PERKIN 2

Sandmeyer reactions. Part 5.[1] Estimation of the rates of 1,5-aryl/aryl radical translocation and cyclisation during Pschorr fluorenone synthesis with a comparative analysis of reaction energetics

Stephen A. Chandler,[a] Peter Hanson,*[a] Alec B. Taylor,[a] Paul H. Walton[a] and Allan W. Timms[b]

[a] *Department of Chemistry, University of York, Heslington, York, UK YO10 5DD*
[b] *Great Lakes Fine Chemicals Ltd., Halebank, Widnes, UK WA8 8NS*

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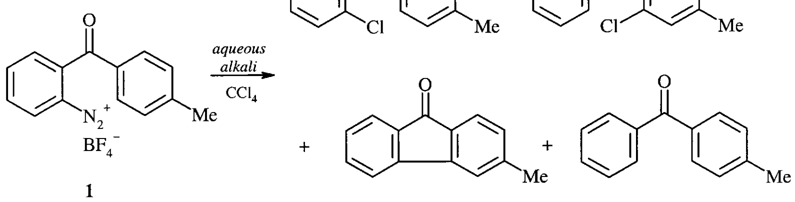
During the Pschorr cyclisation of 2-aroylphenyl radicals, a rearrangement occurs reversibly by 1,5-hydrogen transfer to give 2-benzoylaryl radicals. Rate constants of $(1.2 \pm 0.2) \times 10^6$ s^{-1} at 293 K are estimated for both the forward and back reactions in the equilibrium between 2-(4-methylbenzoyl)phenyl and 2-benzoyl-5-methylphenyl radicals. Assuming an empirical estimate of 1.6×10^{-2} dm^3 mol^{-1} s^{-1} for the hypothetical rate of abstraction of hydrogen from benzene by phenyl radicals, the radical translocation is calculated to occur with a statistically corrected effective molarity of 2.2×10^8 mol dm^{-3}. By contrast, the competing cyclisation, though occurring at a rate of $(8.0 \pm 0.9) \times 10^5$ s^{-1}, exhibits an effective molarity of only 5.3 mol dm^{-3}. The causes of these differences are analysed in terms of reaction mechanism.

Observation of the intermolecular abstraction of hydrogen from aromatic sp^2 C–H bonds is normally restricted to the gas phase at high temperatures; for example, kinetic studies have been reported for abstractions from benzene by methyl and ethyl radicals in the temperature interval 650–700 K,[2] and by hydroxyl radical in the temperature interval 790–1450 K.[3] In the liquid phase, such abstractions cannot compete with additions to the aromatic systems which occur over a wide range of rates between 3.8×10^2 dm^3 mol^{-1} at 352 K for addition of primary alkyl radicals to benzene[4] and 7.9×10^9 dm^3 mol^{-1} s^{-1} at 293 K for addition of hydroxyl radical to the same substrate.[5] Consistent with such observations, additions of aryl radicals to benzene derivatives are well documented[6–8] (typically with rate constants of 10^5–10^7 dm^3 mol^{-1} s^{-1}) whereas a rate constant for the bimolecular abstraction of hydrogen from aromatic sp^2 C–H bonds by aryl radicals does not appear to have been reported for either the gaseous or liquid state.

Abstraction of aromatic hydrogen by an aryl radical does, however, occur *intramolecularly* in a process first reported many years ago by DeTar and Relyea[9,10] who observed four products from the alkaline homolysis of 2-(4-methylbenzoyl)benzenediazonium tetrafluoroborate **1** in mixtures containing CCl_4 (Scheme 1). The occurrence of the isomeric chloroketones was explained by the translocation of the radical centre between the two rings during the lifetime of the initially formed radical. Both isomeric radicals cyclise to 3-methylfluoren-9-one and both are reduced to 4-methylbenzophenone, presumably *via* intermolecular H-abstraction from the hydrofluorenyl π-radical intermediates or from the methyl groups present in other products. Cadogan, Hutchinson and McNab[11] have reported an analogous 1,5-hydrogen exchange in 2-aryloxyphenyl radicals generated in gas-phase pyrolyses.

More recently, Karady and co-workers[12] have examined the rearrangement of benzophenone-derived radicals in more detail (Scheme 2). The diazonium ion **2** was homolysed in various conditions giving rise, initially, to the corresponding radical **3** which could then undergo sequential 1,5-H-transfer reactions to produce the isomeric radicals **4** and **5**. The products arising from bimolecular atom-transfers to the three radicals **3**–**5** varied in their proportions as a consequence of the differing extents to which the 1,5-radical translocations were able to compete with various bimolecular processes. In particular, it was observed that the homolysis of **2** in an acetone solution of potassium triiodide resulted in the formation of three iodinated products, the proportions of which were dependent on the triiodide concentration. From this dependency and Abeywickrema and Beckwith's[13] rate constant of 5×10^9 dm^3 mol^{-1} s^{-1} at 293 K for the transfer of iodine to aryl radicals in these conditions, an upper limit of 10^6–10^7 s^{-1} was estimated for the rate constant for the 1,5-radical translocation.

We have previously described a calibration of the rate of closure of 2-benzoylphenyl radical **6** to fluorenone and the use



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Scheme 1

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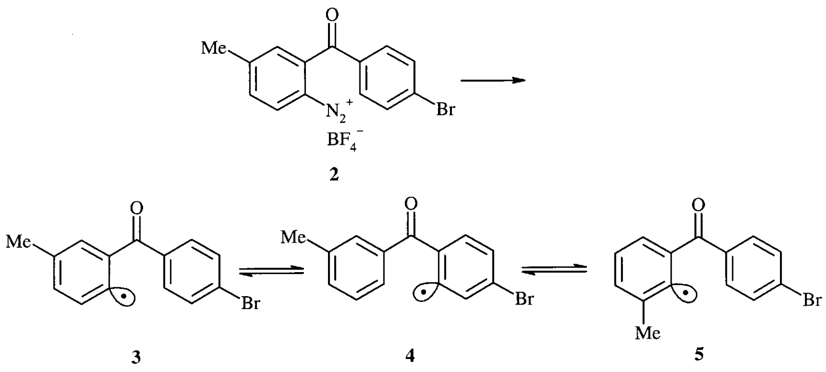
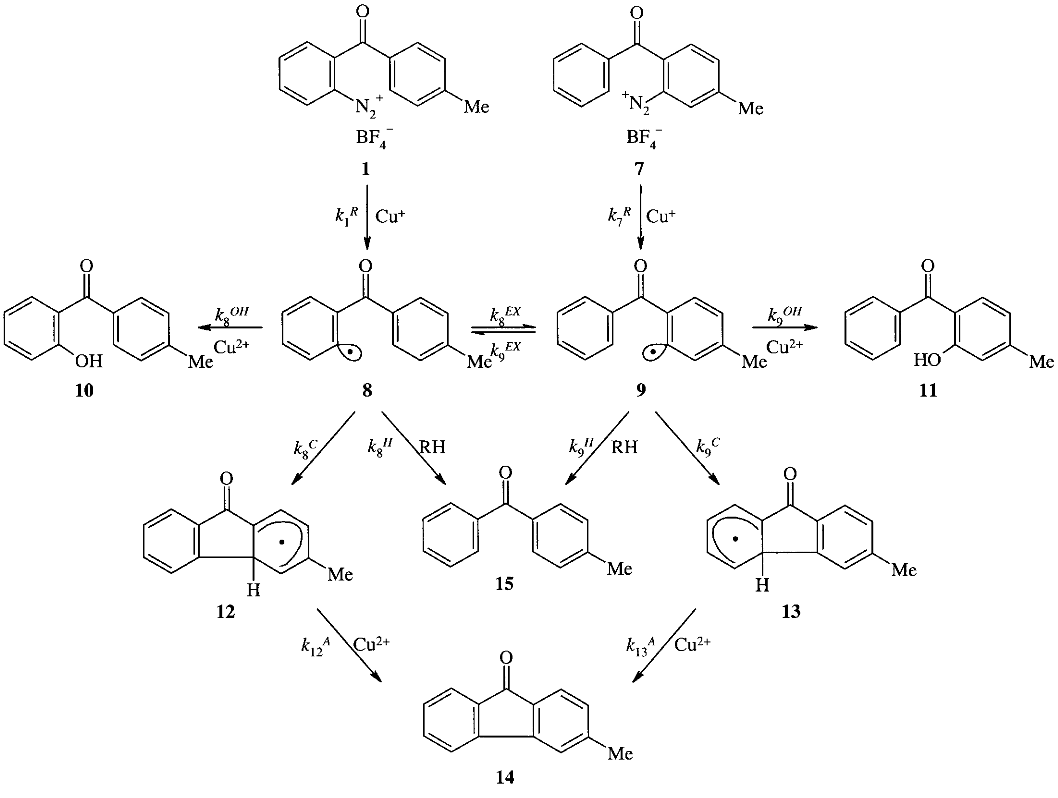
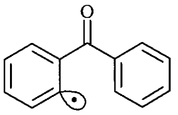


Scheme 2



Scheme 3



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of this process as a radical clock to obtain rate constants for various ligand-transfer reactions from copper(II) complexes to aryl radicals in Sandmeyer reactions.[14,15]

Results

(i) Evaluation of relative rate constants

The investigation described in this paper is based upon the reactions shown in Scheme 3. The two isomeric diazonium ions **1** and **7**, on homolysis, give radicals **8** and **9** which are interchangeable by 1,5-hydrogen transfer. Each of these radicals may undergo bimolecular reactions with hexaaquacopper(II) to produce a characteristic phenol **10** or **11** but both are cyclised to a common product, 3-methylfluoren-9-one, **14**; in the presence of a hydrogen donor both are also reduced to 4-methylbenzophenone **15**. This system offers the following advantages for the study of the radical rearrangement. Depending on the starting material, each of the radicals **8** and **9** can be obtained either as the initial radical or as the rearranged radical; methylation of benzophenone-derived reactants, while providing the label necessary to distinguish the 'normal' and 'abnormal' phenolic products, causes the minimal electronic perturbation of the reacting species which allows a crucial assumption in the evaluation of rate constants, *vide infra*. The choice of homolytic hydroxylation as the radical-trapping reaction [occurring with a rate constant of $(1.47 \pm 0.17) \times 10^6$ dm^3 mol^{-1} s^{-1} in the unmethylated system **6**[14]] gives a better comparator for the rearrangement than the iodine transfer employed by Karady and coworkers[12] which occurs at essentially the diffusion controlled rate. Furthermore, the recycling of the copper catalyst ensures the concentration of the radical-trapping species [hexaaquacopper(II)] remains invariant over the course of the reaction with the consequence that the ratio of phenolic products can be taken as a measure of the relative rate at which the phenols were formed.

Practically, the reactions were brought about by dissolving one or other of the diazonium salts **1** or **7** in aqueous copper(II) nitrate solution of chosen concentration and initiating homolysis by addition of a small portion of ascorbic acid

Table 1 Molar ratios of normal : abnormal phenolic products from the homolyses of diazonium ions **1** and **7** in aqueous copper nitrate solutions

2-(4-Methylbenzoyl)benzenediazonium ion, **1**				2-Benzoyl-5-methylbenzenediazonium ion, **7**			
$[Cu^{2+}]$/mol dm^{-3}	[**10**]/[**11**]	$[Cu^{2+}]$/mol dm^{-3}	[**10**]/[**11**]	$[Cu^{2+}]$/mol dm^{-3}	[**11**]/[**10**]	$[Cu^{2+}]$/mol dm^{-3}	[**11**]/[**10**]
0.138	1.36	0.747	2.03	0.098	2.30	0.593	3.32
0.256	1.52	0.865	2.23	0.197	2.45	0.688	3.50
0.393	1.62	0.904	2.33	0.295	2.62	0.786	3.78
0.505	1.75	0.963	2.40	0.393	2.78	0.885	4.17
0.629	1.93			0.494	3.10	0.963	4.33

Table 2 Gradients and intercepts of the lines of Fig. 1 and derived relative rate constants

2-(4-Methylbenzoyl)benzene-diazonium ion, **1**		2-Benzoyl-5-methylbenzene-diazonium ion, **7**	
Gradient	1.239 ± 0.057	Gradient	2.393 ± 0.161
Intercept	1.163 ± 0.038	Intercept	1.947 ± 0.098
k_8^{EX}/k_8^{OH}	0.807 ± 0.037	k_9^{EX}/k_9^{OH}	0.418 ± 0.028
k_8^{C}/k_8^{OH}	0.007 ± 0.078	k_9^{C}/k_9^{OH}	0.521 ± 0.063

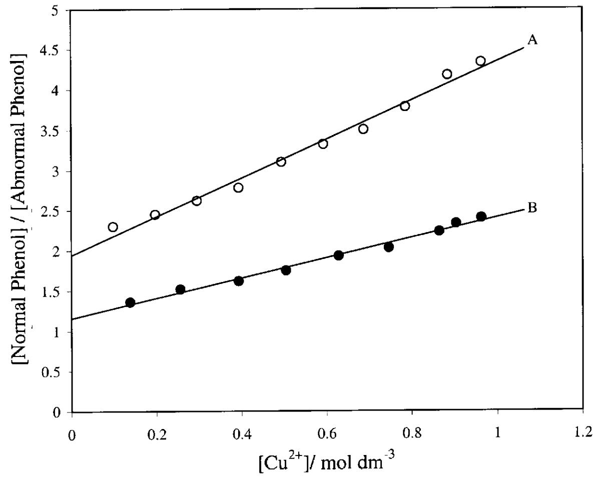


Fig. 1 Variation with the concentration of copper nitrate of the proportions of normal to abnormal phenol from homolyses of **1** (line B) and **7** (line A).

solution. The latter rapidly reduces Cu^{2+} to Cu^{+}[16,17] which, in turn, reduces **1** or **7** to their respective radicals **8** or **9** and dinitrogen. The reaction might involve the formation of diazenyl radical intermediates but these are known to fragment rapidly to the aryl radical and dinitrogen.[18]

Whichever diazonium salt is selected, its reduction is the rate determining step in Scheme 3 [see Section (iii)]. Once formed, the aryl radicals **8** and **9** each undergo three competitive reactions of interest: interconversion, Sandmeyer hydroxylation to the corresponding phenols **10** and **11** and cyclisation to the respective hydrofluorenyl radicals **12** and **13**. (In the absence of an added H-donor, the reduction of **8** and **9** to **15** is negligible.) On account of the great difference in stability between the aryl σ-radicals and the hydrofluorenyl π-radicals, the cyclisation reactions are no doubt rapid and irreversible.[7] Both **12** and **13** are expected to be aromatized rapidly to 3-methylfluoren-9-one in the presence of an excess of hexaaquacopper(II) with a rate constant > 10^7 dm^3 mol^{-1} cm^{-1}.[19]

Since the concentration of aquacopper(II) can be assumed to be invariant over the course of reaction, the molar ratio of the phenolic products is a measure of their relative rates of formation [eqn. (1)].

$$\frac{[\mathbf{10}]}{[\mathbf{11}]}=\frac{d[\mathbf{10}]/dt}{d[\mathbf{11}]/dt}=\frac{k_8^{OH}[\mathbf{8}][Cu^{2+}]}{k_9^{OH}[\mathbf{9}][Cu^{2+}]}=\frac{k_8^{OH}[\mathbf{8}]}{k_9^{OH}[\mathbf{9}]} \qquad (1)$$

When **1** is the diazonium ion homolysed, **8** is the initial aryl radical and **9** the rearranged aryl radical, application of the steady state hypothesis to **9** then results in eqn. (2).

$$\frac{[\mathbf{8}]}{[\mathbf{9}]}=\frac{(k_9^{EX}+k_9^{C})}{k_8^{EX}}+\frac{k_9^{OH}}{k_8^{EX}}\times[Cu^{2+}] \qquad (2)$$

Combining eqns. (1) and (2) gives eqn. (3).

$$\frac{[\mathbf{10}]}{[\mathbf{11}]}=\frac{k_8^{OH}}{k_8^{EX}}\times\left(\frac{k_9^{EX}}{k_9^{OH}}+\frac{k_9^{C}}{k_9^{OH}}\right)+\frac{k_8^{OH}}{k_8^{EX}}\times[Cu^{2+}] \qquad (3)$$

Eqn. (3) indicates the molar ratio of the normal to abnormal phenolic products from diazonium salt **1** to be a linear function of the copper concentration and that the gradient and intercept of the line may be expressed in terms of three relative rate constants.

When diazonium ion **7** is homolysed, a directly analogous treatment leads to eqn. (4) relating the molar ratio of normal to abnormal phenolic products [here inverted relative to eqn. (3)] to the copper concentration.

$$\frac{[\mathbf{11}]}{[\mathbf{10}]}=\frac{k_9^{OH}}{k_9^{EX}}\times\left(\frac{k_8^{EX}}{k_8^{OH}}+\frac{k_8^{C}}{k_8^{OH}}\right)+\frac{k_9^{OH}}{k_9^{EX}}\times[Cu^{2+}] \qquad (4)$$

In Table 1 are presented phenolic product ratios obtained from the homolyses of diazonium ions **1** and **7** in various concentrations of aqueous copper nitrate solution. Each quoted ratio is a mean value obtained from duplicate analyses of duplicate reactions. The isomeric phenols were satisfactorily separated from each other and other products by GC using a 60 m Carbowax capillary column and appropriate temperature programming (see Experimental).

Fig. 1 shows that the anticipated linear relationship in a plot of product ratio *versus* $[Cu^{2+}]$ is obtained for both diazonium ions but that each has a characteristic gradient and intercept (Table 2). Clearly, there must be differences between the competitive reactions of radicals **8** and **9**; simple arithmetic with the gradients and intercepts of the lines of Fig. 1 allows evaluation of the relative rate constants given in Table 2. The uncertainties in the gradients and intercepts are the 95% confidence limits calculated by the regression programme. These uncertainties are propagated as errors or fractional errors, as appropriate, in all subsequent evaluations of relative and absolute rate constants.

(ii) Estimation of absolute rate constants

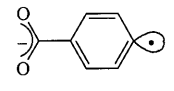
When benzophenone-derived diazonium ions are homolysed in water the yields of the parent benzophenone are low (<5%), the source of hydrogen being adventitious. If, however, an alcoholic H-donor is added to the solvent, the proportion of benzophenone is increased at the expense of the other products. We have previously shown[14] that the rates of abstraction by **6** of hydrogen atoms from simple alcohols, relative to the rate of

Table 3 Evaluation of rate constants for Sandmeyer hydroxylations

Rate constant	MeOH	EtOH	i-PrOH	*t*-BuOH
$k_{17}{}^{H}/k_{17}{}^{OH}$	0.138 ± 0.007	0.799 ± 0.030	1.88 ± 0.29	0.069 ± 0.014
$k_{17}{}^{Hrel}$	1.00 ± 0.07	5.79 ± 0.36	13.62 ± 2.21	0.50 ± 0.10
$k_{16}{}^{Hrel}$ [a]	1.00 ± 0.10	5.49 ± 0.55	12.16 ± 1.22	0.49 ± 0.10
$k_{16}{}^{H}/dm^3\ mol^{-1}\ s^{-1}$ [a]	$(4.3 \pm 0.4) \times 10^5$	$(2.4 \pm 0.3) \times 10^6$	$(5.2 \pm 0.5) \times 10^6$	$(2.1 \pm 0.4) \times 10^5$
$k_{17}{}^{OH}/dm^3\ mol^{-1}\ s^{-1}$ [a]	$(3.11 \pm 0.33) \times 10^6$	$(3.00 \pm 0.39) \times 10^6$	$(2.77 \pm 0.50) \times 10^6$	$(3.04 \pm 0.85) \times 10^6$
Mean $k_{17}{}^{OH}/dm^3\ mol^{-1}\ s^{-1}$	$(2.98 \pm 0.28) \times 10^6$			
Mean $k_{9,8}{}^{OH}/dm^3\ mol^{-1}\ s^{-1}$ [b]	$(2.28 \pm 0.22) \times 10^6$			
Mean $k_{8,9}{}^{OH}/dm^3\ mol^{-1}\ s^{-1}$ [c]	$(2.10 \pm 0.27) \times 10^6$			
Mean $k_{6}{}^{OH}/dm^3\ mol^{-1}\ s^{-1}$ [d]	$(1.47 \pm 0.17) \times 10^6$			

[a] From ref. 6. [b] Radical **9** as initial radical. [c] Radical **8** as initial radical. [d] From ref. 14.

abstraction from methanol, plot linearly and, within experimental error, with unit slope against the corresponding relative rates of abstraction by the 4-carboxyphenyl **16** radical measured by Schuler and co-workers[6] and hence we have concluded that the 2-benzoyl substituent in **6** does not exert any significant proximity effect on hydrogen abstraction reactions, *i.e.* both aryl radicals abstract from a particular alcohol at essentially the same rate. In the present work we find, as expected, that the same situation prevails for the methylated radicals **8** and **9** and for the dimethylated radical **17**.



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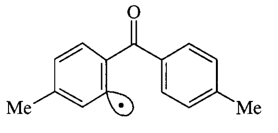

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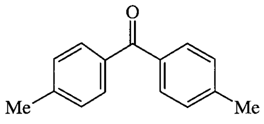

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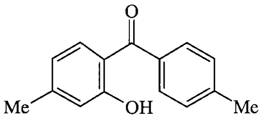

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Fig. 2a shows the variation in the molar ratio of 4,4′-dimethylbenzophenone **18** and 2-hydroxy-4,4′-dimethylbenzophenone **19**, obtained from a homolysis of 2-(4-methylbenzoyl)-5-methylbenzenediazonium tetrafluoroborate, as a function of the concentration of added alcohols at a fixed concentration of copper(II). Routine kinetic analysis shows that the gradients of the lines equal $k_{17}{}^{H}/k_{17}{}^{OH}[Cu^{2+}]$ where $k_{17}{}^{H}$ is the rate constant for abstraction of hydrogen by **17** from a particular alcohol and $k_{17}{}^{OH}$ is that for Sandmeyer hydroxylation. Division of the value for each alcohol by that obtained for methanol gives $k_{17}{}^{H,rel}$ (Table 3). In Fig. 2b the values of $k_{17}{}^{H,rel}$ are plotted against Schuler's corresponding values for **16**. Within the experimental errors, the line has unit gradient. As in our previous work with **6**, **17** does not discriminate any differently from **16** between the various hydrogen environments of the donor alcohols and we infer that their absolute H-abstraction rate constants are essentially equal for a given alcohol.

Since Schuler also obtained absolute values for the H-abstraction rate constants of **16**,[6] we can use these as the fiducial values against which the rates reported in this work are scaled. On this basis, in Table 3, absolute rate constants for Sandmeyer hydroxylation of **17** are evaluated for each alcohol. The values are constant within experimental error, showing that the rate constant is independent of the solvent composition over the ranges of alcohol concentrations employed. Our previous value obtained for **6** is included for comparison and it can be seen that the hydroxylation rate of the dimethylated radical **17** has twice the magnitude of the unsubstituted radical **6**, which is a significant difference. When comparable evaluations are made for the monomethylated substrates, analogous behaviour is found and hydroxylation rate constants intermediate in value between those of the dimethylated and unmethylated systems are found.

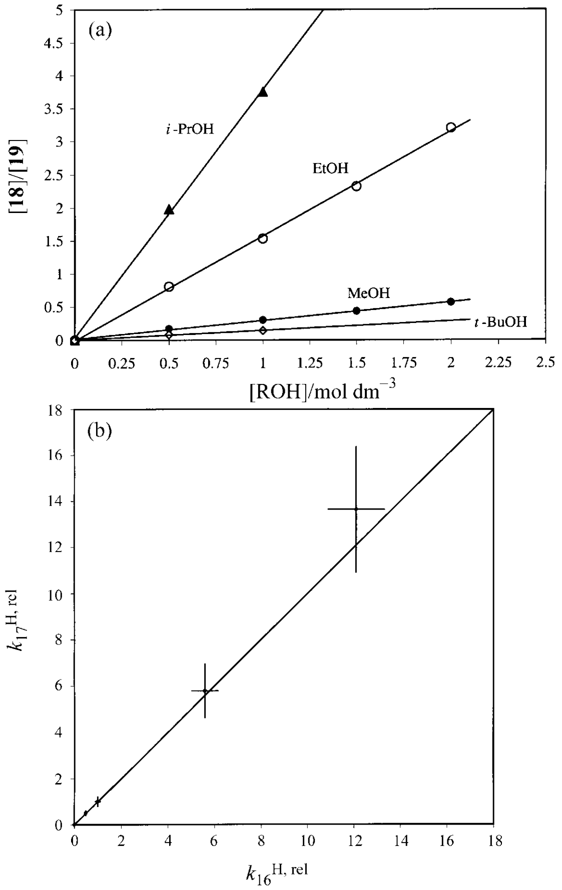


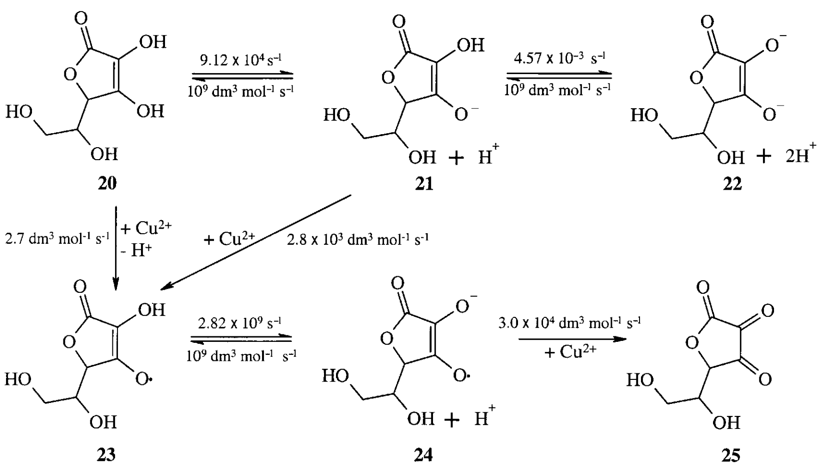
Fig. 2 (a) Variation in the proportion of reduction product to hydroxylation product from the homolysis of 2-(4-methylbenzoyl)-5-methylbenzenediazonium tetrafluoroborate as a function of the concentration of added alcohols. (b) Plot of relative hydrogen abstraction rate constants for **17** *versus* those for **16**; the line has unit gradient.

If, for the monomethylated radicals **8** and **9**, $k^{OH} \gg k^{EX}$, each would give only its own 'normal' phenol and not both phenols **10** and **11**; on the other hand, if $k^{EX} \gg k^{OH}$, the radicals would equilibrate before ligand-transfer and both radicals would give the same ratio of phenolic products. The observation of both phenols in different ratios depending on which radical was initial and which derived, demonstrates that for **8** and **9** k^{OH} and k^{EX} are of comparable magnitudes. The ligand transfer rates found from the homolyses of **1** and **7** are therefore composite, having contributions from both radicals.

Table 4 Absolute rate constants for the reactions of **8** and **9**

2-(4-Methylbenzoyl)phenyl radical, **8**		2-Benzoyl-5-methylphenyl radical, **9**	
k_8^{OH}/dm^3 mol^{-1} s^{-1}	$(1.47 \pm 0.17) \times 10^6$	k_9^{OH}/dm^3 mol^{-1} s^{-1}	$(2.98 \pm 0.28) \times 10^6$
k_8^{EX}/s^{-1}	$(1.19 \pm 0.15) \times 10^6$	k_9^{EX}/s^{-1}	$(1.25 \pm 0.14) \times 10^6$
k_8^{C}/s^{-1}	$(1.0 \pm 11.5) \times 10^4$	k_9^{C}/s^{-1}	$(1.55 \pm 0.24) \times 10^6$

Copper(II) Reduction



Ascorbate Disproportionation

$$\mathbf{24} + \mathbf{24} \xrightarrow{7.0 \times 10^4\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}} \mathbf{22} + \mathbf{25}$$

$$\mathbf{23} + \mathbf{23} \xrightarrow{7.4 \times 10^7\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}} \mathbf{20} + \mathbf{25}$$

$$\mathbf{23} + \mathbf{24} \xrightarrow{2.38 \times 10^8\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}} \mathbf{21} + \mathbf{25}$$

Copper(I) Autoxidation

$$Cu^+ + O_2 \xrightarrow{4.1 \times 10^4\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}} Cu^{2+}$$

Scheme 4

In order to assign ligand-transfer rates to each of **8** and **9** we make the assumption that the methyl groups in the *non-radical* rings of **8** and **17** have a negligible effect on their rates of Sandmeyer hydroxylation. The corollary of this assumption is that **8** reacts at the same rate as **6**, and **9** reacts at the same rate as **17**. The assumption is justified on the following grounds: first, the methyl group has an intrinsically small substituent effect (inductive/field) and the radical centre is separated from the methyl group by seven bonds; and second, although the methyl group will influence the π-system of the ring it substitutes, this is only cross-conjugated with the π-system of the ring which bears the radical centre and, furthermore, the radical being a σ-radical has a SOMO which is orthogonal to the π-system of the latter ring. The methyl groups in the non-radical rings of **8** and **17** are thus so electronically isolated and spatially separated from the radical centres that their presence will be of no consequence for the bimolecular reaction of the radicals with aquacopper(II). Having so assigned values for k_8^{OH} and k_9^{OH}, the relative rate constants of Table 2 can be used to evaluate absolute rate constants for the 1,5-H-transfers (k^{EX}) and the cyclisation (k^{C}) of **8** and **9**. The values are given in Table 4.

(iii) Simulation studies

The evaluation of the rate constants in Table 4 has involved a number of implicit assumptions in addition to the explicit ones discussed above. For example, the kinetics of the reactions of **8** and **9** have been assumed to be independent of the reactions involved in the initiation of homolysis and the applicability of the steady state hypothesis for the rearranged radicals has been assumed. In view of this, we used a kinetic simulation to confirm our conclusions. Practically, initiation was achieved by addition of an aliquot (1 cm^3) of a solution of ascorbic acid (0.5 mol dm^{-3}) to 49 cm^3 of a solution of a diazonium tetrafluoroborate (40 mg) which contained required amounts of $Cu(NO_3)_2$. The reactions likely to be involved in the initiation process and for which rate constants have been reported are indicated in Scheme 4.

Rate constants were assigned to the various acid equilibria involving ascorbate species by assuming arbitrarily that protonations occur with a rate constant of 10^9 dm^3 mol^{-1} s^{-1} and then assigning the deprotonations a rate which reproduced published pK_a values.[20] Rate constants for the reduction of Cu^{2+} by ascorbic acid itself and by ascorbate mono-anion are those of Martinez and co-workers;[16] the rate constant for the reduction of Cu^{2+} by ascorbate radical-anion is that of Moravskii and co-workers.[17] The ascorbate radical disproportionation rates are those of Bielski, Comstock and Bowen[21] and the rate constant for aerial oxidation of Cu^+ is that of Günter and Zuberbühler.[22]

Simulation was performed using the programme *SIMULA*[23] which requires as input the concentrations of initial reactants and the relevant rate constants. For the latter, were used those given in Scheme 4, an arbitrary value of 5×10^4 dm^3 mol^{-1} s^{-1} for k_1^R or k_7^R (Scheme 3), and the rate constants given in Table 4. The reduction of diazonium ions to aryl radicals might conceivably involve intermediate diazenyl radicals:

$$Cu^+ + Ar\text{–}N_2^+ \xrightarrow{1} Cu^{2+} + Ar\text{–}N_2^{\bullet} \xrightarrow{2} Ar^{\bullet} + N_2$$

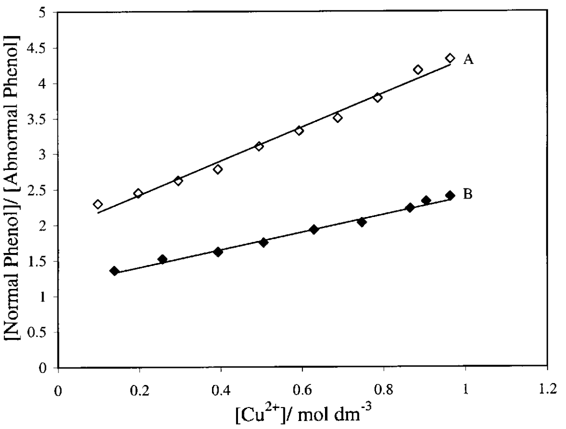


Fig. 3 Variation with the concentration of copper nitrate of the proportions of normal to abnormal phenol from homolyses of **1** and **7**; discrete points are experimental values, the lines simulated values.

Here step 1 is represented by k_1^R or k_7^R as the fragmentation of diazenyl radicals is known to be very rapid ($>10^6$ s^{-1}).[18] Similarly, the combined cyclisation and aromatisation of **8** and **9** were represented by k_8^C and k_9^C, respectively, as the aromatisation steps k_{12}^A and k_{13}^A are also very rapid (*ca.* 10^7 dm^3 mol^{-1} s^{-1}).[19]

Fig. 3 shows that the simulation gives an excellent fit of the experimental phenol ratios which vindicates the various assumptions made, confirms that diazonium ion reduction is the rate-determining step of the overall process and validates the rate constants determined.

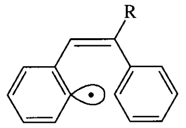
Discussion

(i) Substituent effects

The rate constants k_8^{EX} and k_9^{EX} for the 1,5-translocation are the same within experimental error making the translocation equilibrium constant 1.0 ± 0.2, *i.e.* the presence of a *m*-Me group has no discernible effect on the rates of intramolecular H-transfer between **8** and **9**. The determination of rate constants in this work depends on an assumption of the absence of substituent effects on the rates of abstraction by aryl radicals of hydrogen from C–H bonds in alcohols. While a similar absence might not necessarily pertain for abstraction from a stronger bond, such as an aryl C–H bond (we thank a referee for drawing attention to this point), the finding of no discernible effect of the *m*-Me substituent on the equilibration of **8** and **9** suggests that, if present, any such substituent effect is small.

By contrast, the presence of the *m*-Me substituent *in the radical ring* does have consequences for the Sandmeyer ligand transfer step: $k_9^{OH}/k_8^{OH} = k_9^{OH}/k_6^{OH} = 2$. Application of the Hammett equation to this single ratio gives a ρ value of -4.3 [*i.e.* $\log 2/\sigma_m^{Me} = 0.30/(-0.07)$][24] for the water ligand transfer step. We have previously suggested that the transition states for Sandmeyer ligand transfers, in general, vary in character between extremes of S_H2 atom transfer and electron transfer dependent on the nature of the transferred ligand, the standard reduction potential of the transferring copper complex and the substitution in the aryl ring.[15] On the present albeit slenderest of evidence, it seems that water transfer, which is expected to have less electron transfer character than halide ligand transfers,[15] nevertheless may, itself, experience considerable charge separation in the transition state.

The presence of the Me substituent in **8** and **9** also has an effect on the relative cyclisation rates: $k_8^C < k_9^C$, there being a difference of 1–2 orders of magnitude in the two rates. A more precise figure cannot be given because of the large uncertainty in k_8^C which occurs because this rate constant is found from the difference in two comparable quantities. The slower reaction occurs for **8** where the attacked ring is methylated which, ostensibly, implies Pschorr homolytic fluorenone cyclisation to have nucleophilic character. However, AM1 UHF calculations on **6** indicate the SOMO to lie at *lower* energy than the upper two bonding π-orbitals of the attacked ring. The strongest interactions of the SOMO on ring closure thus involve these bonding orbitals of the attacked ring and the cyclisation is hence electrophilic in character. (We previously found a similar situation in the Pschorr homolytic phenanthrene cyclisation of **26a**.[1]) Methylation of the attacked ring in **6** to give **8** raises the energies of its π-orbitals, so increasing the energy differences between the SOMO and the upper two bonding π-orbitals. This reduces the strength of their interactions and leads to the expectation that **8** should cyclise more slowly than **6**. Conversely, methylation of the radical ring in **6** to give **9** slightly raises the energy of the SOMO relative to the π-orbitals of the attacked ring with the result that **9** is expected to cyclise somewhat more rapidly than **6**. We have previously found[14] **6** to cyclise with a rate constant of 8 × 10^5 s^{-1}; the cyclisation rates found here for **8** and **9** are thus in agreement with this rationale.



26a R = CO_2Me
b R = H

(ii) Calculation of effective molarities

The effective molarity, M_E, of any unimolecular process is calculated as the ratio of the rate constant, k_{uni}, for the process with that, k_{bi}, of a comparable bimolecular process [eqn. (5)].

$$k_{uni}/k_{bi} = |k_{uni}|\ \mathrm{s^{-1}}/|k_{bi}|\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} = |M_E|\ \mathrm{mol\ dm^{-3}} = M_E \quad (5)$$

The linkage between two reactive moieties in a unimolecular process necessarily affects the behaviour of the moieties and, indeed, insight into the mechanism comes from examination of the relationship of a calculated effective molarity to the nature of the linkage.[25] Clearly, the choice of bimolecular comparator reaction is somewhat arbitrary. For the purpose of discussing, in terms of effective molarity, homolytic Pschorr cyclisations giving fluorenone and phenanthrene rings, we have chosen the addition of phenyl radical to benzene as the bimolecular comparator common to both cyclisations. While closer bimolecular analogues of each individual cyclisation might be envisaged, the choice of the simple Ph•/PhH addition allows a cleaner separation of mechanistic influences; furthermore, the requisite absolute bimolecular rate constant is available.[8] Since Ph• can attack benzene at any of its six positions but only two sites are available to the attacking radical in the cyclisations, a statistical correction factor of 3 is required in effective molarity calculation.

(iii) Effective molarity of cyclisation

The rate constant for the addition of phenyl radical to benzene (in Freon 113) has been measured as (4.5 ± 0.3) × 10^5 dm^3 mol^{-1} s^{-1} at 298 K.[8] Using our value of (8.0 ± 0.9) × 10^5 s^{-1} for the cyclisation of **6** (at 293 K)[14] allows a statistically corrected effective molarity of [3 × (8.0 ± 0.9) × 10^5]/(4.5 ± 0.3) × 10^5 = (5.3 ± 0.7) mol dm^{-3} to be calculated for homolytic Pschorr fluorenone cyclisation. This contrasts with the value of (2.0 ± 0.4) × 10^4 mol dm^{-3} which we found for the analogous phenanthrene cyclisation of **26a**.[1] The large effective molarity in the phenanthrene case was explained in terms of a relative attenuation of the bimolecular comparator reaction which arises from π–π repulsion between the aryl radical and the attacked ring for those trajectories of approach where the dihedral angle between the planes of the two aromatic reactants is significantly less than 90°. In a (*Z*)-stilbene radical **26** which cyclises to give a phenanthrene, the rigid alkene bridge holds the radical ring and the attacked ring in a mutual orientation favorable for minimising π–π repulsion. Evidently, for closure to fluorenone, the bridging carbonyl group cannot act in a similar way: the value of the effective molarity shows that for the cyclisation of **6** the intramolecular reaction mode has little advantage over the bimolecular comparator.

(iv) Activation parameters for 1,5-radical translocation (intramolecular H-exchange)

In order to evaluate an effective molarity for the 1,5-radical translocation which occurs between **8** and **9**, and degenerately in **6**, a suitable bimolecular comparator reaction is required but, as stated in the introduction, bimolecular abstraction of an aromatic C–H bond by an aryl radical is an unknown process. A value of effective molarity might be obtainable indirectly, however, if a rate constant for a suitable bimolecular process could be inferred. We therefore estimate below a rate constant for the abstraction of hydrogen from benzene by phenyl radical [the $Ph^{\bullet}/PhH$ identity exchange, reaction (6)] at 298 K.

$$Ph^{\bullet} + H\text{–}Ph \longrightarrow Ph\text{–}H + Ph^{\bullet} \qquad (6)$$

The choice of this hypothetical process as the bimolecular comparator for hydrogen exchange is apposite as then the competing unimolecular reactions of **6** (cyclisation and intramolecular H-exchange) are compared, respectively, to the notionally competing addition and exchange reactions of phenyl radical and benzene. In order to calculate a rate constant by means of the Arrhenius equation, values are required of the activation energy and the pre-exponential factor; each is considered in turn.

Activation energy for phenyl radical/benzene identity exchange. In recent years there have been two approaches to the estimation of activation energies for hydrogen-transfer reactions in general. That of Roberts[26,27] is essentially empirical, being a correlation analysis with roots in the Evans–Polanyi equation.[28] When applied to an identity exchange such as reaction (6), some explanatory variables used by Roberts, such as the enthalpy of reaction and the electronegativity difference between the leading atoms which exchange hydrogen, are zero and his correlation simplifies to eqn. (7).

$$E_a = E_o f + 2\gamma s_{Ph} \qquad (7)$$

Here, the explanatory variable f is defined in terms of bond dissociation enthalpies,[29] $f = [D_{0(Ph\text{–}H)}/D_{0(H\text{–}H)}]^2$ and s_{Ph} is a factor to accommodate structural change at the carbon centre between $Ph^{\bullet}$ and the transition state. Values of s ranged between 0 for atomic radicals and 2.5 for alkyl radicals. From a correlation of 65 reactions Roberts obtained values of 37.614 and 4.227 kJ mol^{-1}, respectively, for the regression coefficients E_o and γ.[27] Unfortunately, his data set did not include any reactions of $Ph^{\bullet}$ and so there is no precedent for s_{Ph}. We calculate a value as follows.

The angle, θ, subtended by two equivalent hybrid bonds is given by $\cos\theta = -1/\lambda^2$ where λ is the coefficient of orbital mixing and λ^2 counts the number of p orbitals mixed with an s orbital in the hybrids.[30] Also, it follows that the percentage of p character in a hybrid orbital is given by $100\lambda^2/(1 + \lambda^2)$. We have carried out an AM1 UHF molecular orbital calculation on the phenyl radical which indicates that the internal angle subtended by the C–C bonds at the radical centre is 129.0°. Use of this value for θ in the above expressions gives $\lambda^2 = 1.589$ for the endocyclic carbon hybrids at the radical centre which shows that these two hybrids each comprise 61.4% p character and 38.6% s character. The coplanar third hybrid orbital which is singly occupied must therefore comprise 77.2% p character and 22.8% s character. (The unhybridised p_z orbital contributes to the aromatic system.) When a hydrogen atom is abstracted from methane to form a methyl radical, the p character of the affected carbon orbital increases from 75% to 100%, *i.e.* by 25%; this change is represented in Roberts' correlation by the structural factor $s_{Me} = 2.5$. On abstraction of hydrogen from a benzene ring to form a phenyl radical, our calculation indicates the p character of the affected orbital to increase from 66.7% to 77.2%, *i.e.* by 10.5%. Linear interpolation between 0 for no change and 2.5 for 25% change suggests 1.0 as the structural factor s_{Ph} for the phenyl radical. When this is used, the activation energy for reaction (6) calculated using eqn. (7) is 52.7 kJ mol^{-1}.

The second approach to the estimation of activation energies for H-transfer reactions is that of Zavitsas; originated almost thirty years ago,[31,32] it has been recently refined to take account of improved modern input data.[33–37] This method treats H-transfer in a three-atom, three-electron model. The transition state for H-transfer from A to B may be represented by four canonical structures, **I**–**IV**. It is assumed that, for maximum resonance, the residual bonding in the breaking A–H bond in **I** equals the energy gain from the formation of the new H–B bond in **II**, *i.e.* $E_I = E_{II}$. Since the spins on A and B must always be parallel, **III** contributes a triplet repulsion term, E_{III}, to the total energy. The contribution of **IV** is a stabilisation, E_{IV}, arising from the delocalisation of the unpaired electron over three atoms. Thus the total energy of the hybrid, $E_{tot,}$ which varies with the interatomic distances assumed, is given by eqn. (8).

$$\underset{\textbf{I}}{[A{\uparrow\downarrow}H\cdots B{\uparrow}]} \longleftrightarrow \underset{\textbf{II}}{[{\uparrow}A\cdots H{\downarrow\uparrow}B]} \longleftrightarrow$$

$$\underset{\textbf{III}}{[{\uparrow}A\cdots H{\downarrow}\cdots B{\uparrow}]} \longleftrightarrow \underset{\textbf{IV}}{[A\cdots H\cdots B]^{\bullet}}$$

$$E_{tot} = 0.5(E_I + E_{II}) + E_{III} + E_{IV} \qquad (8)$$

In order to obtain the value of E_{tot} corresponding to E_{TS}, the energy of the transition state, values of E_I and E_{II} are found using the Morse potential[38] for various extensions of A–H and B–H which maintain an equality of E_I and E_{II}. For each value of the E_I,E_{II} pair, E_{III} is found using a variant of Sato's 'anti-Morse' potential[39] in which the A to B separation is the sum of the extended A–H and B–H bond lengths used in finding E_I and E_{II}; the transition state is taken to occur at the bond extensions for which the sum $[0.5(E_I + E_{II}) + E_{III}]$ is minimised. When A and B have first period leading atoms, E_{IV} is arbitrarily assigned a value equal to the stabilisation of the allyl radical in order to represent the delocalisation in **IV** of the three electrons over three atoms. The activation energy for hydrogen transfer, E_a, is calculated as the difference between E_{TS}, corrected for zero-point energy, and $D_{0(A\text{–}H)}$ the bond dissociation energy of the A–H bond. The zero-point energy correction, E_{ZP}, applied to E_{TS} is taken as the mean zero-point energy of the A–H and B–H bonds, $E_{ZP} = (\zeta_{A\text{–}H} + \zeta_{B\text{–}H})/2$.

For an identity exchange process such as reaction (6), the corrected transition state energy, $E_{TS,corr}$ is thus given by eqn. (9).

$$E_{TS,corr} = (E_I + E_{III})_{min} + \zeta_{Ph\text{–}H} + E_{IV} \qquad (9)$$

The transition state occurs at the C–H bond length, r_{TS}, where $(E_I + E_{III})$ is a minimum (Fig. 4a); the C–C separation in the transition state is $2r_{TS}$. The activation energy for hydrogen transfer, E_a, is thus calculated as in eqn. (10) (Fig. 4b).

Table 5 Evaluation of the activation energy for the phenyl radical/benzene identity exchange by the method of Zavitsas

Bond	r_e/Å	ν_{obs}/ cm^{-1}	D_0/ kJ mol^{-1}	ω_e/cm^{-1}	D_e/ kJ mol^{-1}	a/$Å^{-1}$	r_{TS}	$(E_I + E_{III})_{min}$/kJ mol^{-1} [a]	ζ_{Ph-H}/ kJ mol^{-1} [b]	E_{IV}/ kJ mol^{-1} [c]	E_a/ kJ mol^{-1}
Ph–H	1.101 [d]	3047.3 [e]	473.1 [f]	3164.6 [g]	492.0 [h]	1.825 [i]	1.241	$-467.4 + 77.4 = -390.0$	18.9	−44.3	57.8
Ph–Ph	1.497 [j]	1275 [k]	497.5 [l]	1294.6 [g]	505.2 [h]	1.879 [i]					

[a] Calc. by $E_I = D_e\{\exp[-2a(r - r_e)] - 2\exp[-a(r - r_e)]\}$ with values appropriate to the C–H bond, ref. 38, and $E_{III} = 0.45D_e\{\exp[-2a(r - r_e)] + 2\exp[-a(r - r_e)]\}$ with values appropriate to the C–C bond, refs. 31, 39. [b] $\zeta_{Ph-H} = (D_e - D_0)_{Ph-H}$. [c] Ref. 34. [d] Ref. 29, Table **9**-25. [e] Ref. 40. [f] Ref. 29, Table **9**-64. [g] Calc. by $\omega_e = (\nu_{obs} + \nu_{obs}^2/167.3D_0)$, refs. 33, 34. [h] Calc. by $D_e = (D_0 + \omega_e/167.3)$, ref. 41. [i] Calc. by $a = 0.1218\omega_e(\mu/83.65D_e)^{\frac{1}{2}}$, with reduced mass μ and other values for C–H or C–C bond vibration as appropriate, ref. 31. [j] Ref. 42. [k] Refs. 43, 44. [l] Calc. by: $D_{0(Ph-Ph)} = 2\Delta_f H°_{(Ph^\cdot)} - \Delta_f H°_{(Ph-Ph)}$, values given in refs. 45 and 29, Table **5**-57.

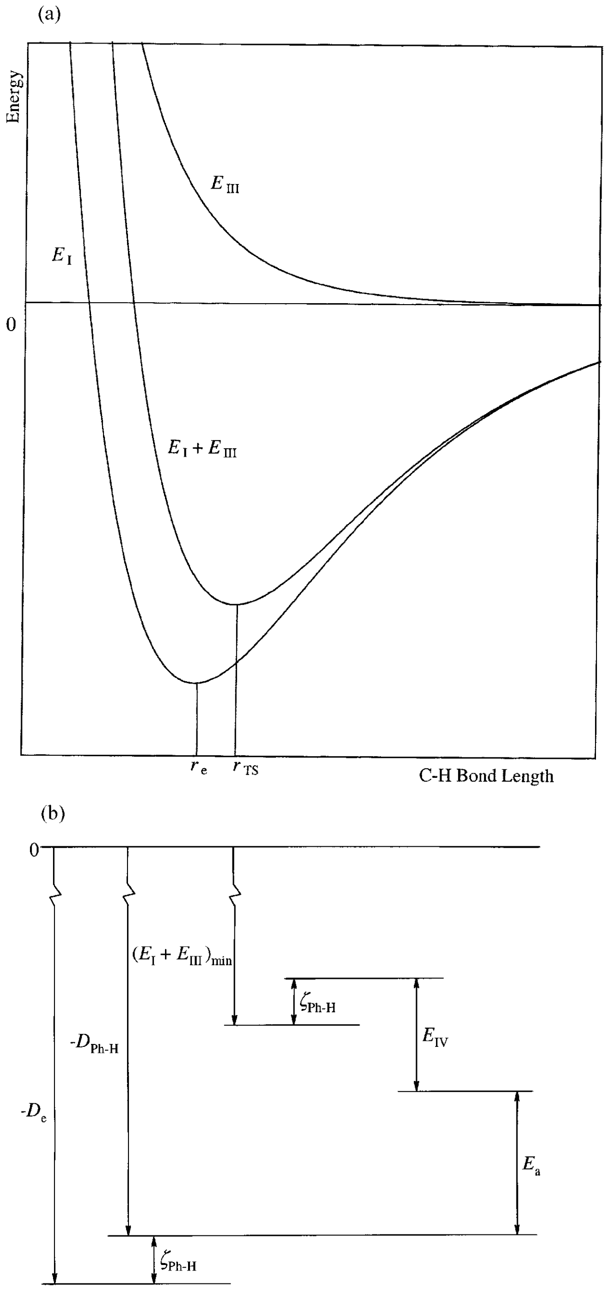


Fig. 4 (a) Potential energy curves for the Ph˙/PhH identity exchange. (b) Energy diagram for evaluation of E_a for the Ph˙/PhH identity exchange, *cf.* Table 5.

$$E_a = [(E_I + E_{III})_{min} + \zeta_{Ph-H} + E_{IV}] - D_{0(Ph-H)} \quad (10)$$

Table 5 gives the terms used in evaluating the activation energy for reaction (6).

The activation energy calculated by this method, 57.8 kJ mol^{-1}, is higher than the value derived from Roberts' correlation by 5.1 kJ mol^{-1}. Zavitsas and Chatgilialoglu[34] found that the average deviation between activation energies calculated by Zavitsas' method and the means of corresponding experimental values was 2.5 kJ mol^{-1}; Roberts[27] found a standard deviation of 2 kJ mol^{-1} for his data set of 65 reactions and he maintained that "the difference between calculated and experimental activation energies rarely exceeds 3.5 kJ mol^{-1}". The difference between the activation energies found by the two methods may not therefore be significant.

Pre-exponential factors for phenyl radical/benzene identity exchange and addition. In order to calculate a rate constant for the identity exchange using the Arrhenius equation with the estimated activation energy, a value of the pre-exponential factor A is required. Benson[46] has suggested that a value of $10^{8.5}$ dm^3 mol^{-1} s^{-1}, *i.e.* 3.2×10^8 dm^3 mol^{-1} s^{-1} applies to hydrogen exchange between non-atomic radicals. We have confirmed this value to be appropriate here and, for later use, have also calculated a pre-exponential factor for the Ph˙/PhH addition reaction of 5.47×10^6 dm^3 mol^{-1} s^{-1} at 298 K (see Appendix). The rate constants found using the activation parameters derived in this section are given along with others in Table 6.

(v) Comparison of reaction energetics

The pre-exponential factor, A_{uni}, for a unimolecular reaction is given by eqn. (11) where e is the base of natural logarithms,

$$A_{uni} = (ek_BT/h)\exp(\Delta S^‡_{uni}/R) \quad (11)$$

k_B is Boltzmann's constant, T is the absolute temperature, h is Planck's constant, $\Delta S^‡_{uni}$ is the entropy change of activation and R is the gas constant.[47]

The corresponding expression for the pre-exponential factor, A_{bi}, of a bimolecular reaction in solution phase is given, with the same notation, by eqn. (12); here, in the second set of

$$A_{bi} = (ek_BT/h)(RT/p^{\ominus})\exp(\Delta S^‡_{bi}/R) \quad (12)$$

brackets, $p^{\ominus} = 1$ atm and the gas constant R is valued as 8.206×10^{-2} dm^3 atm K^{-1} mol^{-1} whereas in the exponent it is valued as 8.314 J K^{-1} mol^{-1}.[47]

From eqn. (5) and the Arrhenius equation, it follows that the effective molarity of a unimolecular process is given by eqn. (13).

$$\begin{aligned} M_E &= A_{uni}\exp(-E_a^{uni}/RT)/A_{bi}\exp(-E_a^{bi}/RT) \\ &= (A_{uni}/A_{bi})\exp(-\Delta E_a/RT) \quad (13) \end{aligned}$$

Since for unimolecular reactions and bimolecular reactions in solution phase, $E_a = \Delta H^‡ + RT$,[47] eqn. (14) holds.

$$M_E = (A_{uni}/A_{bi})\exp(-\Delta\Delta H^‡/RT) \quad (14)$$

Substitution from eqns. (11) and (12) then gives eqn. (15).

$$\begin{aligned} M_E &= (p^{\ominus}/RT)\exp(\Delta\Delta S^‡/R)\exp(-\Delta\Delta H^‡/RT) \\ &= 0.041\exp(\Delta\Delta S^‡/R)\exp(-\Delta\Delta H^‡/RT) \text{ at 298 K} \quad (15) \end{aligned}$$

Table 6 Comparison of reaction energetics for bimolecular and unimolecular addition and exchange reactions

a) Bimolecular reactions

Reactants	Type	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1} [a]	A/dm^3 mol^{-1} s^{-1} [b]	k/dm^3 mol^{-1} s^{-1}	E_a/kJ mol^{-1}
Ph$^\bullet$/PhH	Addition	−150.8	5.47×10^6	$(4.5 \pm 0.3) \times 10^5$ [c]	(6.2 ± 0.2) [d]
	H-exchange	−116.9	3.23×10^8	1.60×10^{-2} [e]	57.8 [f]
				1.30×10^{-1} [g]	52.7 [h]

b) Unimolecular reactions

Reactant	Type	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1} [i]	A/s^{-1} [j]	k/s^{-1}	E_a/kJ mol^{-1} [k]	M_E/mol dm^{-3}
PhCOPh$^\bullet$ **6**	Cyclisation	0	1.66×10^{13}	$(8.0 \pm 0.9) \times 10^5$ [l]	41.0 ± 0.3	5.33
	H-exchange	0	1.66×10^{13}	$(1.2 \pm 0.2) \times 10^6$ [m]	40.0 ± 0.4	2.30×10^8
PhCR=CHPh$^\bullet$ **26a**	Cyclisation	0	1.66×10^{13}	$(3.0 \pm 0.5) \times 10^9$ [n]	21.0 ± 0.4	2.00×10^4

[a] Value estimated (see Appendix). [b] Value for 298 K calculated from estimated $\Delta S^{\ddagger}$ by eqn. (12). [c] Ref. 8. [d] Calc. from k and A by Arrhenius eqn. [e] Calc. by Arrhenius eqn. using estimated A with E_a obtained by eqn. (10). [f] Value obtained by eqn. (10). [g] Calc. by Arrhenius eqn. using estimated A with E_a obtained from eqn. (7). [h] Value obtained from eqn. (7). [i] Value assumed. [j] Value for 293 K, [(ek_BT/h)/s^{-1}]. [k] Calc. by Arrhenius eqn. using A with experimental k. [l] Ref. 14. [m] *cf*. Table 4, value for **8** and **9** assumed for **6**. [n] Ref. 1.

The value of an effective molarity at a given temperature is thus determined by an initial constant [which may incorporate a statistical correction as mentioned in (ii) above] and two exponential factors dependent, respectively, on the difference in entropy change of activation and enthalpy change of activation between the unimolecular process of interest and its bimolecular comparator. As a unimolecular process usually exhibits a small entropy change of activation whereas a bimolecular process exhibits a large negative value, the difference $\Delta\Delta S^{\ddagger}$ is large and positive and the entropy-dependent factor is a large figure. Whenever the unimolecular reaction has an enthalpy change of activation which is greater than that of its bimolecular comparator, the enthalpy-dependent exponent is negative and the enthalpy-dependent factor moderates the effect of the entropy-dependent factor in determining M_E; conversely, should the enthalpy change of activation of the unimolecular process be less than that of the bimolecular comparator, the enthalpy-dependent factor supplements the entropy-dependent factor in increasing M_E.

In addition to the parameters derived above for the hypothetical Ph$^\bullet$/PhH identity exchange and addition reactions, Table 6 also contains comparable data for the unimolecular reactions of interest. For these, values of $\Delta S^{\ddagger}$ were first estimated then activation energies were calculated *via* the Arrhenius equation from the derived A factors and experimental rate constants. On account of the rigidity of the aryl segments in species such as **6** and **26a**, to a reasonable approximation $\Delta S^{\ddagger}$ for all their unimolecular reactions can be taken to be zero whence, *via* eqn. (11) with $\Delta S^{\ddagger}_{uni} = 0$, $A = ek_BT/h = 1.66 \times 10^{13}$ s^{-1} at 293 K. The use of this value for A allows evaluation of the tabulated activation energies for the various processes. (The 5 K difference in temperature between the bimolecular and unimolecular reactions is not significant for present purposes.)

The activation energy for the addition of phenyl radical to benzene is less than those for the cyclisations of **6** and **26a**. For both processes, the conversion of addition from bimolecular to unimolecular mode therefore occurs at some enthalpic cost. If there were no enthalpic costs, the effective molarities of the two cyclisations would be given by the statistically corrected ratio of the appropriate A factors [*cf*. eqn. (13) with $\Delta E_a = 0$ or eqn. (14) with $\Delta\Delta H^{\ddagger} = 0$]; for both cyclisations, the isoenthalpic effective molarity would be $M_E^{iso} = 3 \times 1.66 \times 10^{13}/5.47 \times 10^6 = 9.1 \times 10^6$ mol dm^{-3}. The experimental values for **6** and **26a** are 5.3 and 2×10^4 mol dm^{-3}, respectively. For the cyclisation of **6** the entropic advantage is almost entirely annulled by the enthalpic cost which no doubt arises from the strain incurred by closure of a five-membered ring comprising four sp^2 carbons and one sp^3. The six-membered ring formed in the cyclisation of **26a** is less strained but, nevertheless, the effective molarity is reduced from its isoenthalpic value by a factor of 450. Previously, we have suggested that the relatively large effective molarity for cyclisation of **26a** may arise partly because the addition of phenyl radical to benzene may be attenuated by π–π repulsions between the two reactants for certain trajectories of approach.[1] Any directional constraint on a molecular collision which is required in order for the encounter to be productive is expected to be expressed in the entropy change of activation and hence in the pre-exponential factor. The comparatively large negative value for $\Delta S^{\ddagger}$, and correspondingly small value for A estimated for the bimolecular addition lend credence to this suggestion.

In contrast to the cyclisation reactions, the intramolecular hydrogen exchange in **6** apparently has an activation energy which is *lower* than both estimates deduced for its bimolecular comparator, the Ph$^\bullet$/PhH identity exchange. *A priori*, it is surprising that the activation energy associated with a non-linear approach should be less than that for a collinear C···H···C approach, particularly when there are no obvious effects operative such as intramolecular hydrogen bonding or exothermic Coulombic attractions which might conceivably attenuate the activation energy of the intramolecular reaction. There seem to be three possible causes for this discrepancy: underestimation of the activation energy of the intramolecular process, overestimation of the activation energy of the bimolecular process or neglect of some other factor.

Any underestimation of the activation energy of the intramolecular reaction is unlikely to rest on the assumption that **6** undergoes H-exchange at the same rate as the methylated radicals **8** and **9** since intermolecular hydrogen abstraction shows little substituent dependence.[6,48] The uncertainty in the experimental unimolecular H-exchange rate constant indicated in Table 4 is also clearly too small to account for the observed discrepancy. The question arises as to whether the calibration of the constants in Table 4 might be at fault. Since the work of Schuler and co-workers[6] which we have used in the present and earlier calibrations of aryl radical reactivity, von Sonntag and co-workers[48] have obtained absolute rate constants for the abstraction of hydrogen from alcohols by phenyl radical. These are greater than Schuler's values for abstraction by **16** by a factor of 2.17. If we adopt von Sonntag's data instead of Schuler's to calibrate our reactivities, the unimolecular rate constants given in Table 4 must all be *increased* by the same factor. The consequence of using the alternative calibration, and still assuming zero entropy change of activation, is therefore to *lower* the activation barriers to the reactions of **6** by 1.9 kJ mol^{-1}, *i.e.* the discrepancy is marginally exacerbated. Conceivably, the intramolecular H-exchange might occur by a mechanism which is different from the assumed direct C-to-C transfer of the hydrogen atom such as cyclisation/H-migration/C–C cleavage. This cannot be the explanation as cyclisation is somewhat slower than the H-exchange and so cannot provide a lower energy pathway and, furthermore, C–C bond formation which converts the aryl σ-radical into a delocalised π-radical is most probably irreversible.[7] The assumption of zero entropy change of activation for the intramolecular H-transfer is also unlikely to be the cause of the discrepancy for the following reason. If the discrepancy has arisen as a result of the activation energy of the intramolecular process being underestimated, in order to increase it and yet preserve the experimental rate constant from which it is derived, a larger A factor is necessary. This, in turn, would imply a positive entropy change of activation for the process: an increase in activation energy from 40 to 55 kJ mol^{-1} would require a compensatory change of A factor from 1.66×10^{13} to 7.67×10^{15} s^{-1}, implying $\Delta S^{\ddagger}$ to be 51.0 J K^{-1} mol^{-1}. This is not consistent with increased molecular ordering as **6** enters the transition state for H-transfer. In some processes a positive entropy change of activation can be ascribed to the liberation of molecules of solvation on passage to the transition state. This seems improbable here where the reactive centres are of hydrocarbon character and in an aqueous medium. It thus seems the activation energy for the intramolecular H-transfer is unlikely to be seriously underestimated.

If the activation energy for the bimolecular H-transfer has been overestimated, the method of Zavitsas has given the worst estimate which is surprising since it has worked well in many instances where the calculated value can be compared to experimental data.[34,37] For example, the values of E_a of 56.5 and 60.7 kJ mol^{-1}, respectively, for the Et$^{\bullet}$/EtH and Me$^{\bullet}$/MeH identity exchanges[34] are in excellent agreement with experimental values and are closely comparable to the value of 57.8 kJ mol^{-1} we find for the Ph$^{\bullet}$/PhH identity exchange. There is no significant overestimation of E_a values for the aliphatic exchanges and so no reason for assuming such in the aromatic case. Roberts' method of calculating E_a, when used with a plausible value for s_{Ph}, also gave a value exceeding 52 kJ mol^{-1}. We thus conclude that, for the identity exchange between benzene and the phenyl radical, an activation barrier of at least 55 kJ mol^{-1} is unlikely to be seriously overestimated.

If the activation barriers to the inter- and intra-molecular reactions of interest have not been wrongly estimated, the inverted order of their magnitudes must stem from some hitherto unconsidered factor and the problem reduces to *how* the bridging carbonyl group in **6** might enhance the apparent mutual reactivity of its reactive moieties relative to that of the separate phenyl radical and benzene molecule. As a direct electronic perturbation, the bridge exerts only an electron withdrawing inductive effect at both reactive centres and, in the transition state, these will be equal by reason of symmetry. It was seen above that H-exchange in **8** and **9** is insensitive to the unsymmetrical inductive effect of a *m*-Me group and that bimolecular H-abstraction from alcohols is also insensitive to substituent effects in aryl radicals.[48] It is difficult to see why then the bridging carbonyl group, regarded merely as a substituent on the reacting 'phenyl radical' and 'benzene ring' in **6**, should enhance their mutual reactivity by almost 1500-fold, *i.e.* $\exp(\Delta E_a/RT)$.

A collinear C···H···C approach is intrinsic to the Zavitsas method yet the fact that the intramolecular H-transfer occurs demonstrates that is not essential to hydrogen transfer. This suggests a manner in which the relative activation energy of the intramolecular process might be lowered. For the bimolecular reaction, at a given intermolecular distance the collinear approach allows comparable overlaps of the radical SOMO with both the C–H bond and antibond (Fig. 5). Constraint of the reactive centres to the non-linear approach by the bridging group will have the effect of reducing SOMO/C–H antibond overlap and increasing SOMO/C–H bond overlap, *i.e.* in the intramolecular H-transfer, for geometric reasons, the radical will react somewhat more electrophilically than in the intermolecular comparator. Should enhanced SOMO/C–H bond overlap more than compensate for reduced SOMO/C–H antibond overlap, the result would be a stabilisation of the transition state for intramolecular H-transfer relative to its ground state in a manner not available to the intermolecular reaction.

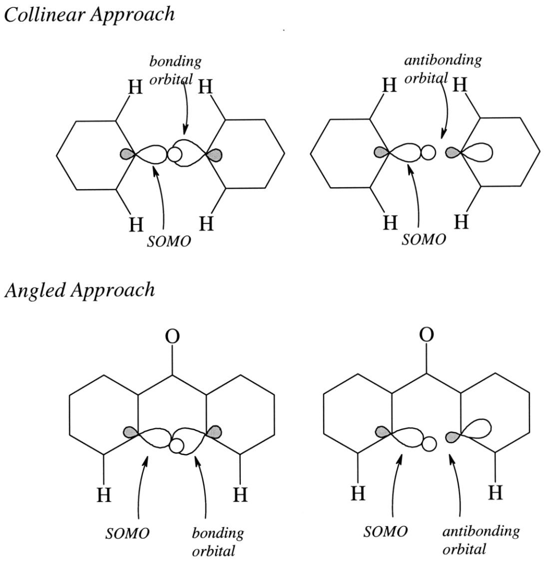


Fig. 5 Schematic diagram of orbital overlap in collinear and angled approaches of the reaction centres in hydrogen exchange between aryl groups. Collinear approach: at a given distance, the radical SOMO has similar overlap with both the H–C at a given distance, the radical SOMO overlaps the H–C bonding orbital more effectively than it overlaps the H–C antibonding orbital.

The reaction of **6** occurs in water and a solvent effect on it might also be considered. For any solvent to influence a reaction rate, there must be a differential effect between the ground and transition states. Since identity exchange reactions are thermo-neutral and scant bond polarisation develops, it is expected that any direct solvent effect on the change occurring in the reaction coordinate should be negligible. However, water molecules can solvate the carbonyl group in **6** by hydrogen bond donation to the carbonyl O-atom and by lone pair donation to the carbonyl C-atom. If such interaction should become stronger as **6** enters the transition state for H-transfer, the transition state would be indirectly relatively stabilised. It is expected that, comparable with benzophenone itself, the ground state conformation of **6** is non-planar and the aromatic rings able to rotate;[49] this may hinder the approach of solvating water molecules, particularly to the lobe of the π* orbital on the carbonyl C-atom. In the H-transfer transition state, the structure becomes planar and nucleophilic access to the π* orbital is less encumbered. It is thus possible that the carbonyl group of **6** might be more strongly solvated in the transition state for H-transfer than in the ground state and this factor could contribute to a relative lowering of the intramolecular barrier to H-transfer.

We tentatively suggest, therefore, that by geometrical effects on orbital overlap or by carbonyl group solvation, or a combination of both, the 1,5-radical translocation in **6** might be constrained by an activation energy barrier which is lower than that expected for the Ph$^{\bullet}$/PhH identity exchange. If this is the case, the effective molarity of the translocation will be greater than the isoenthalpic value. Inserting values into eqn. (13) together with a statistical correction factor of 3 gives $M_E = 2.30 \times 10^8$ mol dm^{-3} at 293 K.

(vi) Molecular orbital calculations

In the hope of throwing light on the processes of present interest we have carried out *MOPAC6* AM1 UHF MO calculations[50] for a number of reactants, derived transition states and products; also, we have carried out corresponding *FORCE* and *THERMO* calculations to obtain their thermodynamic and kinetic properties. The results are summarised in Table 7. In the *THERMO* calculations, in addition to the exclusion of the imaginary frequency in the reaction coordinate of a transition state, the lowest real frequency was excluded when this corresponded to the internal rotation of a phenyl group. In the case of the (*Z*)-stilben-2-yl radical **26b**, the lowest frequency corresponded to a coupled out-of-plane wagging of the two aryl rings. Suppression of this latter adjusts the calculated entropy in the same direction as would suppression of the internal rotation but the adjustment is rather greater than it should be. However, all the entropy adjustments are approximate as no consideration is given to the possibility that the suppressed internal rotations might be hindered to some degree. Enthalpy and entropy changes of reaction, ΔH° and ΔS°, and of activation, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, are the differences in enthalpy and entropy of formation between product or transition state, as appropriate, and the corresponding reactant(s). Activation energies E_a were calculated from the relation, $E_a = \Delta H^\ddagger + RT$, applicable for unimolecular and bimolecular reactions in solution.[47] The values of A were obtained from the calculated entropy changes of activation using eqn. (11) or (12) and the values of k_{calc} were obtained by application of the Arrhenius equation with the calculated E_a and A.

Addition reactions. The enthalpy of formation of benzene accords with that previously obtained by the AM1 approximation[50] and the entropy is in good agreement with the experimental value[51] but the enthalpy of formation calculated for the phenyl radical is smaller than expected[45] by more than 30 kJ mol^{-1}; its entropy is also somewhat less than estimated (see Appendix). Nevertheless, the calculations do indicate the addition of the phenyl σ-radical to benzene, giving the phenylcyclohexadienyl π-radical, to be strongly exothermic, as expected. The entropy change of activation calculated for the addition is in excellent agreement with that estimated (see Appendix). There must be error in the enthalpy of formation calculated for the transition state for addition which compensates that in the calculation for the phenyl radical since the calculated enthalpy change of activation is in good agreement with the estimated figure given in Table 6. Given these agreements, the calculated A factor, activation energy and reaction rate also accord surprisingly well with those in Table 6.

The Pschorr cyclisation of 2-benzoylphenyl radical, **6**, is exothermic although not to the extent of the bimolecular addition of the phenyl radical to benzene, no doubt reflecting the ring strain in the hydrofluorenyl π-radical. As with bimolecular addition, the calculations of the kinetic parameters of the cyclisation of **6** agree remarkably well with the data of Table 6. The calculations indicate the cyclisation of **26b** to be more exothermic than both the cyclisation of **6** and the addition of Ph$^\bullet$ to benzene. This result can be explained qualitatively by the new six-membered ring in the derived π-radical being less strained than in the five-membered case and the conjugation being more extensive than in the bimolecular adduct but, also, it may be that $\Delta_f H$ calculated for **26b** is too large. That this is so, is indicated by the finding that the activation energy calculated for cyclisation of **26b** is improbably small, a failure that could result from the enthalpy of formation calculated for **26b** being too close to that calculated for the cyclisation transition state.

Exchange reactions. The activation energy calculated for the intramolecular hydrogen exchange in **6** is higher than that calculated for the hypothetical bimolecular exchange between benzene and Ph$^\bullet$ and the values of both are less than the estimated values of Table 6. Thus the ordering of the computed activation energies follows intuitive expectation and does not reflect the discrepancy in the estimated values given in Table 6. However, the difference between the two computed activation energies (6.2 kJ mol^{-1}) is not marked, little more than a third of the discrepancy, which suggests, perhaps, that the activation energy for H-transfer may not be strongly dependent on the direction of approach of the radical to the abstracted atom. Since the MO calculations take no cognisance of solvation, these results are also consistent with the hypothesis that the factor which inverts the order of the estimated activation energies might be differential solvation of the carbonyl group between ground and transition states but, in view of the approximations in obtaining both the estimated and computed energies and their small difference, this may be fortuitous. The difference in activation energies for the intramolecular hydrogen exchange and the cyclisation in **6** is also small but favouring the hydrogen exchange whereas that between bimolecular addition and hydrogen exchange is much larger and strongly favouring addition. This reflects the experimental facts.

The AM1 and derived calculations on this set of unimolecular and bimolecular addition and H-exchange reactions thus give a good quantitative account of the energetics of addition processes and a qualitative account of the exchange processes which together reflect the relative ordering of the magnitudes of all the rate constants: cyclisation of (*Z*)-stilben-2-yl radical ≫ H-translocation in 2-benzoylphenyl radical > cyclisation of 2-benzoylphenyl radical > addition of phenyl radical to benzene ≫ phenyl/benzene identity exchange.

Conclusions

2-Aroylphenyl radicals undergo two competitive intramolecular reactions: cyclisation to a hydrofluorenyl π-radical and hydrogen exchange which gives rise to a reversible 1,5-translocation of the radical centre between the aromatic rings. Rate constants have been evaluated for these processes.

When the rate of cyclisation is compared with the known rate of addition of phenyl radical to benzene,[8] a statistically corrected effective molarity of 5.3 mol dm^{-3} can be calculated. This contrasts with the effective molarity of 2×10^4 mol dm^{-3} found previously[1] for the cyclisation of a (*Z*)-stilben-2-yl radical to a hydrophenanthrene π-radical (referred to the same bimolecular comparator). The small effective molarity for Pschorr fluorene closure arises because the entropic advantage of the unimolecular process only just outweighs the enthalpic advantage of the bimolecular addition reaction. The contrasting large effective molarity of Pschorr phenanthrene closure, calculated relative to the same bimolecular comparator, occurs because the entropic advantage of the unimolecular process is less diminished by the enthalpic cost of ring closure; this cost is minimised because the rigid structure of the bridging alkene holds the reactive moieties at such a distance that, with only minor displacement, they can enter a transition state which occurs earlier in its reaction coordinate than does that of the comparator reaction. The calculation of an effective molarity for the hydrogen exchange process requires a rate constant for the hypothetical phenyl radical/benzene identity exchange reaction. By estimating a value for this of 1.60×10^{-2} dm^3 mol^{-1} s^{-1} we calculate a statistically corrected effective molarity of 2.2×10^8 mol dm^{-3}.

Table 7 Results of AM1 UHF semi-empirical MO calculations and their derived thermodynamic and kinetic parameters for 300 K

a) Bimolecular reactions

Ground states	$\Delta_f H$/kJ mol^{-1}	S/J K^{-1} mol^{-1}	$\Delta H°$/kJ mol^{-}	$\Delta S°$/J K^{-1} mol^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	E_a/kJ mol^{-1}	A/dm^3 mol^{-1} s^{-1}	k_{calc}/dm^3 mol^{-1} s^{-1}
PhH	92.25	269.53							
Ph$^{\bullet}$	306.20	283.65							
Ph–$C_6H_6^{\bullet}$ *π-radical*	248.58	387.21	−149.9	−166.0					
Transition states									
[PhH/Ph]$^{\bullet}$ *addition*	405.52	403.24			7.1	−149.9	9.6	6.18×10^6	1.3×10^5
[Ph·H·Ph]$^{\bullet}$ *exchange*	422.14	395.57			23.7	−157.6	26.2	2.45×10^6	67.2

b) Unimolecular reactions

Ground States	$\Delta_f H$/kJ mol^{-1}	S/J K^{-1} mol^{-1}	$\Delta H°$/kJ mol^{-}	$\Delta S°$/J K^{-1} mol^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	E_a/kJ mol^{-1}	A/s^{-1}	k_{calc}/s^{-1}
2-PhCOPh$^{\bullet}$, **6**	298.47	412.95							
cyc-PhCOPh$^{\bullet}$ *π-radical*	178.46	408.58	−120.0	−4.4					
2-PhCH=CHPh$^{\bullet}$, **26b**	467.67	421.80^a							
cyc-PhC=CHPh$^{\bullet}$ *π-radical*	290.34	414.01	−177.3	7.8^a					
Transition states									
[2-PhCOPh]$^{\bullet}$ *cyclisation*	337.06	412.55			38.6	−0.4	41.1	1.58×10^{13}	7.44×10^5
[2-PhCOPh]$^{\bullet}$ *exchange*	328.35	414.06			29.9	1.1	32.4	1.89×10^{13}	3.17×10^7
[2-PhCH=CHPh]$^{\bullet}$ *cyclisation*	471.53	420.83			3.9	−1.0^a	6.4	$1.47 \times 10^{13\,a}$	$1.06 \times 10^{12\,a}$

[a] Lowest frequency vibration suppressed in **26b**.

Semi-empirical molecular orbital calculations (AM1 UHF) and derived thermodynamic calculations account surprisingly well for most of the various addition reaction rates; they are less successful in predicting hydrogen abstraction rates but, nevertheless, do predict correctly the ordering of the rates of all of the processes.

Experimental

(i) Materials

The 2-aminobenzophenones required as precursors to the diazonium ions used in this work were prepared by the reaction of an appropriate 2-aminobenzonitrile with an excess of an appropriate Grignard reagent followed by hydrolysis of the resultant imine.

2-(4-Methylbenzoyl)benzenediazonium tetrafluoroborate, 1. 4-Bromotoluene (42.8 g) in THF (20 cm^3) was added to Mg (10 g) in THF and refluxed under nitrogen to produce the Grignard reagent. 2-Aminobenzonitrile (5.9 g) in THF (20 cm^3) was added slowly and the mixture stirred overnight. The mixture was then added to a saturated solution of ammonium chloride and extracted into ethyl acetate. After evaporation of the solvent and other volatiles, the resultant solid was dissolved in a minimum amount of methanol and added to concentrated hydrochloric acid to complete hydrolysis of the intermediate imine. Following basification, the aqueous layer was re-extracted with ethyl acetate. Evaporation of the extract gave crude 2-amino-4′-methylbenzophenone, 4.5 g (43%), ν_{max}($CHCl_3$)/cm^{-1} 3499, 3362 (NH_2), 1613 (C=O); δ_H(270 MHz, $CDCl_3$) 2.40 (s, 3H), 6.00 (br, NH_2), 6.57 (appt. t, 1H), 6.68 (d, *J* 8.2, 1H), 7.2–7.4 (m, 3H), 7.45 (dd, *J* 8.0, 1.5, 1H), 7.55 (d, *J* 8.3, 2H); δ_C(67.9 MHz, $CDCl_3$) 21.5, 115.5, 116.9, 118.5, 128.9 (2C), 129.4 (2C), 134.0, 134.4, 137.2, 141.7, 150.7, 198.8. The amine (4.3 g) was stirred in hydrochloric acid (20 cm^3, 2.5 mol dm^{-3}) and chilled to 0 °C; $NaNO_2$ (1.5 g) in a minimum of water was added at 0 °C. After stirring for 30 min, the mixture was filtered into a solution of $NaBF_4$ in water. The precipitate was collected, redissolved in acetone and the solution filtered; addition of diethyl ether to the solution precipitated *2-(4-methylbenzoyl)benzenediazonium tetrafluoroborate*, 1.8 g, (29%), mp 104–106 °C [Found: M^+ (FAB) 223.0872. $C_{14}H_{11}N_2O$ requires *M* 223.0871]; *m*/*z* 223 (46%, M^+), 195 (46), 154 (100), 137 (69), and 136 (87); ν_{max}(Nujol)/cm^{-1} 2293 ($N\equiv N^+$), 1655 (C=O), 1052 br (BF_4^-); δ_H[500 MHz, $(CD_3)_2SO$] 2.47 (s, 3H), 7.49 (d, *J* 8.3, 2H), 7.79 (d, *J* 8.3, 2H), 8.18 (dd, *J* 7.8, 1.8, 1H), 8.26 (td, *J* 8.3, 1.3, 1H), 8.36 (td, *J* 7.6, 1.2, 1H), and 9.03 (dd, *J* 8.2, 1.0, 1H); δ_C[125.8 MHz, $(CD_3)_2SO$] 21.3, 115.6, 129.5 (2C), 130.9 (2C), 131.4, 133.5, 134.1, 136.1, 137.4, 140.1, 145.5 and 189.4.

2-Benzoyl-5-methylbenzenediazonium tetrafluoroborate, 7. 4-Methyl-2-nitroaniline (15.2 g) was converted by Sandmeyer cyanation into 4-methyl-2-nitrobenzonitrile, 11.4 g (70%), mp 94–95 °C, lit.[52] 96–98 °C. This nitrobenzonitrile (10 g) was reduced by iron filings in $MeCO_2H$–EtOH (1 : 1 v/v, 140 cm^3) to give 2-amino-4-methylbenzonitrile, 7.1 g (87%), mp 85–86 °C, lit.[53] 93–95 °C. The 2-amino-4-methylbenzonitrile (5.4 g) on reaction with an excess of phenylmagnesium bromide by the procedure above gave crude 2-amino-4-methylbenzophenone 3.5 g (40%), ν_{max}(Nujol)/cm^{-1} 3457, 3351 (NH_2), 1621 (C=O); δ_H(270 MHz, $CDCl_3$) 2.28 (s, 3H), 6.12 (br, NH_2), 6.42 (d, *J* 8.3, 1H), 6.54 (s, 1H), 7.34 (d, *J* 8.0, 1H), 7.4–7.55 (m, 3H) and 7.61 (d, *J* 6.3, 2H); δ_C(67.9 MHz, $CDCl_3$) 21.7, 115.3, 115.9, 117.0, 128.0 (2C), 129.9 (2C), 130.7, 134.7, 140.3, 145.3, 151.2 and 198.7. Diazotisation of the amine (3.2 g) gave *2-benzoyl-5-methylbenzenediazonium tetrafluoroborate*, 1.8 g (38%), mp 93–94 °C [Found: M^+ (FAB) 223.0868. $C_{14}H_{11}N_2O$ requires *M* 223.0871]; *m*/*z* 223 (M^+, 69%), 195 (100), 154 (81), 137 (55) and 136 (73); ν_{max}(Nujol)/cm^{-1} 2282 ($N\equiv N^+$), 1651 (C=O), 1065 br (BF_4^-); δ_H[270 MHz, $(CD_3)_2SO$] 2.61 (s, 3H), 7.6–8.0 (m, 5H), 8.08 (d, *J* 7.6, 1H), 8.18 (d, *J* 7.6, 1H) and 8.87 (s, 1H); δ_C[67.9 MHz, $(CD_3)_2SO$] 21.1, 115.7, 129.3 (2C), 130.9 (2C), 133.9, 134.4, 134.8, 135.1, 136.1, 140.9, 146.0 and 190.1.

2-(4-Methylbenzoyl)-5-methylbenzenediazonium tetrafluoroborate. 2-Amino-4-methylbenzonitrile (4.8 g) in THF was reacted overnight under nitrogen with an excess of 4-methylphenylmagnesium bromide. Following addition to saturated ammonium chloride solution the mixture was extracted with ethyl acetate then, after removal of solvent and other volatiles, the residual solid was dissolved in methanol and added to concentrated hydrochloric acid to ensure hydrolysis of the intermediate imine. The crude product was isolated by basification and extraction with ethyl acetate and, after removal of solvent, the solid was chromatographed on a silica column, eluting with chloroform to give 2-amino-4,4′-dimethylbenzophenone as a yellow solid (5.5 g, 67%), mp 108–109 °C (lit.[54] 119 °C) (Found: M^+ 225.1145. $C_{15}H_{15}NO$ requires *M* 225.1154); *m*/*z* 225 (M^+, 66%), 224 (100), 210 (20), 182 (11), 134 (28) 119 (12) and 91 (18); ν_{max}(Nujol)/cm^{-1} 3449, 3342 (NH_2), 1631 (C=O); δ_H(270 MHz, $CDCl_3$) 2.26 (s, 3H), 2.40 (s, 3H), 6.04 (br, NH_2), 6.40 (ddd, *J* 8.2, 1.7, 0.5, 1H), 6.51 (s, 1H), 7.23 (d, *J* 8.0, 2H), 7.34 (d, *J* 8.2, 1H), and 7.53 (d, *J* 8.0, 2H); δ_C(67.9 MHz, $CDCl_3$) 21.5, 21.7, 116.2, 116.9, 117.0, 128.7 (2C), 129.3 (2C), 134.5, 137.5, 141.3, 145.0, 151.0 and 198.4. This amine (4.0 g) was dissolved in a mixture of 50% fluoroboric acid (11 cm^3) and water (7 cm^3) at 0 °C and diazotised by addition of $NaNO_2$ (1.3 g) in a minimum of water followed by stirring at 0 °C for 0.5 h. The precipitate was collected, dissolved in acetone, filtered and reprecipitated by addition of diethyl ether to give *2-(4-methylbenzoyl)-5-methylbenzenediazonium tetrafluoroborate* as a yellow solid (1.7 g, 30%), mp 96–98 °C [Found: M^+ (FAB), 237.1026. $C_{15}H_{13}N_2O$ requires *M* 237.1028]; *m*/*z* 237 (15), 209 (17), 154 (100), 137 (66) and 136 (72); ν_{max}(Nujol)/cm^{-1} 2282 ($N\equiv N^+$), 1650 (C=O) and 1062 br (BF_4^-); δ_H[270 MHz, $(CD_3)_2SO$] 2.52 (s, 3H), 2.67 (s, 3H), 7.54 (d, *J* 7.7, 2H), 7.84 (d, *J* 7.7, 2H), 8.14 (d, *J* 8.0, 1H), 8.24 (d, *J* 8.0, 1H) and 8.93 (s, 1H); δ_C[67.9 MHz, $(CD_3)_2SO$] 21.0, 21.6, 115.6, 129.8 (2C), 131.0 (2C), 131.8, 133.7, 135.4, 136.0, 140.8, 145.6, 145.8 and 189.6.

2-Hydroxybenzophenones were required as chromatographic standards. 2-Hydroxy-4′-methylbenzophenone was prepared by reaction of 2-hydroxybenzonitrile with an excess of 4-methylphenylmagnesium bromide. It was assumed that its isomer, 2-hydroxy-4-methylbenzophenone would exhibit the same chromatographic response factor. 2-Hydroxy-4,4′-dimethylbenzophenone was isolated from a homolysis of 2-(4-methylbenzoyl)-5-methylbenzenediazonium tetrafluoroborate.

2-Hydroxy-4′-methylbenzophenone, 10. 4-Methylphenylmagnesium bromide was prepared by reaction of 4-bromotoluene (21.4 g) with magnesium (5 g) in THF (120 cm^3). To this was added 2-hydroxybenzonitrile (3 g) in THF (20 cm^3) and the mixture was stirred overnight under nitrogen. Following addition to saturated ammonium chloride, the organic part was extracted into ethyl acetate. After removal of the solvent and other volatiles, the residual solid was dissolved in methanol and treated with conc. HCl to ensure complete hydrolysis of the intermediate imine. The acidity was reduced by addition of sodium hydroxide and the crude product isolated by extraction into ethyl acetate. Chromatography on a silica column, eluting with chloroform, gave *2-hydroxy-4′-methylbenzophenone* (3.2 g, 60%) as a yellow solid mp 57–58 °C, lit.[55] 54–57 °C (Found: M^+ 212.0836. $C_{14}H_{12}O_2$ requires *M* 212.0837); *m*/*z* 212 (M^+, 65%), 211 (63), 197 (100), 121 (50), 120 (37), 119 (52), 91 (52) and 65 (48); ν_{max}(Nujol)/cm^{-1} 3000 br (OH), 1629 (C=O), 1245 (C–O); δ_H(270 MHz, $CDCl_3$) 2.44 (s, 3H), 6.86 (ddd, *J* 8.0, 7.3, 1.2, 1H), 7.06 (dd, *J* 8.5, 1.2), 7.3 (d, *J* 7.7, 2H), 7.49 (appt. td, 1H), 7.59 (d, *J* 8.0, 2H) and 7.61 (dd, *J* 8.0, 1.7, 1H); δ_C(67.9 MHz, $CDCl_3$) 21.6, 118.3, 118.5, 119.2, 129.0 (2C), 129.4 (2C), 133.5, 135.1, 136.0, 142.7, 163.1 and 201.3.

2-Hydroxy-4,4′-dimethylbenzophenone. 2-(4-Methylbenzoyl)-5-methylbenzenediazonium tetrafluoroborate (0.5 g) was dissolved in a solution of $Cu(NO_3)_2$ (500 cm^3, 1 mol dm^{-3}). A solution of ascorbic acid (1 cm^3, 0.5 mol dm^{-3}) was added; the evolution of nitrogen was immediate. After ten minutes, the products were extracted into ethyl acetate. Following removal of the solvent and chromatography of the residue on a silica column, eluting with light petroleum (40–60 °C)–diethyl ether (9 : 1), *2-hydroxy-4,4′-dimethylbenzophenone* was obtained as a yellow solid (0.15 g, 43%), mp 67–68 °C, lit.[54] 73–74 °C (Found: M^+ 226.1000. $C_{15}H_{14}O_2$ requires *M* 226.0994); *m*/*z* 226 (M^+, 91%), 225 (79), 211 (100), 160 (87), 135 (53), 134 (28), 119 (27) and 91 (92); ν_{max}(Nujol)/cm^{-1} 3000 br (OH), 1630 (C=O), 1250 (C–O); δ_H(270 MHz, $CDCl_3$) 2.38 (s, 3H), 2.46 (s, 3H), 6.69 (d, *J* 8.0, 1H), 6.89 (s, 1H), 7.31 (d, *J* 8.0, 2H), 7.50 (d, *J* 8.2, 1H) and 7.59 (d, *J* 8.0, 2H); δ_C(67.9 MHz, $CDCl_3$) 21.6, 22.0, 117.0, 118.4, 119.8, 128.9 (2C), 129.3 (2C), 133.4, 135.4, 142.4, 147.8, 163.3 and 200.8.

(ii) Determination of relative rate constants

As appropriate, diazonium salts **1** or **7** (40 mg) were dissolved in aqueous solutions of $Cu(NO_3)_2$ (49 cm^3) made up by dilution of a master solution (0.9925 mol dm^{-3}), which had been standardised iodometrically.[56] When freshly made, each solution was homolysed upon addition of 1 cm^3 of ascorbic acid (0.5 mol dm^{-3}). Nine or ten different final copper concentrations were used as indicated in Table 1. Effervescence of nitrogen occurred immediately and after ten minutes the products were extracted into ethyl acetate. Following concentration of the extracts on the rotary evaporator, each was analysed in duplicate by GC. Each run was itself also duplicated so that the product ratios given in Table 1 are the means of four analyses. (The individual points rather than their means were used in finding the gradients and intercepts in Table 2 in order to minimise the uncertainties.) The isomeric hydroxybenzophenones **10** and **11** were assumed to have equal response factors, product ratios were thus taken to equal their integrated peak area ratios. The GC analysis was carried out on a Carbowax capillary column (60 m) using the following temperature program: isothermal at 225 °C for 56 minutes then ramped at 5° min^{-1} to 235 °C and held for 20 minutes. Four products were obtained from each homolysis which were identified as in Table 8. The amount of 4-methylbenzophenone under these conditions was minor as the only hydrogen donor added was the ascorbic acid initiator.

Table 8 Identification of products from homolysis of **1** and **7** in $Cu(NO_3)_2$ solutions

Retention time/min	Identification
37.55	4-Methylbenzophenone, **15**; *m*/*z* 196 (M^+, 41%), 181 (6), 119 (100), 105 (34), 91 (43), 77 (44) and 65 (25) in agreement with precedent.[a]
49.33	2-Hydroxy-4′-methylbenzophenone, **10**; MS identical with synthesised material.
49.87	2-Hydroxy-4-methylbenzophenone, **11**; *m*/*z* 212 (M^+, 66%), 211 (100), 135 (90), 105 (37), 77 (86) and 51 (21).
66.62	3-Methylfluoren-9-one, **14**; *m*/*z* 194 (M^+, 100%), 165 (82) and 139 (12).

[a] Ref. 57.

(iii) Calibration of Sandmeyer hydroxylation rates

The following procedure is typical: the diazonium ion of interest (40 mg) was dissolved in a solution of $Cu(NO_3)_2$ (25 cm^3, 0.9925 mol dm^{-3}) to which was added an appropriate amount of a 5 M solution of one of the alcohols (methanol, ethanol, propan-2-ol, *tert*-butyl alcohol) and the volume made up to 49 cm^3 with water. Reaction was initiated by addition of 1 cm^3 of ascorbic acid (0.5 mol dm^{-3}). For methanol and ethanol four final concentrations (0.5, 1.0, 1.5 and 2.0 mol dm^{-3}) were obtained and for the other alcohols two (0.5 and 1.0 mol dm^{-3}; use of a large concentration of propan-2-ol gave peaks of disparate area whereas use of high concentrations of *tert*-butyl alcohol led to phase separation). On initiation, evolution of nitrogen was immediate; after ten minutes the products were extracted into ethyl acetate, the extracts concentrated by rotary evaporation, and analysed by GC as above. Each run was carried out and analysed in duplicate. Response factors were determined for the appropriate benzophenone reduction products and hydroxylation products by use of authentic materials (again the isomeric 2-hydroxymethylbenzophenones were assumed to have equal factors) and used to correct the peak area ratios of reduction product to hydroxylation product(s). The corrected ratios were plotted against the alcohol concentrations (*e.g.* Fig. 2a) and their gradients determined. From the gradients ($k^H/k^{OH}[Cu^{2+}]$) values of k^{OH} for each radical were evaluated using Schuler's k^H values[6] as described in the text.

Table 9 Evaluation of Arrhenius pre-exponential factors for the identity exchange and addition reactions of phenyl radical and benzene

Species of interest	$Ph^\bullet$	$Ph^\bullet/PhH_{exchange}$ TS	$Ph^\bullet/PhH_{addition}$ TS
Symmetry number, $\sigma_{species}$	2	8	2
Model species	PhH	Ph–Ph	Ph–Ph
Symmetry number, σ_{model}	12	8	8
$S^\circ_{298(model)}$/J K^{-1} mol^{-1}	269.2[a]	389.5[b]	389.5[b]
Symmetry correction,[c] S_{sym}/J K^{-1} mol^{-1}	14.9	0	11.5
Spin correction,[d] S_{spin}/J K^{-1} mol^{-1}	5.8	5.8	5.8
Vibrational correction,[e,f] S_{vib}/J K^{-1} mol^{-1}	−1.4[g]	45.3[h]	0
Mass corrections,[f] S_{mass}/J K^{-1} mol^{-1}	0	0	0
$S^\circ_{298\ (species)}$/J K^{-1} mol^{-1}[i]	288.5	440.6	406.8
$\Delta S^\ddagger$/J K^{-1} mol^{-1}[j]		−116.9	−150.9
A/dm^3 mol^{-1} s^{-1}[k]		3.23×10^8	5.47×10^6

[a] Ref. 51. [b] Ref. 58. [c] $S_{sym} = R\ln(\sigma_{model}/\sigma_{species})$, ref. 46. [d] $S_{spin} = R\ln2$, ref. 46. [e] Calc. by the Einstein eqn. $S_{vib} = R\{(\omega hc/k_BT)[\exp(\omega hc/k_BT) - 1]^{-1} - \ln[1 - \exp(-\omega hc/k_BT)]\}$, where ω is the frequency of the oscillator, *h* is Planck's constant, *c* is the velocity of light, k_B is Boltzmann's constant and *T* is the absolute temperature, ref. 59. [f] Corrections of magnitude <1 J K^{-1} mol^{-1} are neglected. [g] Due to 1 CCH bending mode at 673 cm^{-1} in benzene, ref. 40. [h] Due to 2 CHC bending modes at 37 cm^{-1} found by AM1 UHF MO calculations for transition states with both co-planar and orthogonal rings. [i] $S^\circ_{298(species)} = S^\circ_{298(model)} + S_{sym} + S_{spin} + S_{vib} + S_{mass}$, ref. 46. [j] $\Delta S^\ddagger = S^\circ_{298(TS)} - (S^\circ_{298(PhH)} + S^\circ_{298(Ph^\bullet)})$. [k] Calc. by eqn. (12).

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Appendix

Arrhenius pre-exponential factors for the reactions of phenyl radical with benzene were calculated using eqn. (12) from entropy changes of activation estimated by Benson's method.[46] Here a transient entity, such as a transition state or radical, is ascribed the entropy of a structurally comparable stable molecule with corrections applied for any change in symmetry number σ, and, for radical species, for the spin; adjustments for significant vibrational or mass differences between the transient species and its model may also be included. Terms used for the evaluation of the two pre-exponential factors are given in Table 9.

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