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Electron Apportionment in Cleavage of Radical Anions. 2. Naphthylmethyl Phenyl Ethers vs. Naphthyl Benzyl Ethers

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Abstract: Naphthylmethyl phenyl ethers and naphthyl benzyl ethers were found to undergo scission of the H_2C-O bond when treated with radical anions of anthracene or fluoranthene. Under comparable conditions, ethers of the naphthylmethyl phenyl series (α and β) reacted more than 10^4 times faster than ethers of the naphthyl benzyl series (α and β). This preference for regioconservation of spin density in the scission process is interpreted in terms of σ-bond polarization at the transition state.

In our previous paper on this subject,[1] we found that the radical anions of 4-nitrobenzyl phenyl ethers underwent unimolecular scission at least 10^4 times faster than the corresponding 4-nitrophenyl benzyl ethers. This was interpreted in terms of a preference for regioconservation of spin in the scission process. In the nitrobenzyl phenyl systems, the fragments were nitrobenzyl radical plus phenoxide, preserving spin density in the nitrophenyl moiety throughout the process. In the nitrophenyl benzyl systems, energetically accessible products could only be formed with a transfer of spin density out of the nitrophenyl moiety to give a benzyl radical after scission. Radical anions of these latter systems were found resistant to scission. The observed kinetic barrier to what appears to be a thermodynamically favorable process suggested the resistance to spin transfer.

For nitroaryl radical anions, spin density is relatively localized in the nitro group as evidenced by large hfsc's for nitrogen.[1] In a sense, the nitrobenzyl case may be viewed as heterolytic loss of phenoxide ion from a benzyl cation with promotion by the $-NO_2^{-}\cdot$ substituent. The hypothetical nitrophenyl benzyl ether scission cannot be viewed in this way. In order to increase the generality of our proposed principle and to make the role of the unpaired electron less substituent-like, we decided to replace the nitro substituent with a fused benzene ring so that the repository for the added electron is a naphthalene system

Results and Discussion

Ethers α-**1**, β-**1**, α-**2**, and β-**2** all underwent clean reduction by the potassium salt of the radical anion of biphenyl in tetrahydrofuran (THF) to give the expected methylarenes and 1,2-diarylethanes as shown in eq 1. The same products have been

$$\mathrm{ArCH_2OAr'} \xrightarrow{\mathrm{D}^{-}\cdot} \mathrm{ArCH_2CH_2Ar} + \mathrm{ArCH_3} + {}^{-}\mathrm{OAr'} \quad (1)$$

α-**1** Ar = 1-naphthyl, Ar′ = phenyl
β-**1** Ar = 2-naphthyl, Ar′ = phenyl
α-**2** Ar = phenyl, Ar′ = 1-naphthyl
β-**2** Ar = phenyl, Ar′ = 2-naphthyl

reported from the reaction of α-**1** and β-**1** with sodium in toluene.[2] The reaction was too fast for convenient kinetic measurement, being complete in a few seconds even at −78 °C. It was thus decided to investigate the reaction of eq 1 using the more stable radical anions of anthracene ($A^{-}\cdot$) and fluoranthene ($F^{-}\cdot$) as donors with the realization that this would mean following the disappearance of the donor radical ion. Thus radical anions of **1** and **2** would play the role of steady-state intermediates according to Scheme I where $D^{-}\cdot$ is the donor radical anion. This proved to be a satisfactory plan in that with the proper donor all of the ethers underwent scission at measurable rates.[3] Interestingly it was found that under these conditions in either dimethylformamide (DMF) or 1,2-dimethoxyethane (DME), only methylarenes and no diarylethanes were found, presumably reflecting the relatively low concentrations of arylmethyl radicals and high concentration of radical anion reductant. This situation favors formation of the methylarene via the benzylic anion.

Scheme I

$$\mathbf{1} \text{ or } \mathbf{2} + \mathrm{D}^{-}\cdot \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{D} + \mathbf{1}^{-}\cdot \text{ or } \mathbf{2}^{-}\cdot$$

$$\mathbf{1}^{-}\cdot \text{ or } \mathbf{2}^{-}\cdot \xrightarrow{k_2} \text{products}$$

Table I. Reduction Potentials of Some Aromatic Hydrocarbons and Ethers[4]

	reduction potentials					
	DMF (Hg pool)		DMF (SCE)		75% DO[a] (SCE)	
compound	$-E_{1/2}^{1}$[b]	$-E_{1/2}^{2}$	$-E_{1/2}^{1}$	$-E_{1/2}^{2}$	$-E_{1/2}^{1}$	$-E_{1/2}^{2}$
anthracene	1.41	1.88	1.95	2.47	1.96	2.44[c]
biphenyl	2.05		2.58			3.2[d]
fluoranthene	1.23		1.78	2.30	1.77	2.16[c]
naphthalene	1.99		2.52		2.45	
1-methylnaphthalene	2.03				2.46	
2-methylnaphthalene	2.05				2.46	
1-methoxynaphthalene			2.65			
2-methoxynaphthalene	2.03		2.60			
benzene[e]					3.4	

[a] 75% dioxane–25% water. [b] $E_{1/2}^{1}$ = first reduction potential. $E_{1/2}^{2}$ = second reduction potential. [c] 96% dioxane. [d] THF vs. Ag electrode. [e] Estimated.[5]

Based on Scheme I the expected rate expression should be that of eq 2. Assuming $k_{-1}[\mathrm{D}] > k_2$ would lead to a prediction of first-order kinetics with $k_{\mathrm{obsd}}/R = k_1k_2/k_{-1}$ where R = [**1** or **2**]/[D]. Data obtained by following the disappearance of $A^{-}\cdot$

$$\frac{-\mathrm{d}[\mathrm{D}^{-}\cdot]}{\mathrm{d}t} = \frac{k_1k_2[\mathrm{D}^{-}\cdot][\mathbf{1} \text{ or } \mathbf{2}]}{k_{-1}[\mathrm{D}] + k_2} \quad (2)$$

and $F^{-}\cdot$ in the presence of the four ethers under conditions which maintain a relatively constant value of R during each reaction are listed in Table II. Individual runs for α-1, β-1, and α-2 show good agreement with a first-order rate law. There is some scatter in measured values of k_{obsd}/R, but the essential information, independence of $[\mathrm{D}^{-}\cdot]_0$ and dependence on R, is evident.

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(1) Maslak, P.; Guthrie, R. D. *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) Schoringin, P. *Chem. Ber.* **1926**, *59*, 2502.

(3) (a) An analogous cleavage of benzyl phenyl ether by the sodium salt of naphthylene radical anion has been carried out: Angelo, B. *Bull. Soc. Chim. Fr.* **1966**, 1091. (b) Leading references to chemical and electrochemical reductive cleavage reactions of ethers may be found in: Koppang, M. D.; Woolsey, N. F.; Bartak, D. E. *J. Am. Chem. Soc.* **1984**, *106*, 2799.

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Table II. Kinetics of Disappearance of Fluoranthene and Anthracene Radical Anions ($D^{-}\cdot$) in the Presence of $ArCH_2OAr'$ at 22 °C

run	solvent	ether	10^{-2}[ether]$_0$, M	D	10^{-1}[D]$_0$, M	$10^{-3}[D^{-}\cdot]_0$,[b] M	k_{obsd},[a] s^{-1}	k_{obsd}/R, s^{-1}	no. of kinetic pts
1	DME	α-**1**	1.9	F	0.95	1.8	1.8×10^{-2}	9.0×10^{-2}	7
2			5.8		1.9	1.1	3.8×10^{-2}	1.3×10^{-1}	5
3			8.6		1.25	6.5	7.4×10^{-2}	1.1×10^{-1}	3
4			5.8		2.5	2.1	2.4×10^{-2}	1.0×10^{-1}	6
5			5.8		3.4	2.1	2.9×10^{-2}	1.7×10^{-1}	12
6			5.8		2.8	4.3	2.5×10^{-2}	1.2×10^{-1}	8
7			5.9		3.9	6.6	1.9×10^{-2}	1.3×10^{-1}	13
8			8.8		2.6	5.9	3.6×10^{-2}	1.1×10^{-1}	7
9	DMF		7.3		4.1	3.6	1.4×10^{-3}	7.7×10^{-3}	24
10			7.4		2.5	5.2	2.3×10^{-3}	7.7×10^{-3}	12
11			3.7		1.6	5.4	2.2×10^{-3}	9.6×10^{-3}	18
12			1.9		3.8	1.6	3.8×10^{-3}	7.6×10^{-3}	7
13		α-**2**	12.0		0.53	12.0	3.8×10^{-7}	1.7×10^{-7}	14
14			16.0		0.30	66.	1.00×10^{-6}	1.9×10^{-7}	11
15			32.0		0.42	16.	1.20×10^{-6}	1.6×10^{-7}	9
16			7.0	A	0.195	5.7	5.9×10^{-4}	1.6×10^{-4}	10
17			5.0		0.210	1.5	3.7×10^{-4}	1.6×10^{-4}	5
18			4.8		0.28	2.5	4.2×10^{-4}	2.4×10^{-4}	12
19		β-**1**	5.9	F	1.9	2.0	8.0×10^{-5}	2.5×10^{-4}	5
20			5.9		0.22	6.7	4.9×10^{-4}	1.8×10^{-4}	11
21			5.9		0.42	1.5	2.6×10^{-4}	1.8×10^{-4}	9
22		β-**2**	4.8	A	0.16	1.1	2.3×10^{-5} [c]	7.7×10^{-6} [c]	9
23			6.2		0.15	3.6	7.0×10^{-5} [c]	1.7×10^{-5} [c]	9
24			9.5		0.23	2.6	9.8×10^{-5} [c]	2.4×10^{-5} [c]	7

[a] Correlation coefficients were >0.999 for runs 1–4, 7, 15, 21; >0.998 for runs 9–12, 14, 16–18; >0.997 for 5, 6, 8, 20; >0.994 for 13, 19. Standard deviations for individual points within runs were less than the standard deviations between runs. The latter are used as estimated error limits in Table III. [b] Approximate radical anion concentrations were obtained from ESR intensities and are probably within a factor of 2 of true values. [c] These reactions did not follow a first-order rate law. Values are provided for rough comparison and are taken from the high-conversion end of first-order plots. (See text.) Values of $[D^{-}\cdot]_0$ are estimated at the beginning of the data segment used to determine k_{obsd}.

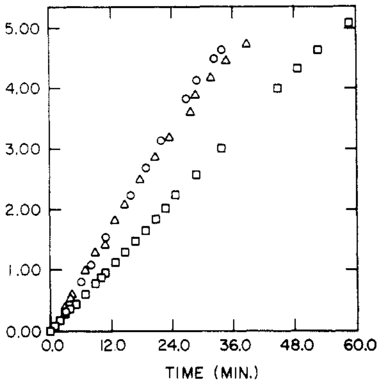

Figure 1. Pseudo-first-order kinetic plot for disappearance of $F^{-}\cdot$ in the presence of α-**1** in DMF at 22 °C. See Table II for rate constants: (□) run 9; (○) run 10; (△) run 11.

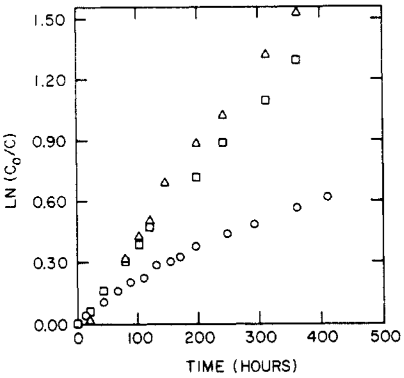

Figure 2. Pseudo-first-order kinetic plot for disappearance of $F^{-}\cdot$ in the presence of α-**2** in DMF at 22 °C. See Table II for rate constants: (○) run 13; (□) run 14; (△) run 15.

Runs 1–8 represent the disappearance of $F^{-}\cdot$ promoted by α-**1** in DME. Values of k_{obsd}/R are reasonably constant at an average value of 1.2×10^{-1} s^{-1} over a 4.6-fold change in R. Using α-**2** under otherwise identical conditions gave a barely measurable rate of change in $[F^{-}\cdot]$. By sealing reaction mixtures in ampules and waiting several days, we were able to establish an upper limit of $k_{obsd}/R < 10^{-7}$ s^{-1}.

For a detailed comparison of the four systems, DMF was selected because of the literature availability of reduction potentials for appropriate model systems (Table I) and the relative protection from ion association problems. Solutions of $A^{-}\cdot$ and $F^{-}\cdot$ in this solvent were stable for days, but treatment with **1** and **2** caused the ESR signal to disappear at a convenient rate.

For α-**1** with $F^{-}\cdot$ in DMF, rate constants were approximately a factor of 10 smaller than for the DME reaction but showed the same concentration dependence, verifying the analysis of Scheme I (runs 9–12 in Table II). The kinetic plot in Figure 1 shows excellent first-order rate law adherence through seven half-lives. In DMF, α-**2** did react with $F^{-}\cdot$ at a measurable but very slow rate (runs 13–15 and Figure 2). To obtain data for two half-lives required taking measurements over a 2-week period, retuning the spectrometer for each measurement. As expected some scatter is observed in the plots, but the fit to a first-order rate law is acceptable. Attempted fitting of the data from runs 14 and 15 to a second-order rate law was clearly unsuccessful. When α-**2** is treated with the more powerful reducing agent $A^{-}\cdot$, the reaction speeds up and its first-order character is easily demonstrable (runs 16–18 and Figure 3).

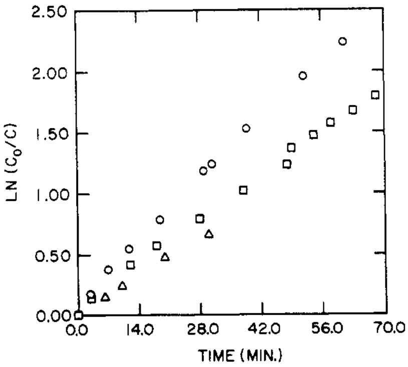

Figure 3. Pseudo-first-order kinetic plot for disappearance of $A^{-}\cdot$ in the presence of α-**2** in DMF at 22 °C. See Table II for rate constants: (○) run 16; (△) run 17; (□) run 18.

The rate for the reaction of $F^{-}\cdot$ with β-**1** in DMF was roughly a factor of 40 slower than with α-**1** in the same circumstances.

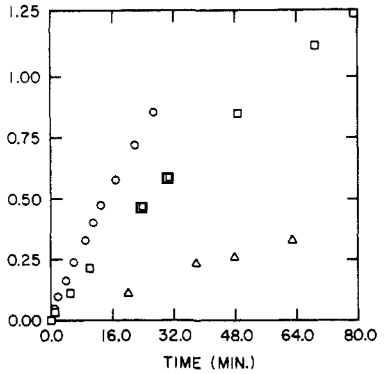

Figure 4. Pseudo-first-order kinetic plot for disappearance of $F^{-}\cdot$ in the presence of β-**1** in DMF at 22 °C. See Table II for rate constants: (△) run 19; (○) run 20; (□) run 21.

Run 19–21 are described in Table II and first-order plots are drawn in Figure 4. All of these runs show a noticeable decrease in the first-order rate constant with time, but the data fit a first-order rate law better than a second-order rate law. Particularly for run 21, which was carried out to the highest extent of conversion, a second-order plot is clearly inadequate, requiring a 2-fold increases in the apparent second-order rate constant in the second half-life.

The slowest-reacting isomer was β-**2**, and meaningful data could not be obtained for reaction with $F^{-}\cdot$. With $A^{-}\cdot$, the reaction was inconveniently slow, but it was possible to collect usable data into the third half-life. To our surprise, the disappearance of $A^{-}\cdot$ showed rather good adherence to a second-order rate law for all three runs (22–24). Clearly a different mechanism is operative for the reaction of $A^{-}\cdot$ with β-**2**, and we are reluctant to guess what this might be at the present time. A^{2-}-promoted scission would be consistent with our data, but it is difficult to see why the reaction should take this path. A supplementary table listing the raw data for runs 22–24 has been provided. The important point for the purposes of this paper is that β-**2** undergoes scission much more slowly than β-**1** under similar conditions. It may be reasonably assumed that as the concentration of $A^{-}\cdot$ decreases, some point will be reached where the observed second-order process will be supplanted by a first-order process which is legitimately comparable to that observed for β-**1**. This point was not reached in the accessible concentration range, so in order to have a basis for comparison, we have reported in Table II maximum first-order rate constants taken as the slope of the low-concentration ends of plots of $\ln([A^{-}\cdot]_0/[A^{-}\cdot])$ vs. time. This provides a range of values, the lowest of which was found, as expected, at the lowest estimated concentration of $A^{-}\cdot$ (run 22). This value may then be regarded as an upper limit to the rate constant of a competing first-order process. Correcting for the increased potency of $A^{-}\cdot$ as a reducing agent makes β-**2** more than 10^4 times less reactive than β-**1**.

In principle it should be possible to use the values of $k_{\text{obsd}}/[R]$ in conjunction with the measured reduction potentials of A and F to calculate values for k_2 in Scheme I. An assortment of relevant electrochemical data is listed in Table I. If counterion and electrolyte concentration differences are ignored, it may be seen that the difference in reduction potential between α-**1** and F is ~0.8 V. This corresponds to an equilibrium constant (Scheme I), $k_{\text{eq}} = k_1/k_{-1} = 10^{-14}$. Because k_{-1} is limited by diffusion, the value of k_1 cannot be much greater than 10^{-4} M^{-1} s^{-1}.[6] With, for example, $[\alpha\text{-}\mathbf{1}]_0 = 7 \times 10^{-2}$ M, the maximum value possible for k_{obsd} would be 7×10^{-6} s^{-1} even for irreversible formation of the radical anion of α-**1**. This is 2–3 powers of 10 smaller than the values of k_{obsd} reported in Table II. It is clear from the rate reduction observed when $[F]_0$ is increased that radical anion formation is at least partially reversible. We are thus left with the conclusion that existing electrochemical data underestimate the value of K_{eq} under the conditions of our experiments. Nevertheless, values of k_2 for the various substrates are approximately proportional to values of $k_{\text{loss}}/R = k_1k_2/k_{-1}$ provided that variations in k_1/k_{-1} are small. Existing reduction potentials for α- and β-methyl- and methoxynaphthalenes (Table I) clearly support this assumption. At most $\Delta E_{1/2}$ is 0.05 V, less than a factor of 10 in k_1/k_{-1}. Thus we arrive at relative rates of 6.3×10^5, 13, 1.5×10^4, and 1.0 for fragmentation of α-**1**, α-**2**, β-**1**, and β-**2**, respectively. The kinetic data are summarized in Table III. Clearly, compounds of type **1** undergo scission more than 10^4 times faster than the corresponding compounds of type **2**, and this preference is reasonably assigned to a more facile scission of $\mathbf{1}^{-}\cdot$ compared to that for $\mathbf{2}^{-}\cdot$.

Table III. Reductive Cleavage of $ArCH_2OAr'$ by Fluoranthene and Anthracene Radical Anions at 22 °C

ether	solvent	$D^{-}\cdot$	$k/[R]$, s^{-1}
α-**1**	DME	$F^{-}\cdot$	$1.2 \pm 0.2 \times 10^{-1}$
α-**2**	DME	$F^{-}\cdot$	10^{-7} (max)
α-**1**	DMF	$F^{-}\cdot$	$8.2 \pm 1.0 \times 10^{-3}$
α-**2**	DMF	$F^{-}\cdot$	$1.7 \pm 0.2 \times 10^{-7}$
α-**2**	DMF	$F^{-}\cdot$[a]	$1.6 \pm 0.4 \times 10^{-7}$[a]
α-**2**	DMF	$A^{-}\cdot$	$1.9 \pm 0.5 \times 10^{-4}$
β-**1**	DMF	$F^{-}\cdot$	$2.0 \pm 0.4 \times 10^{-4}$
β-**2**	DMF	$F^{-}\cdot$[a]	$1.3 \pm 1.0 \times 10^{-8}$[a]
β-**2**	DMF	$A^{-}\cdot$	$1.6 \pm 1.0 \times 10^{-5}$

[a] Values were calculated for $F^{-}\cdot$ from data obtained with $A^{-}\cdot$ in the following entry in the table.

We argued in the preceding paper in this issue that the overall energetics for scission of benzyl phenyl ethers should favor the case in which an $-NO_2^{-}\cdot$ substituent is positioned on the phenoxyl side as compared to the benzyl side of the scissile bond. The fused benzene ring of the present study should have a smaller influence than NO_2 because the extra benzene ring should manifest relatively small inductive effects and thus be nearly equally effective in stabilizing the phenoxide ion and the benzyl radical. The pK_a difference between phenol and 1-naphthol is 1.8 units in Me_2SO[7] or about 2.4 kcal/mol, favoring naphthoxide. The 1-naphthylmethyl radical is more stable than the benzyl radical by 3–4 kcal/mol.[8] Although this might suggest a small thermodynamic preference for the kinetically favored scission process, it seems unlikely that this would exert much kinetic influence in these highly exothermic reactions. Clearly the rate factor of 10^4 favoring reaction of **1** over **2** reflects a property of the transition state for radical anion scission which is unrelated to product stability.

Summary and Conclusions

There are several significant differences between the systems examined in this paper and nitroarenes of our initial study in the preceding paper. Based on estimated reduction potential, the naphthalene-type radical anions are of higher energy than the nitroarene radical anions, relative to their respective neutral precursors, by about 1.5 V or roughly 35 kcal/mol. The energies of the respective C–O σ^* states seem likely to be less disparate. This means that the naphthalene radical ions start out with energies which are rather close to σ^* energies. Moreover, it seems likely that there is little energy difference between the σ^* forms of radical ions $\mathbf{1}^{-}\cdot$ and $\mathbf{2}^{-}\cdot$ because of the relatively nonpolar nature of the substituent group which changes position. Certainly the difference between the corresponding σ^* states of the nitro-substituted ethers should be much greater. It is therefore remarkable that we still observe a strong preference for scission with regio-

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(4) Values taken from: Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Solutions*; Marcel Dekker: New York, 1970.

(5) Streitwieser, A. D., Jr. *Molecular Orbital Theory*; Wiley: New York, 1962; p 176.

(6) This limit could possibly be as high as 10^{-3} M^{-1} s^{-1} if a diffusion limit of $k = 10^{11}$ M^{-1} s^{-1} were operative. Such large diffusion rates are possible for exothermic electron-transfer reactions with large cross sections. See: Johnson, R. W.; Widlanski, T.; Breslow, R. *Tetrahedron Lett.* **1976**, 4685.

(7) (a) pK_a's of naphthols in Me_2SO are: 1-naphthol, 16.2; 2-naphthol, 17.1. Bordwell, F. G., private communication. (b) See also: Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1981**, *46*, 3570.

(8) McMillen, D. F.; Trevor, P. L.; Golden, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 7400.

conservation of spin density. We must conclude that polar contributions at the transition state are again responsible and that $\cdot^{-}\mathrm{NaphCH_2}^{+-}$:OPh is a significant contributor at the transition state for scission of α-**1** and β-**1**, whereas forms $\cdot^{-}\mathrm{NaphO}^{+-}$:$\mathrm{CH_2Ph}$ and $\cdot^{-}$NaphO:$^{-+}\mathrm{CH_2Ph}$ are much less important in the scission of α-**2** and β-**2**. It seems plausible that the extra-electron-induced polarization of the σ bond is actually greater for α-$\mathbf{1}^{-}\cdot$ and β-$\mathbf{1}^{-}\cdot$ than for their nitroarene counterparts because of greater concentrations of negative charge near the scissile bond. This would explain why the effect is still significant for these relatively exothermic cases. Observation of the same effect over such a wide range of thermodynamic driving forces suggests that the phenomenon will prove quite general.

Experimental Section

Solvents and Solutions. Tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were purified by distillation from sodium benzophenone ketyl and collection under argon just prior to use. Dimethylformamide (DMF) was purified by distillation from calcium hydride under reduced pressure (ca. 16 torr) and stored over molecular sieves (3 Å) under argon. Solutions of the radical anions of anthracene, biphenyl, and fluoroanthene were prepared by addition of freshly cut potassium metal to THF solutions of the corresponding hydrocarbons under argon. These solutions were degassed and kept in an argon atmosphere. Their concentrations were estimated by dropwise addition of the solutions to a stirred solution of diphenyl disulfide in THF assuming a two-to-one stoichiometry.[9]

Naphthylmethyl phenyl ethers, α-**1** and β-**1**, were prepared by dissolving the corresponding naphthylmethyl chloride (15 mmol) and phenol (30 mmol) in 40 mL of a 2:1 (v/v) mixture of $\mathrm{CH_2Cl_2}$ and acetonitrile. This was treated with 40 mL of 25% aqueous NaOH and a drop of Aliquat 360 (methyltricaprylammonium bromide), General Mills. Reaction mixtures were diluted with 200 mL of water. The organic layer was separated and washed with 5% aqueous NaOH and water and then dried over $\mathrm{Na_2SO_4}$.

In the case of α-**1**, warming at 60 °C for 16 h gave colorless crystals: 60% yield after recrystallization from ethanol, mp 76–77 °C [lit.[2] mp 76–77 °C]. ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$) δ 8.2–7.0 (m, 12 H), 5.48 (s, 2 H). MS, *m/e* 234, *141*, 115, 94.

In the case of β-**1**, stirring at ca. 25 °C for 72 h produced white crystals: 91% yield after recrystallization from ethanol, mp 116–118 °C [lit.[2] mp 115–116 °C]. ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$) δ 8.0–6.9 (m, 12 H), 5.20 (s, 2 H). MS, *m/e* 234, *141*, 115, 105, 94.

Naphthyl benzyl ethers, α-**2** and β-**2**, were prepared by stirring benzyl chloride (1.26 g, 10.0 mmol) with sodium naphthoxide (prepared from 1.44 g, 10.0 mmol of naphthol, and 10 mmol of sodium methoxide in methanol, evaporation, and drying at 0.1 torr) in 20 mL of dry $\mathrm{Me_2SO}$[10] at 25 °C for 12 h. The reaction mixture in 200 mL of water was extracted with 100 mL of 10% (v/v) $\mathrm{CH_2Cl_2}$ in pentane. Drying and evaporating of solvent gave pure product after recrystallization from ethanol.

By this procedure, α-**2** was prepared in 90% yield: mp 75–77 °C [lit.[11] mp 77.2–77.8 °C]. ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$) δ 8.4 (m, 1 H), 7.9–7.2 (m, 10 H), 6.9 (m, 1 H), 5.23 (s, 2 H). MS, *m/e* 234, 115, *91*, 65.

In the same way, β-**2** was produced in 92% yield: mp 102–103 °C [lit.[12] mp 100 °C]. ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$) δ 7.8–7.2 (m, 12 H), 5.16 (s, 2 H). MS, *m/e* 234, 115, 91, 65.

Product Studies in Cleavage of 1 and 2 by $\mathbf{K^+Ph_2^{-}\cdot}$ in THF. A 2–3-mL portion of a THF solution of $\mathrm{ArCH_2OAr'}$ (0.03–0.3 M) containing *n*-$\mathrm{C_{24}H_{50}}$ as a GC standard was treated with a solution of $\mathrm{K^+Ph_2^{-}\cdot}$ (0.03–0.15 M) in THF. The blue color was discharged immediately, and after 3 min of stirring, the solution was poured into 100 mL of water and acidified with 1% aqueous HCl. Extraction with two 50-mL portions of pentane/$\mathrm{CH_2Cl_2}$ (5:2, v/v), drying, partial evaporation, and dilution with ether gave a solution for GC analysis. Products were collected and identified by NMR, MS, and melting point comparison with authentic samples.[2,13] Compounds α-**1** and β-**1** each gave the corresponding methylnaphthalene and 1,2-dinaphthylethane in nearly equal yields (30–40%). This result was independent of mixing rate, temperature (25 to −78 °C), and excess $\mathrm{Ph_2^{-}\cdot}$ (up to 2:1). No other products were detected by GC or NMR. Recovery of starting ether plus hydrocarbon products was 84–100% for α-**1** and 67–84% for β-**1** (runs 6 and 4, respectively). Phenol recovery ranged from 30% to 85%.

In the case of α-**2**, the major product was 1,2-diphenylethane in yields from 40% to 75% (run 7). The yield of toluene was 3–15%, and recovery of the hydrocarbons plus α-**2** was 60–95%. The recovery of 1-naphthol was 70–90%. For β-**2**, the major product was toluene, 40–50% yield, and 1,2-diphenylethane was produced in only 5–20% yield (run 4). The recovery of hydrocarbons plus β-**2** was 65–100%. The recovery of 2-naphthol was 40–55%.

Reductions carried out using anthracene or fluoranthene radical anions (see Kinetics section) gave only methylarenes and no diarylethanes.

Kinetic Studies of the Reaction of 1 and 2 with the Radical Anions of Anthracene and Fluoranthene. An "H"-shaped glass cell attached to a length of 3-mm Pyrex tubing was placed under argon. With a gas-tight syringe, radical anion solution and reaction solvent were loaded into one side of the apparatus, and a solution of the appropriate ether and hydrocarbon corresponding to the radical anion solution used was placed in the other. Reaction was initiated by mixing and shaking the resultant solution into the 3-mm cell and reaction progress was monitored by following the decrease in the ESR peak intensity. When the various aryl ethers of this study were omitted, the resultant ESR signals were of constant intensity for more than 3 days in either DMF or DME.

Registry No. α-**1**, 6245-96-1; β-**1**, 68299-58-1; α-**2**, 607-58-9; β-**2**, 613-62-7; A (radical anion), 34509-92-7; F (radical anion), 34512-55-5.

Supplementary Material Available: A listing of raw data for the reaction of β-**2** with $\mathrm{A^{-}\cdot}$, Table IV (1 page). Ordering information is given on any current masthead page.

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