)-2,3-diphenylpropenoate **20a**; retention time and MS identical with authentic material, *cf.* (i) above.
3 (0.7)	1382	Methyl (*Z*)-2,3-diphenylpropenoate; MS identical with that of (*E*) isomer.
4 (5.1)	1604	Methyl 9,10-dihydrophenanthrene-9-carboxylate **23**; retention time and MS identical with that of authentic material.
5 (4.5)	1850	Methyl 3-(2-iodophenyl)-2-phenylpropanoate **22b**; *m/z* 366 (M^+, 2.5%), 307 (7), 239 (100), 217 (65), 180 (17), 179 (37), 178 (24), 165 (14) and 121 (27).
6 (47.8)	2094	Methyl (*E*)-3-(2-iodophenyl)-2-phenylpropenoate **20b**; MS identical with that of starting material, *cf.* (i) above.
7 (6.8)	2398	Methyl (*Z*)-3-(2-iodophenyl)-2-phenylpropenoate; *m/z* 364 (M^+, 3%), 333 (0.5), 3.05 (0.5), 237 (100), 222 (10), 206 (6), 194 (15) and 178 (27), *cf.* MS of authentic (*E*)-isomer.
8 (26.4)	2906	Methyl phenanthrene-9-carboxylate **21**; MS identical with that of authentic material, *cf.* (i) above.

[a] As a percentage of total product; estimated from GC peak areas.

under dinitrogen, was added tributyltin hydride (250 mg) in benzene (2.5 cm^3) and refluxing was continued for thirty minutes, then the mixture was cooled and the solvent evaporated. The residue, dissolved in diethyl ether (10 cm^3), was stirred for 24 h with 10 cm^3 of a solution of 10% aqueous KF after which the precipitate was removed by filtration. The ether and aqueous layers were separated and the latter extracted with a further 10 cm^3 of ether; the combined ethereal fractions were then washed with brine (10 cm^3) and dried ($MgSO_4$). Following filtration and solvent removal, the residue was chromatographed on silica gel 60 (70–200 micron) eluting with hexane–dichloromethane, 1 : 1. After elution of tin compounds, organic reaction products (235 mg) were eluted with ethyl ethanoate and identified by GC-MS. The chromatography was performed using a Carbowax capillary column initially isothermal at 160 °C for four minutes then ramping at 8 °C min^{-1} to 250 °C. Under these conditions the significant substances given in Table 7 eluted.

It is apparent that when the reaction was stopped approximately 55% of the initial **20b** remained unreacted but about 7% of this had undergone isomerisation to the (*Z*)-isomer. Phenanthrene ring-closure had occurred for over 30% of the initial reactant and 5% of this had undergone reduction of the C(9)–C(10) bond. Almost 10% of the initial reactant had undergone deiodination without cyclisation; of this reduced component half was also reduced in the alkene function and a small proportion (<1%) was isomerised about the same function.

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