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Steric effects of nucleophile-radical coupling reaction. Determination of rate constants for the reaction of aryl radicals with 2-naphthoxide anion†

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The absolute rate constants for the reaction of different aryl radicals with 2-naphthoxide anion were determined using an indirect method, a competition of the coupling reaction with the H-atom abstraction. We here show that the radical-ambident nucleophile reactions are sensitive to steric hindrance. A lower reactivity is found for 2-anisyl radical with respect to 4-anisyl and for 2-methoxy-1-naphthyl radical with respect to 1-naphthyl ($k_{\mathbf{2b}} < k_{\mathbf{2a}}$ and $k_{\mathbf{2d}} < k_{\mathbf{2c}}$). The *ortho* substitution to the radical centre decreases the rate constant. The reactivity is in agreement with energy barriers determined by theoretical calculations.

Introduction

The last decades have witnessed an explosive growth in the use of radical reactions in organic synthesis. Aryl radicals are important reactive intermediates in many reactions of synthetic relevance. For example, they can react with nucleophiles by the $S_{RN}1$ mechanism to form a substitution product (eqn (1)).[1]

$$Ar^{\bullet} + Nu^{-} \rightarrow\rightarrow ArNu \qquad (1)$$

In the $S_{RN}1$ process,[1] a photostimulated electron transfer from the nucleophile anion to the substrate (aryl halide, ArX) generated a radical anion of the precursor. The fragmentation of the C–halogen bond originates the aryl radical. The radicals thus formed can couple with the nucleophile to give the radical anion of the product (eqn (2)–(4)).

$$ArX + Nu^{-} \xrightarrow{h\nu} ArX^{\bullet -} + Nu^{\bullet} \qquad (2)$$

$$ArX^{\bullet -} \rightarrow Ar^{\bullet} + X^{-} \qquad (3)$$

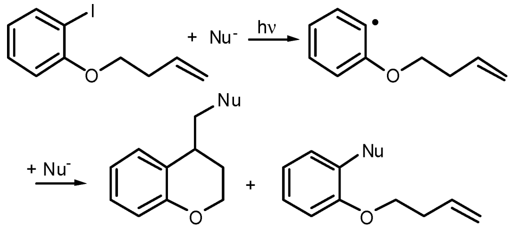
$$Ar^{\bullet} + Nu^{-} \rightarrow ArNu^{\bullet -} \qquad (4)$$

$$ArNu^{\bullet -} + ArX \rightarrow ArNu + ArX^{\bullet -} \qquad (5)$$

Nevertheless, not many kinetic data are available for the fundamental steps in which the aryl radicals are involved. The determination of the rate constant of the radical coupling reactions (eqn (4)) can contribute to the understanding of the course of processes as well as to the achievement of valuable synthetic results.

The absolute value of the rate constant for the reaction of aryl radicals with some nucleophiles has been determined electrochemically. The phenyl radical appears to be less reactive than other aryl radicals. The rate constants for its reaction with nucleophiles (PhS^{-}, $(EtO)_2PO^{-}$ and $^{-}CH_2COMe$) are in the range 10^{7-8} M^{-1} s^{-1} in liquid ammonia at −33 °C (2.6×10^7, 3.8×10^8 and 2.7×10^8 M^{-1} s^{-1}, respectively). Other radicals, such as 1-naphthyl, 3-pyridyl and 3- or 4-quinolyl radicals, react with rates close to the diffusion limit (10^9 to 10^{10} M^{-1} s^{-1}).[2]

The rate constants can be obtained by an indirect method using a radical probe (eqn (6)). In this case the substitution competes with the intramolecular cyclization. The phenyl type radicals react with PhS^{-} and $(EtO)_2PO^{-}$ with a rate of 2.6×10^8 and 2.5×10^9 M^{-1} s^{-1} in DMSO at 25 °C.[3,4]



(6)

Another alternative to determining the coupling rate by two competitive processes of the radical intermediate is by employing the coupling with the nucleophile (eqn (4)) *vs.* H-atom abstraction from the solvent. The rate constants for the reaction between phenyl, 1-naphthyl or 9-anthryl radicals and pinacolone anion in DMSO have been reported using this methodology (3.3×10^9, 2.9×10^9 and 4.4×10^8 M^{-1} s^{-1}, respectively).[5]

On the other hand, it is known that the nucleophile–radical coupling reaction is less sensitive to steric hindrance than expected. The *ortho* substituted aryl radicals react quite well with many nucleophiles even when they have an important steric demand. In the reaction of the enolate anion of acetone with 2,4,6-triethylphenyl radical, a 70% yield of coupling has been determined. However, the yield

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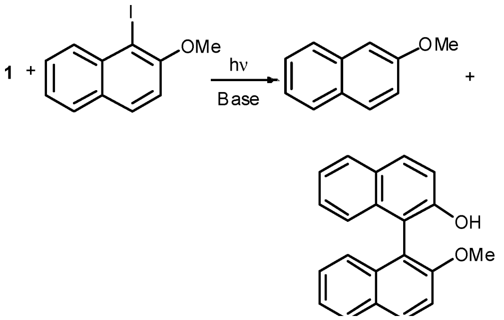
† Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra of compound **3e**. The energy of PES relevant points of the reaction of the anion of **1** with different aryl radicals and solvents. The hybridization change (sp^2 to sp^3) in the reaction path for the coupling of 2-naphthoxide anion and 2-methoxy-1-naphthyl radical. See DOI: 10.1039/b820374a

decreases considerably (16%), accompanied by an increase in the reduction product (ArH) when two *i*-Pr groups are adjacent to the radical centre.[6] The reaction of pinacolone anion with 2,6-dimethylphenyl radical in DMSO afforded reduction and substitution products in a ratio as high as 1 : 4. In contrast, the reaction with halobenzene (phenyl radical) provides less than 1% of the H-abstraction product.[7] These results suggest that the approach of the enolate ion is more difficult when the hindrance at the radical centre increases.

Recently, we have studied the reaction of the anion of 2-naphthol (**1**) with the 2-methoxy-1-naphthyl radical to obtain a disubstituted binaphthyl system (eqn (7)). Thus the reaction offers an alternative route to synthesize BINOL. We showed qualitative experimental evidence of the steric effects.[8] We observed a decrease in product yield compared with the reaction of this anion with 1-naphthyl radical in similar conditions (35 and 52%, respectively), accompanied by an increase in the reduction (56 and 20%).



(7)

In order to determine the importance of the steric hindrance, in this paper we report a first quantitative study of the steric effect in the coupling reactions (eqn (4)). The coupling rate constants for the reaction of aryl radicals with the anion of 2-naphthol (**1**) were determined in DMSO using hydrogen abstraction from the solvent as a competitive reaction. Theoretical calculations were performed in order to provide support for the experimental results reported here.

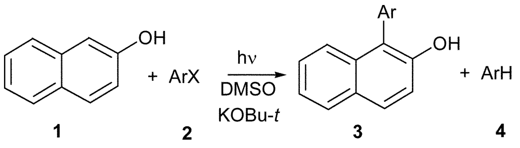
Results

In an $S_{RN}1$ process,[1] the radicals formed (eqn (2) and (3)) can couple with the nucleophile to form the radical anion of the substitution product or can abstract a H-atom from the solvent (eqn (8)).

$$S^{\bullet} + ArH \xleftarrow[k_H]{+\,SH} Ar^{\bullet} \xrightarrow[k_{Nu}]{+Nu^-} ArNu^{\bullet -} \qquad (8)$$

The k_{Nu} value can be determined by product analysis according to the approximation previously reported,[9,5] whenever the reduced products (ArH) can be detected accurately and the rate constant k_H is known.

We studied the photoinitiated reactions of the anion of **1** with different aryl halides (**2**) (eqn (9)).



(9)

2a: Ar= 4-$MeOC_6H_4$
2b: Ar=2-$MeOC_6H_4$
2c: Ar=1-$C_{10}H_7$
2d: Ar=2-MeO-1-$C_{10}H_6$
2e: Ar= 9-anthracenyl

We began our studies by examining the reaction of the anion of **1** with the 4-anisyl radical (**2a**). The substitution product **3a** and anisole are obtained in 54.0 and 8.6% yield, respectively (see Scheme 1).

When the methoxy group is *ortho* to radical centre, the percentage of substitution product decreased and that of anisole increased (39.9 and 14.9%) (Scheme 1).

Similar results were observed in the reactions of 1-naphthyl (**2c**) and 2-methoxy-1-naphthyl (**2d**) radicals. The first gave 65.1% of substitution and 10.1% of naphthalene. For **2d** the reduction increased to 45.9% and the substitution decreased to 34.9% (see Scheme 1). These values confirm the effect of *ortho* substitution on the radical centre.

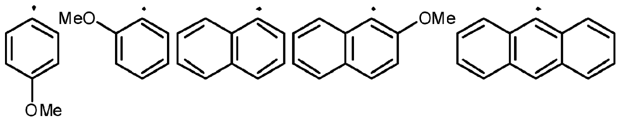
The anthracenyl radical reacts with 2-naphthoxide anion affording 55.1% of **3e** and 39.9% of anthracene.

Kinetic analyses of the reactions of aryl radicals with the anion of **1** were performed. All the reactions were carried out in DMSO at 25 °C. The yield of the products (ArNu and ArH) formed were then accurately determined by gas chromatography. In all cases, blank assays to verify the complete recovery of reduced products were performed.[10] The substituted aryl radicals bear the same substituent (the OMe group) to enforce the same electronic effect by the substituent. The concentration of nucleophile, by far larger than that of **2a–e**, remained sufficiently constant throughout the experiments. Under these conditions both competing processes (eqn (8)) were pseudo-first order events. The yield of the products formed was determined and k_{Nu}/k_H calculated.

We calculated values of k_{Nu} from k_{Nu}/k_H and knowledge of the k_H value in DMSO obtained by radical clock and electrochemical experiments. The k_H used is $2.8 \times 10^6\ M^{-1}\ s^{-1}$ for anisyl radicals,[5] $6.4 \times 10^6\ M^{-1}\ s^{-1}$ for naphthyl radicals[5] and $6.0 \times 10^5\ M^{-1}\ s^{-1}$ for anthracenyl radicals.[11] The results are summarized in Table 1.

According to Table 1, k_{Nu} for **2a** ($5.1 \times 10^8\ M^{-1}\ s^{-1}$) is 2.5 times higher than that for **2b** ($1.9 \times 10^8\ M^{-1}\ s^{-1}$).

The naphthyl radicals **2c** and **2d** provide a further example of the effect of *ortho* substitution to a radical centre. The value



3	54.0	39.9	65.1	34.9	55.1
4	8.6	14.9	10.1	45.9	39.9

Scheme 1

Table 1 Values of k_{Nu} obtained for the reaction of the anion of **1** with aryl halides[a]

Substrate	$[NuH]_0$/M	$[ArX]_0$/M	$[ArH]^b$/M	$[ArNu]^b$/M	k_{Nu}/k_H	k_{Nu}
2a, X = I	0.509	0.0520	0.0045	0.028	177.1	$(5.1 \pm 0.1) \times 10^8$
	0.474	0.0551	0.0039	0.024	187.7	
2b, X = I	0.519	0.0676	0.0101	0.027	74.5	$(1.9 \pm 0.2) \times 10^8$
	0.346	0.0564	0.0147	0.021	60.0	
2c, X = I	0.491	0.0476	0.0057	0.031	161.2	$(10.2 \pm 0.2) \times 10^8$
	0.510	0.0462	0.0051	0.028	156.0	
2d, X = I	0.505	0.0544	0.0250	0.019	21.6	$(1.41 \pm 0.05) \times 10^8$
	0.489	0.0488	0.0241	0.019	23.1	
2e, X = Br	0.510	0.0526	0.0210	0.029	39.2	$(2.42 \pm 0.07) \times 10^7$
	0.503	0.0510	0.0201	0.029	41.6	

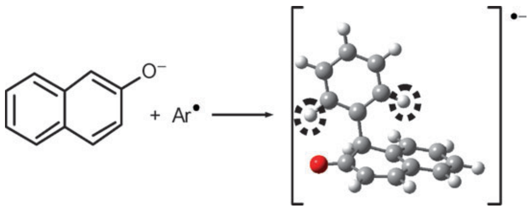
[a] Photoinitiated reactions carried out under nitrogen at 25 °C; reaction time = 120 min. [b] Determined by GLC and the internal standard method.

of k_{Nu} for **2d** is sevenfold lower than that for **2c**. In this case the effect of substitute is higher than that observed for anisyl radicals.

Anthracenyl radicals show a lower reactivity toward the anion of **1** than that of radicals **2a** and **2b**. Similar results for this radical were obtained with pinacolone anion.[5]

Discussion

In these reactions, the aryl radicals ($Ar^\bullet$) react regioselectivity with the anion of **1** at the C1 of the naphthyl moiety. A change in hybridization from sp^2 to sp^3 occurs in this position in the formation of the radical anion of the substitution products (eqn (10)). This radical anion has a rigid structure with substituents in both positions adjacent to the coupling centre (C1).



(10)

The lower reactivity of radicals **2b** and **2d** compared with **2a** and **2c**, respectively, can be explained in terms of the steric hindrance to the coupling at the radical centre to form the radical anion intermediates. In the radical **2d**, the two hydrogens near the radical centre are replaced by two substitutes, the OMe group, and the aryl moiety. In consequence the steric compression exerted by the *ortho* substituents is more severe for **2d**. This radical has the lowest reactivity of the series (**2c** > **2a** > **2b** > **2d**).

In order to complement the experimental results, the potential energy surfaces (PES) for the coupling step were calculated. We have demonstrated that the reactions of the ambident nucleophiles and the radical are kinetically controlled[12] and that the TSs are located early along the reaction coordinates. The rehybridization at the C1 of the naphthyl moiety takes place at shorter C–C distances than those of the localized TSs (see Fig. ESI 1†).

The PESs were inspected from the most stable conformer of the radical anions formed by AM1 and B3LYP methods.[13] Table 2 shows the difference in energy between the critical structures located along the PESs. The energy information for the main structures is provided in the ESI.†

Similar PES profiles were obtained with AM1 and B3LYP for the coupling reaction of the anion of **1** and radicals **2a–e**. The radicals combined exothermically with the anion to form the radical anion of the product. In the PES, radicals **2b** and **2d** combined with the anion of **1** to form an electrostatic encounter complex (IT) (Fig. 1) in which the hydrogen atoms of the methoxy group interact with the oxygen centre of the nucleophile. In the IT for the radicals **2a** and **2c**, the hydrogen *ortho* to the radical centre interacts with this oxygen.

In the gas phase, the reactions take place without energy barriers (negative ΔE) evaluated as the energy difference between of the TS and the reactive. Different results are obtained considering the IT (see Table 2). The ΔE_{TS-IT} calculated by AM1 and B3LYP shows a similar tendency.

The 1-naphthyl radical **2c** is the most highly reactive radical and its energy barrier calculated is the smallest. The *ortho* substitution at the radical centre increased the barrier. In

Table 2 Energy differences between PES relevant points of the reaction of the 2-naphthoxide anion with different aryl radicals derived from ArX

	AM1			B3LYP (6-31G*)			B3LYP (6-31G*) Continuum solvent[d]		
Ar	$\Delta E_r{}^a$	ΔE^b	$\Delta E_{TS-IT}{}^c$	$\Delta E_r{}^a$	ΔE^b	$\Delta E_{TS-IT}{}^c$	ΔE_r	ΔE^b	$\Delta E_{TS-IT}{}^c$
2a	−46.69	−0.72	3.17	−36.56	**−4.50**	**1.60**	−33.03	**−1.28**	**0.47**
2b	−46.40	−0.91	3.40	−32.98	**−1.92**	**0.13**	−30.55	**1.52**	**2.00**
2c	−43.99	−1.68	1.86	−34.97	**−5.84**	**0.02**	−30.52	**−1.05**	**0.35**
2d	−43.55	−0.66	4.37	−29.82	**−1.31**	**1.68**	−28.05	**2.23**	**2.92**

[a] ΔE_r (kcal mol^{-1}) = reaction energy (energy difference between radical anion and reactants (anion of **1** + radical, distance = 10 Å for AM1 and 15 Å for B3LYP). [b] ΔE (kcal mol^{-1}) = energy difference between transition states and reactants (anion of **1** + radical, distance = 10 Å for AM1 and 15 Å for B3LYP). [c] ΔE_{TS-IT} (kcal mol^{-1}) = energy difference between transition state and intermediate (IT). [d] Continuum solvent model for DMSO, without geometry optimization. Differences in the total solution phase energies informed.

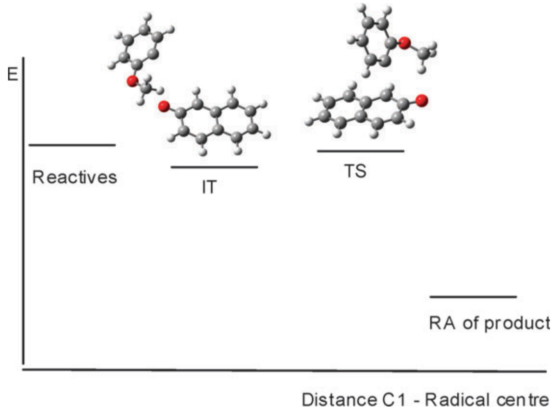


Fig. 1 Reaction path, in the gas phase, for the coupling of 2-naphthoxide anion and aryl radical.

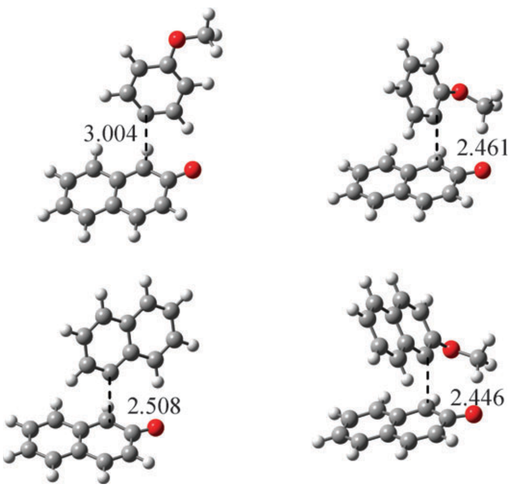


Fig. 2 TSs of **2a–d** with distance C_1 of anion of **1** to the radical centres indicated.

consequence the reactivity decreases in agreement with the experimental results.

The different results obtained by **2b** and **2d** (*ortho* substituted radicals) are attributed to higher steric constraints (Fig. 2). This effect increased in **2d** and the ΔE correlated with this.

The solvent effect was taken into consideration in the DFT methodology.[14] In the presence of DMSO, the solvent of the experimental reactions, the PESs are similar to those calculated in the gas phase. The reactants are more stabilized than all the other species, as expected from the higher charge localization of the anion (see Tables in ESI†). The solvent affects the TS of the reaction, but this effect is similar for all the radicals and the barriers ordering determined in the gas phase maintains under a continuum solvent; the ΔE for the *ortho* substituted radicals being higher (**2b** > **2a** and **2d** > **2c**). The reactivity order is **2c** > **2a** > **2b** > **2d** in agreement with the experimental findings.

Conclusions

The absolute rate constant determined for the addition of the anion of 2-naphthol to radicals **2a–e** are 5.1×10^8, 1.9×10^8, 1.0×10^9, 1.4×10^8 and 2.4×10^7 M^{-1} s^{-1}, respectively. From the results obtained we conclude that the radical-ambident nucleophile reactions are sensitive to steric hindrance. The *ortho* substitution to the radical centre decreases the rate constant ($k_{\mathbf{2b}} < k_{\mathbf{2a}}$ and $k_{\mathbf{2d}} < k_{\mathbf{2c}}$). This effect is more significant when the aryl system is a highly congested radical centre (1-naphthyl > phenyl) $k_{\mathbf{2d}} < k_{\mathbf{2b}}$.

The theoretical calculations show that the order of the energy barriers is 2-methoxy-1-naphthyl > 2-anisyl > 4-anisyl > 1-naphthyl, in agreement with the experimental results.

These results are of great interest to show the limitation of this reaction type in the syntheses of disubstituted biaryl compounds.

Experimental

General experimental methods

^1H and ^{13}C NMR spectra were recorded on a nuclear magnetic resonance spectrometer with $CDCl_3$ as solvent. Gas chromatographic analyses were performed on a chromatograph (Hewlett Packard 5890 Series II) with a flame-ionization detector and using a HP-1 capillary column (methyl silicone, 10 m × 0.53 mm × 2.65 μm film thickness). The GS/MS analyses were carried out on a Shimadzu GC-MS QP 5050 spectrometer, employing a 30 m × 0.12 mm DB-5 MS column. The distillation at reduced pressure was performed with a Kügelrohl. Irradiation was conducted in a reactor equipped with two 400-W lamps emitting maximally at 350 nm ((Philips Model HPT, air and water refrigerated). Potentiometric titration of halide ions was performed in a pH meter using an Ag/Ag^+ electrode. Melting points were not corrected. Column chromatography was performed on silica gel (70–270 mesh ASTM).

Materials

Potassium *tert*-butoxide, 4-iodoanisole, 2-iodoanisole, 1-iodonaphthalene and 9-bromoanthracene were commercially available and used as received. 2-Naphthol was recrystallized from ethanol–water.[15] DMSO was stored under molecular sieves (4 Å). 1-iodo-2-methoxynaphthalene (**2dI**) was prepared from reaction of 1-iodo-2-naphthol, potassium *tert*-butoxide in DMSO with methyl iodide. 1-iodo-2-naphthol was prepared from reaction of 2-naphthol, iodide and H_2O_2 in ethanol.[16]

Photoinitiated reaction of the anion of 2-naphthol (1) with haloaryls

The following procedure is representative of these reactions. The reactions were carried out in a 25 mL three-neck round-bottomed flask equipped with nitrogen inlet and magnetic stirrer into the thermostatic bath. To 10 mL of dry and degassed DMSO under nitrogen were added potassium *tert*-butoxide (887 mg, 7.92 mmol) and then 2-naphthol (733 mg, 5.09 mmol). After 15 min 4-iodoanisole (121.7 mg, 0.52 mmol) was added and the reaction mixture was irradiated for 120 min. The reaction was quenched with an excess of ammonium nitrate and water (30 mL). The mixture was extracted twice with methylene chloride (20 mL); the organic extract was washed twice with water, dried ($MgSO_4$), and quantified by GLC. The iodide ions in the aqueous solution were determined potentiometrically. The reduction products (ArH) were compared by CGL with authentic commercial samples.

All products are known and exhibited physical properties identical to those reported in literature. Also, they were isolated by column chromatography [petroleum ether–acetone (9 : 1)] from the reaction mixture and characterized by ^{1}H and ^{13}C NNR and mass spectrometry.

1-(4-Anisyl)-2-naphthol (3a).[17] m/z = 251 (17); 250 (100); 235 (22); 218 (9); 207 (22); 189 (12); 179 (15); 178 (23); 176 (10); 152 (13); 94 (11); 76 (11); 55 (10).

1-(2-Anisyl)-2-naphthol (3b).[18] ^{1}H NMR: δ_H 3.67 (s, 3H); 5.18 (s, 1H); 7.04–7.12 (m, 2H); 7.17–7.25 (m, 5H); 7.38–7.47 (m, 1H); 7.71–7.75 (m, 2H). ^{13}C NMR: δ_C 55.84; 112.01; 117.69; 117,85 (c); 121.55; 122.55 (c); 123.17; 124.81; 126.24; 128.02; 128.10 (c); 129.13; 129.50; 130.23; 133.38; 133.46 (c); 150.63 (c). m/z 251 (18); 250 (100); 235 (10); 219 (15); 218 (16); 207 (18); 191 (12); 190 (9); 189 (25); 179 (15); 178 (25); 176 (9); 152 (9); 95 (11); 94 (13); 76 (12).

1-Naphthyl-2-naphthol (3c).[17] m/z = 271 (18); 270 (100); 269 (50); 268 (12); 255 (14); 253 (39); 252 (27); 251 (16); 250 (13); 241 (10); 240 (11); 239 (38); 135 (11); 126 (26); 125 (21); 120 (11); 119 (26); 113 (16).

2-Methoxy-2′-ol-1,1′-binaphthalenyl (3d).[8,19] ^{1}H NMR: δ_H 3.79 (3H, s); 4.90 (1H, s); 7.01–7.50 (8H, m); 7.83–7.92 (3H, m); 8.05 (1H, d). ^{13}C NMR: δ_C 56.82; 113.90; 115.03 (c); 115.41 (c); 117.45; 123.22; 124.19; 124.81; 124.92; 126.40; 127.32; 128.13; 129.15 (c), 129.44 (c); 129.77; 131.06; 133.78 (c); 137.03, 151.25 (c); 156.02 (c). m/z 301 (16); 300 (100); 268 (8); 239 (7).

1-(9-Anthracenyl)-2-naphthol (3e). Isolated by column chromatography and eluted with petroleum ether: acetone (90:10). M.p. 214–215 °C. ^{1}H NMR: δ_H 4.67 (s, 1H); 6.80 (d, 1H); 7.10–7.18 (m, 1H); 7.27–7.54 (m, 8H); 7.92 (d, 1H); 8.02 (d, 1H); 8.13 (d, 2H); 8.67 (s, 1H). ^{13}C NMR: δ_C 116.62 (c); 117.54; 123.49; 125.06; 125.70; 160.00; 126.62; 126.75; 128.07; 128.42; 128.61; 128.75; 129.15; 130.26; 131.58 (c); 131.82 (c); 151.63 (c). m/z 321 (25); 320 (100); 319 (19); 317 (11); 316 (9); 303 (12); 302 (9); 289 (13); 252 (14); 250 (9); 158 (12); 151 (20); 150 (36); 145 (11); 144 (18); 143 (10); 138 (13); 132 (11); 131 (10). HRMS: calc. for $C_{24}H_{16}O$ 320.12012; found: 320.12033.

Computational procedure

All calculations were carried out with the semiempirical AM1 and B3LYP methods as implemented in Gaussian 03 within the UHF (opened shell systems) or RHF (closed shell systems) formalisms in order to properly account for the electronic nature of the species under study. First, the most stable conformers of the radical anions $RNu^{-\cdot}$ were evaluated through an AM1 conformational search by scanning the two or three main torsion angles. The conformers thus obtained were then refined with complete geometry optimization. The geometries thus found were used as starting points to study the PEs corresponding to the C–C bond breaking/formation. The equilibrium geometries were obtained with complete geometry optimization. The intermediates and transition states were first located through the reaction coordinate method and then refined with the appropriate procedure. The stationary points were located by Hessian matrix calculations: all positive eigenvalues for a minimum energy species and one imaginary frequency for transition states. PEs explorations within the B3LYP DFT functional and the 6-31G* basis set were carried out by the same procedure. The solvent effect was modeled with a continuum model as implemented in the G03 program. The solvent stabilization was evaluated from single point calculations on the gas-phase optimized geometries at the B3LYP/6-31G* theory level; electrostatic and non-electrostatic contributions being considered.

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9 The equation used in the relative reactivity determination of coupling reaction of nucleophiles *vs.* H-atom abstraction from the solvent was:

$$\frac{k_{\mathrm{Nu}}}{k_{\mathrm{H}}} = \frac{\ln\left([\mathrm{Nu}^-]_0/\left([\mathrm{Nu}^-]_0 - [\mathrm{ArNu}]_t\right)\right)}{\ln\left([\mathrm{SH}]_0/\left([\mathrm{SH}]_0 - [\mathrm{ArH}]_t\right)\right)}$$

where $[\mathrm{Nu}^-]_0$ and $[\mathrm{SH}]_0$ are initial concentrations and $[\mathrm{ArNu}]_t$ and $[\mathrm{ArH}]_t$ are concentrations at time t of both products. This equation is based on first-order reactions of the radicals, see J. F. Bunnett, in *Investigation of Rates and Mechanisms of Reactions*, ed. E. S. Lewis, Wiley-Interscience, New York, 3rd edn, 1974, part 1, p. 159.

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