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Electron Apportionment in Cleavage of Radical Anions. 1. Nitro-Substituted Benzyl Phenyl Ethers

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Abstract: The radical anions of 4-nitrobenzyl phenyl ethers undergo cleavage at least 10^4 times faster than the radical anions of corresponding 4-nitrophenyl benzyl ethers despite a perceived thermodynamic advantage for the latter set of reactions. It is suggested that this result reflects a kinetic advantage for cleavage reactions which take place with regioconservation of spin density.

Reactions that involve the making or breaking of formal three-electron bonds have attracted increased attention from organic chemists in the last few years. These reactions are critical components of the $S_{RN}1$ mechanism and occur in nonchain processes as well.[1] We would like to call attention to a fundamental but hitherto unexplored aspect of the cleavage process.

Consider radical anions $\mathbf{1}^{-}\cdot$ and $\mathbf{2}^{-}\cdot$. Each is the radical anion of a nitro-substituted benzyl phenyl ether. They differ only in the position of the $-NO_2^{-}\cdot$ group in relation to the C–O bond direction. If cleavage of either of these radical ions is to occur, it may be reasonably assumed that the weakest bond (the C–O bond) will break. For each radical ion, there exist two conceivable scission modes marked 1A and 1B for $\mathbf{1}^{-}\cdot$ and 2A and 2B for $\mathbf{2}^{-}\cdot$ (Scheme I). The A and B paths differ only in the way electrons are apportioned in the product fragments.

It is clear that the A path is thermodynamically favored over the B path in each case simply because of negative charge stabilization in the phenoxide fragment as contrasted to the benzyl fragment. One might also compare path 1A with path 2A in an attempt to predict the thermochemical driving force for scission in $\mathbf{1}^{-}\cdot$ vs. $\mathbf{2}^{-}\cdot$. Clearly path 2A should be favored. This choice may be justified by comparing eq 1 and 2.[2] The DE° values for

$$\Delta H^\circ \text{ (path 1A)} = \mathrm{DE}^\circ(\mathbf{1}) - \mathrm{EA}(C_6H_5O\cdot) + \mathrm{EA}(\mathbf{1}) \quad (1)$$

$$\Delta H^\circ \text{ (path 2A)} = \mathrm{DE}^\circ(\mathbf{2}) - \mathrm{EA}(O_2NC_6H_4O\cdot) + \mathrm{EA}(\mathbf{2}) \quad (2)$$

neutral **1** and **2** are not known, but existing literature suggests that the nitro group does not have a significant effect on the stability of benzyl radicals.[3] Thus DE°(**1**) and DE°(**2**) should be approximately equal. In contrast, the gas-phase acidity of 4-nitrophenol is greater than that of phenol by a free-energy difference of 21 kcal/mol.[4] In Me_2SO or *N*-methylpyrrolidone solution, the difference is only 8 pK_a units[5a] (~10 kcal/mol) but is still a convincing indicator of anion stabilization by the nitro group. It thus seems clear that $\mathrm{EA}(O_2NC_6H_4O\cdot) > \mathrm{EA}(C_6H_5O\cdot)$ may be safely assumed. That EA(**1**) is slightly greater than EA(**2**) also seems certain, based on reduction potentials determined for 4-nitrotoluene and 4-nitroanisole ($\Delta E_{1/2} = 0.05$ V in acetonitrile).[6] One must therefore conclude that ΔH° (path 2A) is smaller or more negative than ΔH° (path 1A).

Table I. Hyperfine Coupling Constants for $\mathbf{1}^{-}\cdot$ and $\mathbf{2}^{-}\cdot$ in Me_2SO[a]

radical ion	a^N, G	a_0^H, G	a_m^H, G	a_{benzyl}, G
$\mathbf{1a,f}^{-}\cdot$	9.4	3.3	1.0	2.6
$\mathbf{1e}^{-}\cdot$	9.4	3.2	1.0	2.6
$\mathbf{1b}^{-}\cdot$	9.4	3.3	1.0	1.9
$\mathbf{1c}^{-}\cdot$	9.4	*b*	1.0	*b*
$\mathbf{1g}^{-}\cdot$	9.5	3.3	1.0	2.6
$\mathbf{2a,b}^{-}\cdot$	10.7	3.4	1.1	0.3
$\mathbf{2c}^{-}\cdot$	10.9	3.4	1.1	0.2
$\mathbf{2g}^{-}\cdot$	9.0	3.3	1.0	<0.1

[a] Radical ions were prepared as Li salts with the exception of $\mathbf{2c}^{-}\cdot$ which was prepared as the potassium salt; $\mathbf{1c}^{-}\cdot$ was prepared as both Li and K salts without noticeable affect on the spectrum. The observed coupling constants are consistent with those reported for structurally similar compounds. See: Berndt, A. In *Landolt-Börnstein, Zahlenwerte und Funktionen aus Naturwissenshaften und Technik*, *neue Serie*; Fischer, H., Hellwege, K.-H., Eds.; Springer-Verlag: Berlin 1980; vol. 9, Part d1, pp 430–572. [b] It is difficult to assign these coupling constants with certainty because the spectrum is complicated by additional coupling with the methyl group, $a_{Me}^H \simeq 0.3$ G. The observed spectrum is consistent with a_0^H and a_{benzyl}^H equal to the corresponding values in $\mathbf{1a}^{-}\cdot$ however.

Despite this clear prediction of a greater thermochemical driving force for scission of $\mathbf{2}^{-}\cdot$ over $\mathbf{1}^{-}\cdot$, we will show that under conditions where several modifications of $\mathbf{1}^{-}\cdot$ readily react following path 1A, the corresponding $\mathbf{2}^{-}\cdot$ radical ions *do not undergo scission of any kind*. If reaction of the various $\mathbf{2}^{-}\cdot$ by path 2A does occur, it is at least 10^4 times slower than reaction of $\mathbf{1}^{-}\cdot$ by path 1A. Why should this be so?

We will attempt to answer this question in the Summary and Conclusions section. First, however, we must describe in detail the behavior of radical ions $\mathbf{1}^{-}\cdot$ and $\mathbf{2}^{-}\cdot$. The chemistry associated with one-electron reduction of **1** and **2** turned out to be more complicated than we had anticipated.

Results and Discussion

Radical ions $\mathbf{1}^{-}\cdot$ and $\mathbf{2}^{-}\cdot$ were produced by treatment of **1** or **2** with 2,4,6-tri-*tert*-butylnitrobenzene radical anion (TBNB$^{-}\cdot$, K^+

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(1) Reviews touching on radical anion cleavage are: (a) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413. (b) Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734. (c) Rossi, R. A. *Acc. Chem. Res.* **1982**, *15*, 164. (d) Rossi, R. A.; de Rossi, R. H. *Aromatic Substitution by the $S_{RN}1$ Mechanism*; ACS Monograph 178; American Chemical Society: Washington, DC, 1983.

(2) These equations represent the following thermochemical cycle: $[ArCH_2OAr']^{-}\cdot \rightarrow ArCH_2OAr' \rightarrow ArCH_2\cdot + \cdot OAr' \rightarrow ArCH_2\cdot + {}^{-}{:}OAr'$. Note that DE°(**1**) and DE°(**2**) refer to dissociation of **1** and **2**, not $\mathbf{1}^{-}\cdot$ and $\mathbf{2}^{-}\cdot$.

(3) (a) Szwarc, M.; Leigh, C.; Sehon, A. *Proc. R. Soc. London, Ser. A* **1951**, *A209*, 97. (b) Bartlett, P. D.; Ruchardt, C. *J. Am. Chem. Soc.* **1960**, *82*, 1757. (c) Dust, J. M.; Arnold, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 1221. (d) Wayner, D. D. M.; Arnold, D. R. *Can. J. Chem.* **1984**, *62*, 1164. (e) Hydrogen abstractions from substituted toluenes almost invariably show negative ρ values: Russell, G. A. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, p 293. However, such "polar" effects are exhibited by reactions with early transition states and probably do not reflect product stability.

(4) (a) Fujio, M.; McIver, R. T., Jr.; Taft, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 4017. (b) Mashima, M.; McIver, R. R., Jr.; Taft, R. W.; Bordwell, F. G.; Olmstead, W. N. *J. Am. Chem. Soc.* **1984**, *106*, 2717.

(5) (a) Bordwell, F. G.; Branca, J. C.; Hughes, D. L.; Olmstead, W. N. *J. Org. Chem.* **1980**, *45*, 3305. (b) Mathews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margalin, A.; McCallum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006. (c) Bordwell, F. G., private communication. pK_a of 4-nitrotoluene in Me_2SO is 20.4.

(6) Maki, A. H.; Geske, D. H. *J. Am. Chem. Soc.* **1961**, *83*, 1852.

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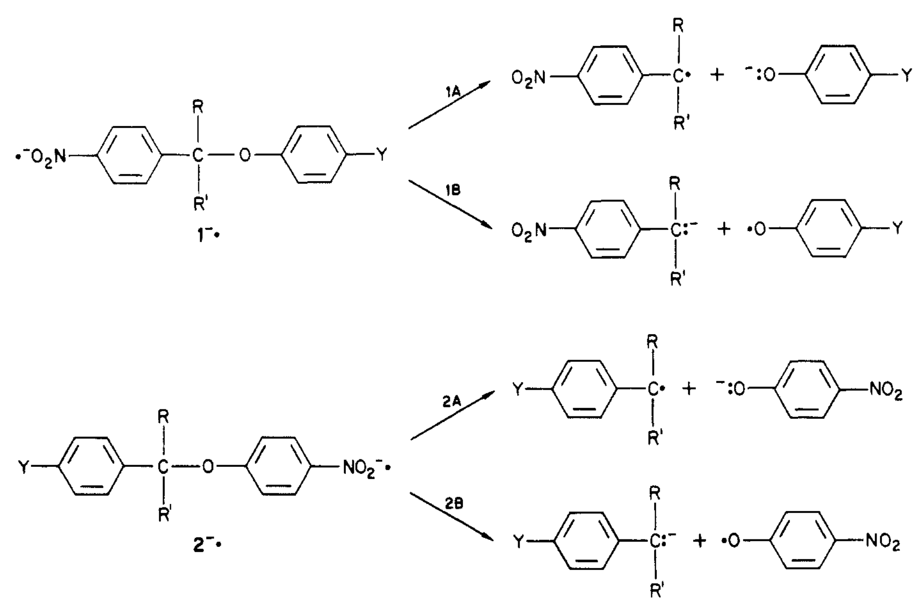
Scheme I



a, R=R'=Y=H
b, R=Ph, R'=Y=H
c, R=CH₃, R'=Y=H
d, R=R'=Ph, Y=H
e, R=R'=H, Y=CH₃
f, R=R'=H, Y=Cl
g, R=R'=Y=H (thioether)

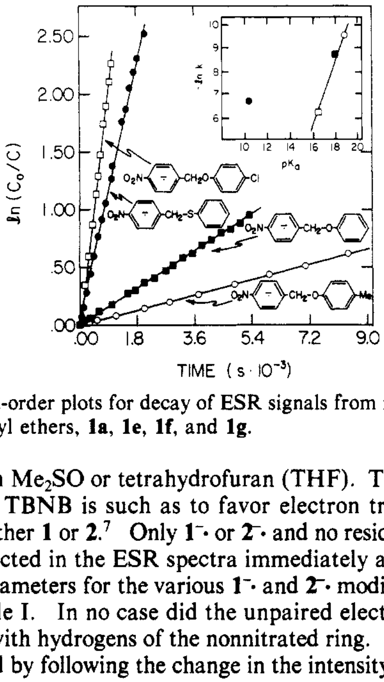


Figure 1. First-order plots for decay of ESR signals from radical anions of 4-nitrobenzyl ethers, **1a**, **1e**, **1f**, and **1g**.

or Li^+ salt) in Me_2SO or tetrahydrofuran (THF). The reduction potential for TBNB is such as to favor electron transfer from $TBNB^-\cdot$ to either **1** or **2**.[7] Only $\mathbf{1}^-\cdot$ or $\mathbf{2}^-\cdot$ and no residual $TBNB^-\cdot$ could be detected in the ESR spectra immediately after mixing. The ESR parameters for the various $\mathbf{1}^-\cdot$ and $\mathbf{2}^-\cdot$ modifications are listed in Table I. In no case did the unpaired electron interact measurably with hydrogens of the nonnitrated ring. Kinetic data were obtained by following the change in the intensity of the ESR signal. The presentation which follows will be in the sequence **1a**, **2a**; **1b**, **2b**; etc., in order to emphasize the effect of localizing the odd electron on different sides of the scissile bond.

Nitrobenzyl Phenyl Ethers, 1a,f,e,g. The fate of $\mathbf{1a}^-\cdot$ in Me_2SO is highly concentration dependent. To obtain direct information on its unimolecular decay, initial concentrations of $\mathbf{1a}^-\cdot$ must be below 1.5×10^{-3} M. Under these conditions, only the spectrum of $\mathbf{1a}^-\cdot$ is observed, and it decays to noise level following a first-order rate law. Rate constants obtained under these conditions are listed in Table II for $\mathbf{1a}^-\cdot$, $\mathbf{1e}^-\cdot$, $\mathbf{1f}^-\cdot$, and $\mathbf{1g}^-\cdot$, and kinetic plots are shown in Figure 1. The 4-nitrobenzyl radicals generated in the scission (path 1A, Scheme I) are presumably reduced by unreacted $\mathbf{1a}^-\cdot$ to 4-nitrobenzyl anions removing a second equivalent of $\mathbf{1a}^-\cdot$. The measured rate constant for disappearance of all $\mathbf{1}^-\cdot$ in this paper must therefore be divided by a factor of 2 to obtain the true rate constants for scission. As expected a direct relationship between phenoxide pK_a and $-(\ln k)$ is found for $\mathbf{1a}^-\cdot$, $\mathbf{1e}^-\cdot$, and $\mathbf{1f}^-\cdot$ (see insert, Figure 1).[8] The sulfur analogue does not fit on this plot. Workup after such kinetic runs gives 4-nitrotoluene as the only detected neutral product.

Table II. First-Order[a] Rate Data for 4-Nitrobenzyl Phenyl Ethers in Me_2SO at 22 °C

run	1	$10^3[1]_0$, M	$10^3[TBNB^-\cdot]_0$, M	$10^4k(SD)$,[b] s^{-1}	$t_{1/2}$
1	**1a** (4-H)	1.6	1.4	1.85 (0.02)	1.2
2	**1a**	0.84	0.80	1.53 (0.05)	0.3
3	**1a**	1.6	1.6	1.62 (0.02)	1.0
4	**1a**	0.84	0.80	1.75 (0.02)	1.4
5	**1a**	0.43	0.41	1.75 (0.02)	1.8
6	**1a**	1.7	0.80	1.93 (0.05)	1.1
7	**1e** (4-CH₃)	1.4	1.0	0.87 (0.15)	1.1
8	**1e**	0.68	0.68	0.725 (0.005)	0.9
9	**1f** (4-Cl)	1.4	1.0	26.3 (0.3)	6
10	**1f**	0.55	0.60	22.8 (0.2)	5
11	**1g** (-S-)	1.4	0.7	12.5 (0.1)	4
12	**1g**	1.4	1.4	16.3 (0.5)	c
13	**1g**	2.8	1.8	18.5 (0.5)	c

[a] All runs showed correlation coefficients of >0.997. [b] SD = standard deviation of slope. [c] These runs showed interference from the radical anion of 4-nitrotoluene and were followed for less than one half-life.

At initial $[\mathbf{1a}^-\cdot]$ of 10^{-2} M and above, both the kinetic behavior and the product mixtures are more complex. ESR studies show $\mathbf{1a}^-\cdot$ being rapidly replaced by the radical anion of 4-nitrobenzaldehyde. Workup of these reaction mixtures yields 4-nitrobenzaldehyde, 1-phenoxy-1,2-bis(4-nitrophenyl)ethene, 4-nitrotoluene, 1,2-bis(4-nitrophenyl)ethane, 1,2-bis(4-nitrophenyl)ethene (the major surviving product at long reaction times), and phenol. It seems likely that the 4-nitrobenzyl anion and phenoxide ion (a relatively strong base in Me_2SO, pK_a = 18[5]) are capable of deprotonating **1a** and various reaction intermediates to give the observed products. Although these reactions of unreduced **1a** are

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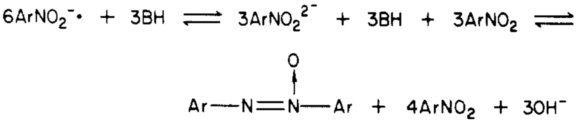
[7] $E_{1/2}$ = −1.203 for 4-nitrotoluene and $E_{1/2}$ = −1.250 for 4-nitroanisole: Maki, A. H.; Geske, D. H. *J. Am. Chem. Soc.* **1961**, *83*, 1852. These should be reasonably good models for **1a–1f** and **2a–2e**, respectively. $E_{1/2}$ = −1.500 for TBNB: Geske, D. H.; Ragle, J. L.; Bambenek, M. A.; Balch, A. L. *J. Am. Chem. Soc.* **1964**, *86*, 987. All of the above values were obtained in acetonitrile vs. SCE.

[8] Generation of phenoxyl radicals from substituted phenols with *tert*-butoxy radicals follows σ^+ with a negative ρ value: Das, P. K.; Encinas, M. V.; Steenken, S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4162.

Scheme II



$$6ArNO_2^{-}\cdot + 3BH \rightleftharpoons 3ArNO_2^{2-} + 3BH + 3ArNO_2 \rightleftharpoons Ar{-}N{=}\overset{\overset{O}{\uparrow}}{N}{-}Ar + 4ArNO_2 + 3OH^- + 3B^-$$

Table III. Kinetics of Decay of ESR Signal from 4-Nitrophenyl Benzyl Ether Radical Anion, **2a**$^{-}\cdot$, in Me_2SO at 22 °C

run[a]	10^{-2}[**2a**]$_0$, M	10^{-2}[TBNB$^{-}\cdot$]$_0$, M	k_{obsd},[b] $M^{-1}\ s^{-1}$	k_{calcd}[c]
14[d]	3.4	0.7	0.62	1.9
15	7.5	0.4	0.21	1.6
16	5.6	0.4	0.31	1.7

[a] Number of points was 23, 13, and 15, respectively. [b] Pseudo-second-order rate constant using concentrations estimated from ESR comparison with nitroxide standard. The absolute values are subject to substantial uncertainty. [c] $k_{calcd} = k_{obsd}$[**2a**]$_0$. [d] See Figure 2, first 22 points.

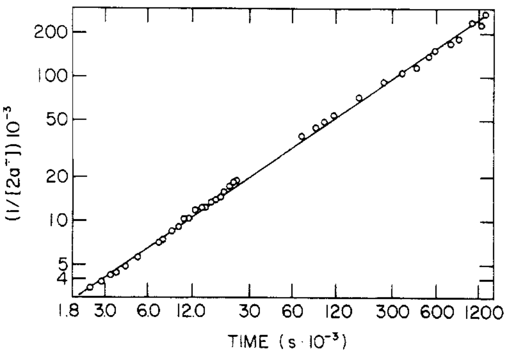


Figure 2. Second-order plot for decay of ESR signal from 4-nitrophenyl benzyl ether radical anion, **2a**$^{-}\cdot$, run 14.

of interest in their own right, they are incidental to the main theme of this paper. Similar product mixtures have been observed from the base-induced decomposition of 4-nitrobenzyl halides.[9]

In THF, disappearance of **1a**$^{-}\cdot$ is faster than in Me_2SO. The initially formed 4-nitrobenzyl radicals are present at higher concentration due both to the higher rate of production and possibly a slower rate of their reduction (less favorable electron-transfer equilibrium in the less polar solvent).[10] This leads to an increase in production of 1,2-bis(4-nitrophenyl)ethane (major product). The lithium phenoxide, probably present as a tight ion pair in THF, is likely to be a weaker base, and this limits the side reactions. Unfortunately, ESR spectra of our radical anions are not well-resolved in this solvent.

4-Nitrophenyl Benzyl Ether, 2a. In contrast to **1a**$^{-}\cdot$, the radical anion of **2a** decomposes slowly in both Me_2SO and THF to give 4,4-bis(phenylmethoxy)azoxybenzene as the only identified product. This suggests that **2a**$^{-}\cdot$ is in equilibrium with a dianion intermediate which is protonated and follows the usual sequence leading to azoxy compounds as generalized in Scheme II. 1,2-Diphenylethane and toluene were shown to be absent, and only a trace of 4-nitrophenol was detected. In the presence of excess **2a**, the ESR signal from **2a**$^{-}\cdot$ decays by a second-order rate law. Figure 2 shows a plot of run 14. Table III shows data obtained at several concentrations of **2a**. In runs where **2a** was completely converted to **2a**$^{-}\cdot$, the second-order plot was curved, being too steep in its initial stages but more gradual as **2a** is generated by the process of Scheme II. The rate-retarding effect of **2a** suggests reversible dianion formation followed by rate-limiting protonation. Approximate data were also obtained in THF as described in the Experimental Section. The last few data points in runs similar to those in Table III but carried out over several months allowed estimation of a maximum first-order component in the decay of **2a**$^{-}\cdot$ of $k_{max} = 1.7 \times 10^{-8}\ s^{-1}$ in Me_2SO. The corresponding value in THF is $k_{max} = 3 \times 10^{-6}\ s^{-1}$.

Table IV. Kinetics of Decay (4-Nitrophenyl)phenylmethyl Phenyl Ether Radical Anion, **1b**$^{-}\cdot$, in Me_2SO at 22 °C

run	10^{-2}[**1b**]$_0$, M	10^{-2}[TBNB$^{-}\cdot$]$_0$, M	10^2k[a]-(SD),[b] s^{-1}	$t_{1/2}$
17	1.0	1.0	0.934 (0.010)	1.5
18	1.0	1.0	1.008 (0.009)	2.0
19	1.0	1.0	1.104 (0.011)	3.1
20	2.2	0.56	1.112 (0.009)	3.4

[a] All runs showed correlation coefficients of greater than 0.999. The number of kinetic points was 8, 8, 14, and 16 for the four runs. [b] Standard deviation of slope.

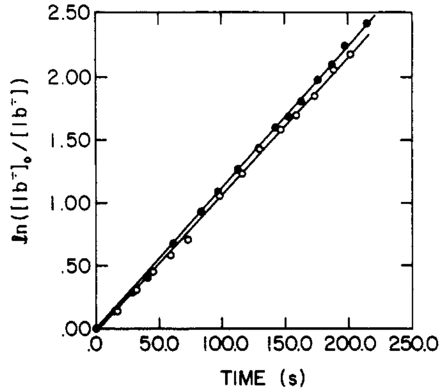
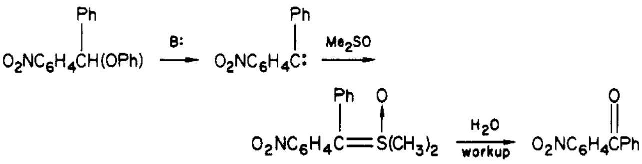


Figure 3. First-order plots for decay of ESR signal from radical anion of (4-nitrophenyl)phenylmethyl phenyl ether, **1b**$^{-}\cdot$, runs 19 (○) and 20 (●).

Scheme III



$$O_2NC_6H_4CH(OPh) \xrightarrow{B:} O_2NC_6H_4\overset{Ph}{C}: \xrightarrow{Me_2SO} O_2NC_6H_4\overset{Ph}{C}{=}\overset{O}{S}(CH_3)_2 \xrightarrow[\text{workup}]{H_2O} O_2NC_6H_4\overset{O}{\overset{\|}{C}}Ph$$

2a$^{-}\cdot$ was allowed to decay to 20% of its initial concentration in the presence of deuterium-labeled 4-nitrophenoxide in Me_2SO. No detectable deuterium-containing component was found in recovered **2a**, demonstrating that the lack of scission products cannot be explained by reversible scission.

A brief kinetic investigation of the radical anion of 4-nitrophenyl benzyl thioether, **2g**$^{-}\cdot$, the sulfur analogue of **2a**$^{-}\cdot$, was carried out. A plot of 1/[**2g**$^{-}\cdot$] vs. time is linear in the concentration range below 3×10^{-5} M, demonstrating second-order kinetics for destruction of **2g**$^{-}\cdot$. After the first day, a spectrum of essentially constant intensity was visible for more than five days. It is clear that any unimolecular scission of **2g**$^{-}\cdot$ is much slower than that observed for **1g**$^{-}\cdot$. The products from **2g**$^{-}\cdot$ were not investigated, but no toluene or 1,2-diphenylethane was detected.

Sulfur analogues such as **1g** and **2g** are deserving of further study. Although our preliminary results indicate that **1g**$^{-}\cdot$ and **2g**$^{-}\cdot$ fit the pattern for the oxygen ethers, Vianello and co-workers[13] have found that 4-nitrophenyl diphenylmethyl sulfide, the sulfur analogue of **2b**, undergoes electrochemical one-electron reduction to give its radical anion which then decays by a first-order process.

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[9] (a) Hanna, S. B.; Iskander, Y.; Riad, Y. *J. Chem. Soc.* **1961**, 217. (b) Hanna, S. B.; Iskander, Y.; Salona, A. *J. Chem. Soc.* **1961**, 221. (c) Swain, C. G.; Thorton, E. R. *J. Am. Chem. Soc.* **1961**, *83*, 4033. (d) Rothberg, I.; Thorton, E. R. *J. Am. Chem. Soc.* **1964**, *86*, 3296, 3302. (e) Doleib, D. M.; Iskander, Y. *J. Chem. Soc. B* **1967**, 1159. (f) Closs, G. L.; Goh, S. H. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2103. (g) Closs, G. L.; Goh, S. H. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1473.

[10] Triphenylmethyllithium undergoes equilibrium-favored electron transfer to 2,4,6-tri-*tert*-butylnitrobenzene in THF but not in di-*n*-propyl sulfoxide. Guthrie, R. D.; Hartmann, C., unpublished results.

[11] Guthrie, R. D.; Cho, N. S. *J. Chem. Soc.* **1979**, *101*, 4698.

[12] Guthrie, R. D.; Wesley, D. P.; Pendygraft, G. W.; Young, A. T. *J. Am. Chem. Soc.* **1976**, *98*, 5870.

[13] Farnia, G.; Severin, M. G.; Capobianco, G.; Vianello, E. *J. Chem. Soc., Perkin Trans. 2* **1978**, 11.

Scheme IV

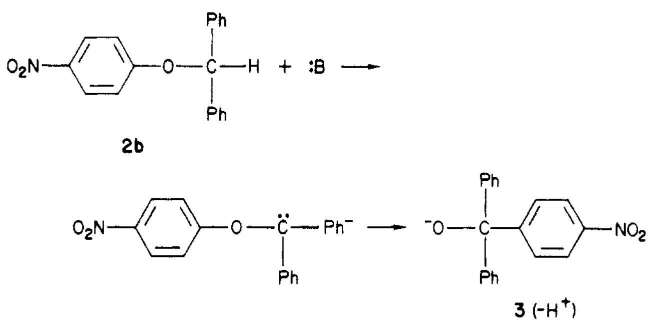

Table V. Products of Reaction of **2b** with TBNB$^-$· in Me_2SO[a]

[**2b**]$_0$, mM	[**2b**]$_0$/[TBNB$^-$·]$_0$	% yield[b] Ph_2CH_2	**3**
7.1	7.6	7	93
7.1	3.50	11	77
7.1	2.04	18	35
16.7	0.46	65	14
12.5	0.26	87	8

[a] Reaction temperature ca. 25 °C. [b] Determined by GC analysis vs. an added standard. 1,1,2,2-Tetraphenylethane was also formed in small amounts ranging from 1% to 15%. Only trace amounts of **2b** remained in all cases. Nitrophenol could be extracted from the water–Me_2SO layer of the workup in ca. 25% of the amount predicted based on Ph_2CH_2 plus $(Ph_2CH)_2$.

This would appear to be an example of a reaction of the type designated 2A. It seems possible that the sulfur analogues of the 1A and 2A reactions are more comparable in rate.

(4-Nitrophenyl)phenylmethyl Phenyl Ether, 1b. The ESR signal produced by treating **1b** with TBNB$^-$· in Me_2SO is clearly that of **1b**$^-$· (Table I) and decays rapidly following a first-order rate law. Data for four runs are listed in Table IV, and plots of runs 19 and 20, carried out at two different initial TBNB$^-$· concentrations, are shown in Figure 3. The scission rate for **1b**$^-$· is ca. 60 times faster than that for **1a**$^-$·, consistent with production of a more stable radical.

Workup in the absence of air gave two products, (4-nitrophenyl)phenylmethane and 4-nitrobenzophenone. Significantly, the ESR spectra obtained during kinetic runs in both Me_2SO and THF show no 4-nitrobenzophenone radical anion during or after the decay of the **1b**$^-$· signal to noise level. Considering that 4-nitrobenzophenone is a substantially better electron acceptor[14] than **1b**, it is clear that it cannot be present as the ketone during the fragmentation of **1b**$^-$· and must therefore be produced in the workup. A logical explanation is found in the sequence of Scheme III. Carbenes are known to react with Me_2SO to form sulfur ylides,[15] and the carbene could be produced through the action of reaction-generated base on **1b**. In support of this explanation, it was shown that 4-nitrobenzophenone is obtained when **1b** is treated with lithium phenoxide in Me_2SO. Also, the generation of 4-nitrobenzophenone could be largely avoided by using excess TBNB$^-$· to completely convert **1b** to **1b**$^-$·. Unfortunately it was not practical to follow the disappearance of **1b**$^-$· in the presence of excess TBNB$^-$·, so kinetic measurements were made under conditions where the sequence of Scheme III was occurring simultaneously with the scission of **1b**$^-$·. Fortunately the side reaction does not interfere with the first-order decay of the ESR signal of **1b**$^-$·.

The scission of **1b**$^-$· can also be carried out in THF. Under conditions comparable to Me_2SO runs, the ESR signal decays too rapidly for kinetic measurements. The rate constant is greater than 10^2 s^{-1}. Workup in the absence of air (quenching with $MeOH/H_2O$) gives exclusively (4-nitrophenyl)phenylmethane for runs carried out in THF. If reaction mixtures are quenched by passing in O_2, 4-nitrobenzophenone is the only product in both THF and Me_2SO. As with **1a**$^-$·, the initially formed radical reacts with intact radical ion to form the corresponding carbanion. This is converted to the ketone on introduction of O_2.[16]

Table VI. Minimum Constant Ratios for Corresponding Examples of Equations 1 and 2

radical ions compared	$k(1^-\cdot)/k(2^-\cdot)$[a] Me_2SO	THF[b]
1a$^-$·/**2a**$^-$·	10^4	10^3
1b$^-$·/**2b**$^-$·	10^2	10^3
1c$^-$·/**2c**$^-$·	10^4	
1g$^-$·/**2g**$^-$·	10^3	

[a] Values of $k(1^-\cdot)$ are first-order rate constants as reported in tables and text. Values of $k(2^-\cdot)$ are maximum observable first-order components as calculated from the last points of the second-order plots. [b] Data assume that observed ESR spectra are those of **1**$^-$· and **2**$^-$·, poor resolution of spectral lines notwithstanding.

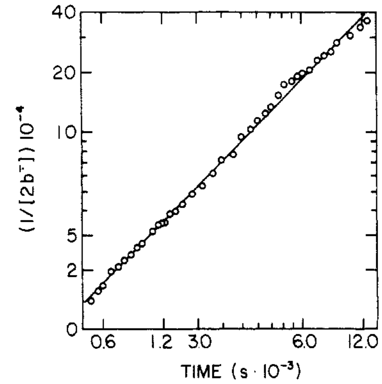

Figure 4. Second-order plot for decay of ESR signal from radical anion of 4-nitrophenyl diphenylmethyl ether, **2b**$^-$·.

Scheme V

$$2\,\mathbf{2b}^{-}\cdot \longrightarrow \mathbf{2b}^{2-} + \mathbf{2b}$$

$$\mathbf{2b}^{2-} \longrightarrow O_2NC_6H_4O^- + Ph_2CH^-$$

$$Ph_2CH^- + \mathbf{2b} \longrightarrow Ph_2CH\cdot + \mathbf{2b}^{-}\cdot$$

4-Nitrophenyl Diphenylmethyl Ether, 2b. Study of the radical anion from **2b** was complicated by the competing conversion of **2b** to (4-nitrophenyl)diphenylmethanol, **3**. As with the systems described above, this side product results from reaction of **2b** with base. In this case the problem is a Wittig- or Smiles-type rearrangement possibly proceeding through a carbanion as shown in Scheme IV. 1,1,2,2-Tetraphenylethane and 4-nitrophenol were also formed. Diphenylmethane supplants **3** as the major product when excess TBNB$^-$· is employed (see Experimental Section and Table V).

When the reaction was monitored by ESR, the initial spectrum was that of **2b**$^-$· (see Table I) and the disappearance of this signal was clearly second order as shown in Figure 4. Rate constants for this case were not as consistent as for other reactions with three runs giving values of 18.9, 27.8, and 32.7 M^{-1} s^{-1} at 22 °C in Me_2SO, possibly reflecting uncertainty in ESR determination of starting concentrations (correlation coefficient of 0.997, 0.995, and 0.999, respectively). These reactions were run at $[\mathbf{2b}]_0 = 1.8$, 1.6, and 1.7×10^{-2} M and $[TBNB^-\cdot]_0 = 1.2$, 1.4, and 0.8×10^{-2} M. The upper limit for the rate constant of a hypothetical competing first-order process was estimated at 6.7×10^{-5} s^{-1}, being necessarily somewhat higher than that for **2a**$^-$· because the emergence of the spectrum of **3**$^-$· limits the length of time over which the spectrum of **2b**$^-$· can be observed.

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(14) $E_{1/2}$ for 4-nitrobenzophenone is −0.80 V vs. SCE in DMF: Ziebig, Von R.; Pragst, F. *Z. Phys. Chem. (Leipzig)* **1979**, *260*, 795.

(15) (a) Dost, F.; Gosselck, J. *Tetrahedron Lett.* **1970**, *58*, 5091. (b) Oda, R.; Mieno, M.; Hayashi, Y. *Tetrahedron Lett.* **1967**, *25*, 2363. (c) Huchins, R. O.; Hoke, D.; Keogh, J.; Koharski, D. *Tetrahedron Lett.* **1969**, *40*, 3495. (d) Trost, B. M.; Melvin, L. S. Jr. *Sulfur Ylides*; Academic: New York, 1975.

(16) Guthrie, R. D. In *Comprehensive Carbanion Chemistry*; Buncel, E., Durst, T., Ed.; Elsevier: New York, 1980; pp 199–208.

The second-order character of the disappearance kinetics demands involvement of 2 equiv of **2b**$^{-\cdot}$ in the fragmentation sequence, and barring the presence of a reversible scission reaction, both molecules of **2b**$^{-\cdot}$ must be utilized prior to the fragmentation. **2b**$^{-\cdot}$ was shown not to be involved in reversible scission by carrying out partial reactions in the presence of deuterium-labeled nitrophenoxide; thus it may be concluded that both **2a**$^{-\cdot}$ and **2b**$^{-\cdot}$ react by paths involving two molecules of radical anion. A logical sequence for **2b**$^{-\cdot}$ is that of Scheme V whereby a dianion intermediate fragments to give two anions. This fragmentation is not observed for **2a**$^{2-}$ probably because of the stability difference between the benzyl anion and benzhydryl anion. The presence of 1,1,2,2-tetraphenylethane suggests that some of the diphenylmethide ions produced as shown in Scheme V are oxidized by **2b** to diphenylmethyl radicals regenerating one of the 2 equiv of **2b**$^{-\cdot}$ required for initial generation of the carbanion. To demonstrate the feasibility of this sequence, we treated **2b** with diphenylmethyllithium. The ESR spectrum of **2b**$^{-\cdot}$ was observed, and the set of products found was the same as that previously obtained when **2b** was treated with TBNB$^{-\cdot}$. The overall stoichiometry for the combined reactions of Scheme V is the same as that for scission of **2b**$^{-\cdot}$ by path 2A, supporting our contention that the difficulty with path 2A is of kinetic and not thermodynamic origin.

In THF solution, the products do not include **3**. The somewhat ill-defined spectrum presumed to be that of **2b**$^{-\cdot}$ disappears in a second-order fashion with an approximate rate constant of 0.15 M^{-1} s^{-1} (THF, 22 °C). A maximum value for any competing first-order process could be set at 3×10^{-6} s^{-1}.

It is important to recognize that the mechanism is not a critical issue in systems with structure **2**$^{-\cdot}$ because all of these with the exception of **2d**$^{-\cdot}$ are highly persistent at low concentration. In the demonstrated absence of reversible cleavage, *persistence alone is sufficient to prove the nonoccurrence of unimolecular fragmentation* and justifies the main conclusions of this paper.

Other Systems. A few systems that were not investigated as extensively are nevertheless consistent with the emerging picture. The radical anion from **1c** disappears in a cleanly first-order fashion at a rate about 4 times greater than that observed for **1a**$^{-\cdot}$, $k = 7.4 \pm 0.4 \times 10^{-4}$ s^{-1} in Me_2SO at 22 °C (three runs, ca. 15 points per run, four half-lives).[17] The ESR signal from **1c**$^{-\cdot}$ decays to noise level and leaves no residual spectrum. The kinetics of **2c**$^{-\cdot}$ disappearance was not studied in any detail, but the essential features are similar to those of **2a**$^{-\cdot}$. After an initial period of decay, the spectral intensity becomes essentially constant and persists for weeks. The maximum possible first-order rate constant is estimated as 1×10^{-7} s^{-1} at 22 °C in Me_2SO.

Both **1d** and **2d** were treated with TBNB$^{-\cdot}$ in Me_2SO but the radical anions, if formed, react too rapidly for kinetic study using techniques available to us. An upper limit for the half-life of **1d**$^{-\cdot}$ is 10 s. The only products of this reacton are (4-nitrophenyl)diphenylmethane (quantitative yield) and phenol. The reaction with **2d** results in immediate generation of triphenylmethyl radical (ESR).

It was found that **2d** undergoes measurable solvolysis (10% in 6 h at 25 °C) even in *t*-BuOH/THF (20/3, v/v). This suggests that the reaction of **2d** with TBNB$^{-\cdot}$ in the better ionizing solvent Me_2SO could well be a reduction of the trityl cation.[18] To provide evidence on this question, the reaction of **2d** with fluoradenide ion (9-(2,1-phenylene)-fluoren-9-ide ion), a carbanion known to produce one-electron reduction of aromatic nitro compounds,[11] was studied. When this reaction mixture is examined by ESR in *t*-BuOH/THF (1/1, v/v), no **2d**$^{-\cdot}$ is observed. A strong and stable spectrum of triphenylmethyl radical immediately appears. 2,4,6-Trichlorophenyl triphenylmethyl ether, **4**, was also found to react with fluoradenide ion in the same solvent to produce triphenylmethyl radical. It is unlikely that the trichlorophenyl moiety in **4** is a sufficiently good electron acceptor to oxidize fluoradenide ion, considering that 2,4,6-trichlorophenyl diphenylmethyl ether, **5**, was found not to react under the same conditions. The most reasonable explanation is that both **2d** and **4** undergo ionization to give triphenylmethyl cation which is reduced to triphenylmethyl radical.[18]

In another relevant experiment, 3-nitrophenyl triphenylmethyl ether, **6**, was found to react with fluoradenide ion in *t*-BuOH/THF to give **6**$^{-\cdot}$ which, by contrast to **2d**$^{-\cdot}$, is persistent. Compound **6** is known to give triphenylmethyl cation on irradiation,[19] and when the mixture containing fluoradenide ion, **6** and **6**$^{-\cdot}$, is irradiated, the ESR spectrum of the triphenylmethyl radical appears. Photoinduced ionization of **6** followed by one-electron reduction of the triphenylmethyl cations produced, while certainly not a unique mechanism for the formation of triphenylmethyl radical from photolysis of this mixture, is an explanation which is consistent with the observed behavior of **2d** and **4**.

Summary and Conclusions

Although the situation is somewhat complicated by side reactions, the important difference between **1**$^{-\cdot}$ and **2**$^{-\cdot}$ is clear. Radical anions of type **1**$^{-\cdot}$ readily undergo fragmentation by path 1A, whereas those of type **2**$^{-\cdot}$ are resistant to scission of any kind.

The scission of radical ions and the reverse process in which radicals react with nucleophiles are of central significance in the important class of $S_{RN}1$ substitution reactions.[1] The usual representation of these processes depicts the σ-bonding electrons moving as a pair. It is therefore fascinating that insistence on such pairwise apportionment leads to a correct prediction of our observed preference for scission of **1**$^{-\cdot}$ over **2**$^{-\cdot}$. If the odd electron is conceptually localized in the $-NO_2^{-\cdot}$ group, then path 1A may be viewed as analogous to the first step in an S_N1 reaction with the $-NO_2^{-\cdot}$ group being simply an unusual substituent, enforcing formation of a radical rather than a cation. The electronically analogous process for **2**$^{-\cdot}$ is path 2B, but this leads to energetically inaccessible products, benzyl anion plus 4-nitrophenoxyl radical. In fact, no pairwise apportionment of σ electrons in **2**$^{-\cdot}$ leads to the more stable product set in a direct manner.

Formal electron apportionment to effect the thermodynamically favorable outcome of path 2A may be accomplished in two ways. Either one electron is transferred from $-NO_2^{-\cdot}$ to the unsubstituted phenyl ring in **2**$^{-\cdot}$, in which case subsequent pairwise movement of the σ electrons leads directly to 4-nitrophenoxide plus benzyl radical, or the electrons constituting the σ bond must be separated and one electron apportioned to each fragment. The former alternative appears unattractive by reason of the highly endothermic character of the electron-transfer component. The latter is not so easily discounted; however, it might be argued that this would be analogous to C–O bond homolysis in neutral **2** (or **1**) and, to the extent of the similarity, would be strongly endothermic. This argument would continue by claiming that pairing of the single electron generated by σ-bond scission with the single electron in $-NO_2^{-\cdot}$ is restricted to an advanced state of bond rupture. Path 2A would then experience minimal kinetic benefit from the development of low-energy 4-nitrophenoxide ion.

Although the foregoing analysis is tempting for its simplicity and its support of the traditional preference of organic chemists for pairwise electron movement, it is based largely on analogy to the behavior of molecules containing only paired electrons. It seems dangerous to regard the scission reactions of radical ions as comparable to "heterolytic" or "homolytic" processes when in one sense they are neither and in another sense they are both.

A more rigorous approach requires a description of the configuration interactions involved as **1**$^{-\cdot}$ or **2**$^{-\cdot}$ proceeds to products. Each reaction profile is composed of energetically ascending and descending configuration surfaces. As an aid to conceptualization of these surfaces, we adopt the methodology of Epiotis, Pross, and

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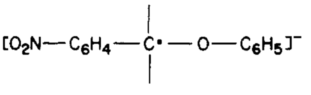
[17] Data analysis was complicated somewhat by the fact that the outermost peaks in the ESR spectra appeared as poorly resolved quartets which were affected by line width changes in a complicated way. This was solved by computer modeling as described in the Experimental Section.

[18] There is evidence for electron-transfer reduction of triphenylmethyl cation by 2,4,6-tri-*tert*-butylphenoxide: Bilevitch, K. A.; Bubnov, N. N.; Okhlobystin, O. Yu. *Tetrahedron Lett.* **1968**, 3465.

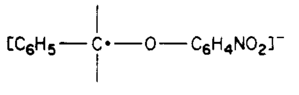
[19] Zimmerman, H. E.; Somasekhara, S. *J. Am. Chem. Soc.* **1963**, *85*, 922.

Shaik[20] which depicts the molecular configurations in valence bond notation. Thus the descending surface for $\mathbf{1}^{-\cdot}$ starts at **7**, the $\pi \rightarrow \sigma^*$ excited state of $\mathbf{1}^{-\cdot}$, and ends at phenoxide plus 4-nitrobenzyl radical. For $\mathbf{2}^{-\cdot}$ the corresponding surface starts at **8** and ends at 4-nitrophenoxide and the benzyl radical. Because the higher energy atomic orbital contributor to the C–O σ bond will be the carbon orbital in each case and the NO_2 substituent lowers the energy of this orbital in **1** relative to **2**, the energy of the σ^* orbital in **7** will be lowered. It may therefore be argued that **8** is a higher energy species than **7**. On the other hand, **8** lies on a surface leading to the lower energy product set, 4-nitrophenoxide plus benzyl radical. It seems likely that the nitro group lowers the energy of the phenoxide ion at least as much as it separates the energies of **7** and **8**. Thus while the descending surface component of the fragmentation profile for $\mathbf{2}^{-\cdot}$ is clearly steeper than that for $\mathbf{1}^{-\cdot}$, starting at higher energy and ending at lower energy, it is not clear that there will be a substantial difference in the mid-range near the transition-state geometry.



$[O_2N-C_6H_4-\overset{|}{\underset{|}{C}}\cdot-O-C_6H_5]^-$

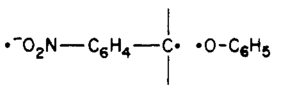
7 (π -> σ)



$[C_6H_5-\overset{|}{\underset{|}{C}}\cdot-O-C_6H_4NO_2]^-$

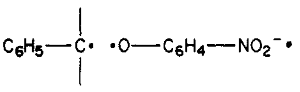
8 (π -> σ*)

If we then turn to the ascending surface components, the intended product from $\mathbf{1}^{-\cdot}$ is **9** and that from $\mathbf{2}^{-\cdot}$ is **10**. These are electron-localized approximations of product excited states for each reaction. Given that the unpaired electrons do not interact, **9** and **10** would seem to be comparable in energy making the ascending surfaces $\mathbf{1}^{-\cdot} \rightarrow \mathbf{9}$ and $\mathbf{2}^{-\cdot} \rightarrow \mathbf{10}$ energetically similar. We would argue, however, that for the products from $\mathbf{1}^{-\cdot}$, there is available a lower energy excited state than **9** which is represented by **11**. Strictly speaking, **11** cannot be said to be on the same surface as $\mathbf{1}^{-\cdot}$, rather **11** connects to a modification of $\mathbf{1}^{-\cdot}$ in which the electrons in the C–O bond are polarized toward the oxygen atom. Nevertheless, the surface leading to **11** should be low in energy relative to corresponding surfaces leading from $\mathbf{2}^{-\cdot}$ to **12** or **13** . We argue, therefore, that the surface connecting $\mathbf{1}^{-\cdot}$ to **9** intersects the surface leading to **11** at low energy. Configuration interaction then permits avoided crossing, and **11** makes a major energy-lowering contribution to the transition state for scission of $\mathbf{1}^{-\cdot}$ by path 1A. By contrast, **12** and **13** are much less involved at the transition state for the hypothetical path 2A which is therefore left at relatively high energy. Although the current emphasis on single electron movement as a basis for chemical reactivity[20f,g] suggests a more direct relationship between reactants and products in path 2A as compared to 1A where both σ electrons must be moved to one product fragment, the availability of a low-lying polarized configuration (**11**) facilitates 1A. Thus while 1A is electronically more complicated than 2A, involving three configurations rather than two, it is nevertheless the lower energy path. It is, in a sense, accidental that the organic chemist's predisposition to pairwise movement of electrons gives a correct prediction.



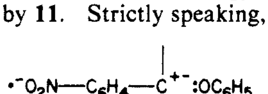
$\cdot^{-}O_2N-C_6H_4-\overset{|}{\underset{|}{C}}\cdot\ \cdot O-C_6H_5$

9



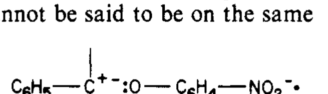
$C_6H_5-\overset{|}{\underset{|}{C}}\cdot\ \cdot O-C_6H_4-NO_2{}^{-}\cdot$

10



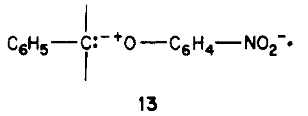
$\cdot^{-}O_2N-C_6H_4-\overset{|}{\underset{|}{C}}{}^{+-}{:}OC_6H_5$

11



$C_6H_5-\overset{|}{\underset{|}{C}}{}^{+-}{:}O-C_6H_4-NO_2{}^{-}\cdot$

12



$C_6H_5-\overset{|}{\underset{|}{C}}{:}^{-+}O-C_6H_4-NO_2{}^{-}\cdot$

13

Based on this analysis it may be predicted that for the general case of a polar scissile bond, X → Y (more precisely, a bond X:Y for which X:Y → X + :Y is thermodynamically favored over X:Y → X: + Y), scission will be relatively facilitated in the corresponding radical anion when the extra electron is positioned on the electropositive side of the scissile bond. In other words, $\cdot^{-}$Z–X:Y will undergo unimolecular cleavage more rapidly than X:Y–Z$^{-}\cdot$. For operational expedience, this translates into an inherent preference for radical anion scission reactions which occur with regioconservation of spin density, that is, where the unpaired electron remains on the same side of the scissile bond throughout the fragmentation process. This is not to say that reactions proceding with transfer of spin density are forbidden; indeed the sulfur analogue of $\mathbf{2b}^{-\cdot}$ seems to be such a case,[13] and we provide another example in the following paper.[21] It does appear, however, that such reactions suffer a kinetic disadvantage when compared to their spin-localized counterparts.

An important question remains as to whether the observed preference for regioconservation of spin density will extend to systems with nonpolar scissile bonds. One might even consider a hypothetical example of the type $\cdot^{-}$Z–X–X′–Z′ constructed in such a way that the two possible scission modes, (1) Z–X· + :X′–Z′ and (2) Z–X: + ·X′–Z′, were thermodynamically equivalent. Would the polarization induced by the extra electron, $\cdot^{-}$Z–X → X′–Z′, still confer a kinetic advantage to mode 1 over mode 2? The experiments required to answer such questions unequivocally will be difficult to design but are necessary for complete understanding of the fundamental issues raised in this paper.

Experimental Section

Solvents and Reagents. Dimethyl sulfoxide (Me_2SO) was purified following the procedure of Bordwell.[5b] Tetrahydrofuran (THF) was distilled from a solution of sodium benzophenone ketyl and collected under argon just prior to use. Solutions of $TBNB^{-}\cdot Li^{+}$ were prepared from methyllithium and TBNB as described elsewhere.[22] Me_2SO solutions of $TBNB^{-}\cdot$ were prepared by adding methyllithium (0.10 mL of a 1.5 M solution in ether) to a degassed solution of TBNB in hexane (ca. 0.15 mmol in 10 mL of hexane). The precipitated $TBNB^{-}\cdot Li^{+}$ was washed with hexane (syringe) and the appropriate volume of Me_2SO added. Due to the low solubility of TBNB in Me_2SO, the concentration of $TBNB^{-}\cdot$ could be estimated (after exposure of the Me_2SO solution to air and workup as described below) by determination of TBNB obtained (GC analysis vs. an internal standard – various saturated hydrocarbons used). Solutions of $TBNB^{-}\cdot K^{+}$ were prepared by treatment of a THF solution of TBNB with potassium metal, evaporation of the THF, and dissolution in Me_2SO.

Kinetics. Solutions were prepared in an oxygen-free argon atmosphere and transferred by means of gas-tight syringe to a two-chamber mixing reservoir attached to a cylindrical 3-mm Pyrex electron spin resonance (ESR) cell. Reagents were mixed and shaken into the ESR cell, and radical ion decay occurred followed by peak intensity at constant peak width. For second-order kinetics, calibration with standard solutions of 4-acetamido-2,2,6,6-tetramethylpiperidino-1-oxyl was performed. Second-order rate constants should be viewed as order-of-magnitude values but are probably internally consistent. Kinetic runs were carried out at 22 ± 3 °C for all runs and (±0.2 °C) for runs of <3 h using a Varian E-109 Century Series spectrometer.

Analytical Methods. ^1H NMR spectra were taken on Varian EM-390 (90 MHz), Varian T-60 (60 MHz), and Varian XL-200 (200 MHz) NMR spectrometers (^{13}C). Chemical shifts are in parts per million units from Me_4Si. Mass spectra were taken on a Hitachi Perkin-Elmer RMU-7 double-focusing mass spectrometer and, for negative ions, on a VG Micromass ZAB-2F. Gas chromatographic analyses were performed on a Varian 3700 gas chromatograph with a flame ionization detector

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[20] (a) Epiotis, N. D. *Pure Appl. Chem.* **1979**, *51*, 203. (b) Epiotis, N. D.; Shaik, S.; Zander, W. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 2. (c) Shaik, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 3692. (d) Pross, A.; Shaik, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 3702. (e) Pross, A.; Shaik, S. S. *J. Am. Chem. Soc.* **1982**, *104*, 1129. (f) Pross, A. *Acc. Chem. Res.* **1985**, *18*, 212. (g) Pross, A. In *Advances in Physical Organic Chemistry*; Academic: London, 1985, Vol. 21, p 99.

[21] Analogous behavior has been observed for the cleavage reactions of naphthyl and naphthyl methyl ethers which suggest that the phenomenon is not limited to the "$-NO_2$" radical anions. Maslak, P.; Guthrie, R. D. *J. Am. Chem. Soc.*, following paper in this issue.

[22] Guthrie, R. D.; Hartmann, C., unpublished results. It was shown that RLi reacts stoichiometrically with TBNB to give $TBNB^{-}\cdot Li^{+}$. R_2 is formed. Excess RLi does not increase the ESR intensity of the TBNB spectrum.

connected to a HP 3390A integrator using a column of 3% OV-101 on Partisorb and on a Varian Aerograph 90-P with thermal conductivity detector equipped with a column of 15% SF-96 on Chromosorb W. The latter served also as a semipreparative instrument for isolation of analytical samples. Melting points are uncorrected unless otherwise specified. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Inc. (Woodside, NY), and Mic Anal (Tucson, AZ).

Phase-Transfer Procedure for Synthesis of Substituted Benzyl Phenyl Ethers. 4-Nitrobenzyl Phenyl Ether, 1a. 4-Nitrobenzyl bromide (3.24 g, 0.015 mol) and phenol (2.8 g, 0.030 mol) were dissolved in 40 mL of CH_2Cl_2 and treated with 40 mL of 25% aqueous NaOH and 1 drop of Aliquat 360 (methyltricaprylylammonium bromide), General Mills. The mixture was stirred for 24 h at ca. 25 °C and treated with 200 mL of water. The organic layer was separated, washed with 5% aqueous NaOH and water, and dried over Na_2SO_4. The residue after solvent evaporation was recrystallized from 95% ethanol, giving 3.3 g (96%) of colorless crystals mp 89–91 °C [lit.[23,24] mp 91 °C]. ^1H NMR (90 MHz, $CDCl_3$) δ 8.15 (d, 2 H, J = 9 Hz), 7.52 (d, 2 H, J = 9 Hz), 7.28 (m, 2 H), 6.95 (m, 3 H), 5.10 (s, 2 H). MS (positive ions), *m/e* 229, *136*, 106, 94, 90, 78, 65. MS (negative ions, EI), *m/e* 228, 181, 136, 120, 118, 105, *93*, 46. MS (negative ions, CI, CH_4), *m/e* 228, 212, 181, 151, 136, 120, *93*, 46.

4-Nitrobenzyl 4-Methylphenyl Ether, 1e. This was prepared from 4-nitrobenzyl bromide and 4-methylphenol by the procedure described for **1a** in 89% yield: mp 92–93 °C (ethanol) [lit.[25] mp 91 °C]. ^1H NMR (90 MHz, $CDCl_3$) δ 8.18 (d, 2 H, J = 9 Hz), 7.52 (d, 2 H, J = 9 Hz), 7.07 (d, 2 H, J = 9 Hz), 6.82 (d, 2 H, J = 9 Hz), 5.09 (s, 2 H), 2.25 (s, 3 H). MS, *m/e* 243, 197, *136*, 107, 106, 90, 78.

4-Nitrobenzyl 4-Chlorophenyl Ether, 1f. This was prepared from 4-nitrobenzyl bromide and 4-chlorophenol using the procedure described for **1a** in 93% yield: mp 102–103 °C (ethanol) [lit.[26] mp 101–103 °C]. ^1H NMR (90 MHz, $CDCl_3$) δ 8.18 (d, 2 H, J = 9 Hz), 7.52 (d, 2 H, J = 9 Hz), 7.20 (d, 2 H, J = 9 Hz), 6.88 (d, 2 H, J = 9 Hz), 5.08 (s, 2 H). MS, *m/e* 265, 263, *136*, 106, 78.

4-Nitrobenzyl Phenyl Thioether, 1g. This was prepared from 4-nitrobenzyl bromide and thiophenol by using the procedure described for **1a** under N_2 for 1 h. The product was obtained in 62% yield: mp 73–75 °C (hexane) [lit.[27] mp 79 °C]. ^1H NMR (90 MHz, $CDCl_3$) δ 8.18 (d, 2 H, J = 9 Hz), 7.41 (d, 2 H, J = 9 Hz), 7.30 (s, 5 H), 4.19 (s, 2 H). MS, *m/e* 245, 199, *136*, 108, 106, 90.

4-Nitrophenyl Benzyl Ether, 2a. This was prepared from benzyl chloride and 4-nitrophenol by using the procedure described for **1a** except the reaction mixture was heated at ca. 50 °C for 5 h. The product was obtained in 82% yield: mp 105–107 °C (ethanol) [lit.[23,28] mp 106–108 °C]. ^1H NMR (90 MHz, $CDCl_3$) δ 8.08 (d, 2 H, J = 9 Hz), 7.28 (s, 5 H), 6.91 (d, 2 H, J = 9 Hz), 5.08 (s, 2 H). MS (positive ions), *m/e* 229, 199, 181, 153, 152, 108, *91*, 77, 65. MS (negative ions), *m/e* 228, *138*, 122, 120, 107, 91, 46.

4-Nitrophenyl Diphenylmethyl Ether, 2b. This was prepared from benzhydryl bromide and 4-nitrophenol by the procedure described for **1a** in 98% yield. The reaction mixture was stirred for 5 days at 25 °C. Heating resulted in production of benzydrol which was difficult to separate from the desired product. The crude product was recrystallized from methanol–ethanol (1:1): mp 157–158 °C [lit.[29] mp 157–158 °C]. ^1H NMR (90 MHz, $CDCl_3$) δ 8.02 (d, 2 H, J = 8.5 Hz), 7.30 (br s, 10 H), 6.90 (d, 2 H, J = 8.5 Hz), 6.21 (s, 1 H). MS (positive ions), *m/e* *167*, 165, 152, 139, 128, 115, 77, 63, 51. MS (negative ions, EI), *m/e* 304, 259, 227, 217, 192, 185, 167, 153, *138*, 122, 108, 96, 92. MS (negative ions, CI, CH_4), *m/e* 304, 277, 261, 228, 227, 167, *138*, 122, 107, 46.

2,4,6-Trichlorophenyl Diphenylmethyl Ether, 5. This was prepared from diphenylmethyl chloride and 2,4,6-trichlorophenol by using the procedure described for **1a** in 64% yield: mp 74–76 °C (heptane). ^1H NMR (90 MHz, $CDCl_3$) δ 7.32 (m, 10 H), 7.11 (s, partially overlapping with m at 7.32), 6.49 (s, 1 H), IR (KBr) 3062, 2920, 1448, 1387, 1242, 1138, 978, 850, 799, 750, 698 cm^{-1}. MS, *m/e* 293, 198, 196, 168, *167*, 152, 118, 116.

Anal. Calcd for $C_{19}H_{13}Cl_3O$: C, 62.75; H, 3.60; Cl, 29.24. Found: C, 62.75; H, 3.74; Cl, 29.59.

(4-Nitrophenyl)phenylmethyl Phenyl Ether, 1b. (4-Nitrophenyl)phenylmethanol was prepared from 4-nitrobenzophenone by reduction with an excess of sodium borohydride in methanol: mp 73–74 °C [lit.[30] mp 73–75 °C]. The carbinol (7.65 g, 0.033 mol) in 50 mL of $CHCl_3$ was treated with PBr_3 (3.8 mL, ca. 0.04 mol in 10 mL of $CHCl_3$) dropwise over 1 h at −5 to −10 °C. The mixture was then stirred an additional hour at 0 °C and then for 2 h at ca. 25 °C. Excess PBr_3 was destroyed by slow addition of methanol, and the reaction mixture was poured into 300 mL of water. Workup in CH_2Cl_2 gave 9.55 g (99%) of nearly pure bromide: ^1H NMR (60 MHz, $CDCl_3$) δ 8.05 (d, 2 H, J = 9 Hz), 7.52 (d, 2 H, J = 9 Hz), 7.28 (m, 5 H), 6.21 (s, 1 H). MS, *m/e* *212*, 165, 143, 119, 117.

The unpurified bromide (5.12 g, 0.0175 mol) and phenol (3.3 g, 0.035 mol) in 10 mL of acetonitrile/20 mL of CH_2Cl_2 was added to 10 mL of aqueous sodium hydroxide (1.4 g, 0.035 mol), 2 drops of Aliquat 360, and a few milligrams of tetraethylammonium bromide and stirred at ca. 50 °C for 16 h. Workup as described for other phase-transfer reactions gave a brown oil. The ether was eluted from a short silica gel column by 400 mL of 10% CH_2Cl_2 in pentane following 800 mL of pentane. Recrystallization from methanol gave 2.8 g (52%) of colorless crystals: mp 102–103 °C. ^1H NMR (90 MHz, $CDCl_3$) δ 8.22 (d, 2 H, J = 9 Hz), 7.54 (d, 2 H, J = 9 Hz), 7.20 (m, 7 H), 6.89 (m, 3 H), 6.18 (s, 1 H). IR (KBr) 3040, 2900, 1590, 1488, 1345, 1227, 1030, 852, 750, 692 cm^{-1}. MS (positive ions), *m/e* 305, *211*, 166, 165, 154, 153, 152, 139, 127, 115, 94, 77. MS (negative ions), *m/e* 304, 273, 242, 227, 212, 196, 165, 164, 153, 137, 122, 109, *93*, 46. Exact mass calcd for $C_{19}H_{15}NO_3$ 305.1052, found 305.1045.

4-Nitrophenyl triphenylmethyl ether, 2d, and 3-nitrophenyl triphenylmethyl ether, 6, were prepared as described by Zimmerman[19] and had correct physical and spectral characteristics.

2,4,6-Trichlorophenyl Triphenylmethyl Ether, 4. This was prepared following the procedure described by Zimmerman[19] for other trityl ethers. It was obtained in 63% yield, mp 149–153 °C, and was unstable to moisture. ^1H NMR (90 MHz, $CDCl_3$) δ 7.80 (m, 6 H), 7.37 (m, 6 H), 7.11 (s, 2 H). IR (KBr) 3060, 3020, 1430, 1238, 1134, 902, 850, 778, 748, 700, 631 cm^{-1}. MS, *m/e 243* (M − $C_6H_2Cl_3O$), 200, 198, 196, 165.

Anal. Calcd for $C_{25}H_{17}Cl_3O$: C, 68.28; H, 3.90; Cl, 24.18. Found: C, 68.27; H, 3.90; Cl, 24.05.

(4-Nitrophenyl)diphenylmethyl Phenyl Ether, 1d. This was again prepared by the method of Zimmerman[19] and purified as described for **1b**, giving white crystals in 55% yield: mp 118–119 °C. ^1H NMR (90 MHz, $CDCl_3$) δ 8.09 (d, 2 H, J = 9 Hz), 7.62 (d, 2 H, J = 9 Hz), 7.28 (m, 10 H), 7.00–6.52 (m, 5 H). MS, *m/e* 381, *288*, 257, 242, 215, 180, 165, 94. IR (KBr) 3045, 3020, 1580, 1480, 1440, 1340, 1218, 1002, 989, 843, 742, 696 cm^{-1}.

Anal. Calcd for $C_{25}H_{19}O_3N$: C, 78.72; H, 5.02; N, 3.67. Found: C, 78.50; H, 5.26; N, 3.67.

Preparation of 1-Phenylethyl 4-Nitrophenyl Ether, 2c. Potassium hydride (604 mg, 14.7 mmol) was slurried in 10.0 mL of dry THF and 1-phenylethanol (9.2 mmol after correction for acetophenone contamination) added over 15 min at 25 °C. The reaction mixture was stirred at 25 °C for 15 min, cooled to 0 °C, and treated with 4-fluoronitrobenzene (1.42 g, 10.0 mmol) dropwise over 15 min. The mixture was treated with O_2 gas for several minutes and centrifuged. The THF solution was added to 100 mL of H_2O and 100 mL of 80:20 pentane/ether (v/v). The organic extracts were dried. Rotary evaporation for 15 min at 100 °C gave 1.39 g of material which showed mostly one peak by GC. The product (1.04 g) was eluted from 30 g silica gel in 300 mL of 10% CH_2Cl_2/pentane and recrystallized from hexane/CH_2Cl_2: mp 67–68 °C. ^1H NMR (90 MHz, CH_2Cl_2) δ 8.11 (d, 2 H, J = 9.5 Hz), 7.35 (s, 5 H), 6.92 (d, 2 H, J = 9.5 Hz), 5.40 (q, 1 H, J = 6.5 Hz), 1.69 (d, 3 H, J = 6.5 Hz).

Anal. Calcd for $C_{14}H_{13}O_3N$: C, 69.12; H, 5.39; N, 5.76. Found: C, 69.05; H, 5.27; N, 5.63.

1-(4-Nitrophenyl)ethyl trifluoroacetate was prepared following the procedure of Okamoto.[31]

Preparation of 1-(4-Nitrophenyl)ethyl Phenyl Ether, 1c. Sodium phenoxide, prepared from the reaction of phenol with sodium methoxide in methanol and dried at 155 °C for 3 h at 1 torr (1.15 g, 9.9 mmol) in 20 mL of dry (distilled from CaH) DMF, was treated with 1-(4-nitrophenyl)ethyl trifluoroacetate (1.72 g, 6.54 mmol) in 5 mL of DMF rapidly with stirring at ca. 25 °C. After 5 min the mixture was added to 100 mL of diethyl ether/100 mL of water. The ether layer was washed with 50 mL of water, 30 mL of 5% aqueous HCl, 30 mL of 10% aqueous NaOH, twice with 20 mL of saturated NaCl, and dried over Na_2SO_4. Evaporation gave 1.00 g of oil. A small amount of solid insoluble in 25% CH_2Cl_2/hexane was recrystallized from $CHCl_3$/ethanol and appeared to be *meso*-1,2-bis(4-nitrophenyl)butane: mp 258–259 °C [lit.[32] mp 256 °C]. MS, *m/e* 300, 190, *151*, 104. The soluble part was

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placed on a column of 15 g of silica gel, and 625 mg eluted in 160 mL of 10% CH_2Cl_2/hexane. **1c** was collected from GC and subjected to short-path distillation. ^1H NMR ($CDCl_3$) δ 8.20 (d, 2 H, J = 9 Hz), 7.56 (d, 2 H, J = 9 Hz), 6.7–7.3 (m, 5 H), 5.42 (q, 1 H, J = 6.5 Hz), 1.65 (d, 3 H, J = 6.5 Hz). MS, m/e 243, 150, *94*. Exact mass calcd for $C_{14}H_{13}O_3N$ 243.0895, found 243.0901. This compound was prepared previously,[31] but the general procedure given required modification as described above.

Phenol-d_5 and 4-nitrophenol-*2,6*-d_2 were prepared by heating the undeuterated compound for 3–4 days in a sealed tube at 120 °C with a excess of D_2SO_4 prepared by heating sulfuryl chloride with 2 equiv of D_2O. The phenol was ca. 38% d_5 and 35% d_4 with decreasing percentages of d_3–d_0. The nitrophenol was ca. 96% d_2.

Products of the Cleavage of 4-Nitrobenzyl Phenyl Ether Radical Anion, 1a$^{-}\cdot$, at High Concentrations in Dimethyl Sulfoxide. In a typical reaction, **1a** (114.5 mg, 0.5 mmol) was treated with 10 mL of 0.025 M TBNB$^{-}\cdot$ solution in Me_2SO at ca. 25 °C. The solution rapidly changed color from brown-red to orange to green. After 15 min of stirring, oxygen was bubbled through and the mixture poured into water (300 mL) and CH_2Cl_2 (200 mL). The organic layer was washed 3 times with water and dried and solvent removed to give 194 mg of orange solid which contained many components (NMR). Some of these were separated by silica gel chromatography and their amounts in the initial reaction mixture determined by GC vs. an added standard. TBNB was recovered (70 mg) along with 4-nitrotoluene (2%), 4-nitrobenzaldehyde (trace), **1a** (8%), 1,2-bis(4-nitrophenyl)ethane, DNE, (1%), 4,4-dinitrostilbene, and DNS, (16%). A new compound was also isolated (11 mg): mp 168–171 °C (methanol). ^1H NMR (90 MHz, $CDCl_3$) δ 8.20 (2d, 4 H, J = 9 Hz for both), 7.83 (d, 2 H, J = 9 Hz), 7.73 (d, 2 H, J = 9 Hz), 7.42–6.91 (m, 5 H), 6.80 (s, 1 H). MS, m/e 362, 333, 270, 239, 223, 212, 196, 176, 165, 150, *94*. Exact mass calcd for $C_{20}H_{14}N_2O_5$ 362.0903, found 362.0899. This compound was assigned the structure of 1-phenoxy-1,2-bis(4-nitrophenyl)ethylene (configuration not established). Phenol was identified by GC isolation from CH_2Cl_2 extracts of the acidified aqueous layer. Reactions followed by GC showed that recovery of **1a** dropped below 1% after 6 h. 4-Nitrotoluene yield is ca. 10% at this time but is gradually consumed.

Products of the Cleavage of 4-Nitrobenzyl Phenyl Ether Radical Anion, 1a$^{-}\cdot$, in THF. Treatment of **1a** (114.5 mg, 0.5 mmol) in 5.0 mL of THF with 10 mL of 0.05 M TBNB$^{-}\cdot$Li$^+$ in THF for 0.5 h at ca. 25 °C and workup as described for the Me_2SO reaction gave starting material (12.4%) and 1,2-bis(4-nitrophenyl)ethane, DNE (47% isolated yield) along with a small amount (20 mg) of unidentified, insoluble yellow solid.

Products of Cleavage of 4-Nitrobenzyl Phenyl Ether Radical Anions, 1a,e,f,g$^{-}\cdot$, at Low Concentration in Me_2SO. At concentrations where first-order kinetics were observed, [**1a**$^{-}\cdot$] $\leq 10^{-3}$ M, product isolation studies were prohibitive, but GC analysis of reaction products using flame ionization detection showed only 4-nitrotoluene. No significant amount of DNE or DNS was present. This was observed for runs 7 and 9 using compounds **1e** and **1f** and verified for a run comparable to runs 1 and 3 for **1a**$^{-}\cdot$. Similar results were obtained for **1g**$^{-}\cdot$.

ESR Study of the Cleavage of 1a$^{-}\cdot$. Mixing Me_2SO solutions of TBNB$^{-}\cdot$ and **1a** gave well-resolved spectra of **1a**$^{-}\cdot$ with hfsc's shown in Table I. At [**1a**$^{-}\cdot$] $\geq 10^{-2}$ M, the spectral changes were not very reproducible. In general, an initial slow decay of the spectral lines for **1a**$^{-}\cdot$ gradually accelerated, and its spectrum was replaced by the spectrum of 4-nitrobenzaldehyde radical anion (comparison with independently prepared solution; $a^N = 5.25$, $a_o{}^H = 2.93$, $a_{o'}{}^H = 2.23$, $a_m{}^H = 0.39$, $a_{m'}{}^H = 0.27$, $a_{O=C}{}^H = 1.31$ G) in 20–30 min. For solutions with 1×10^{-3} M < [**1a**$^{-}\cdot$] < 10^{-2} M, the spectrum of the 4-nitrotoluene radical anion was observed (comparison with independently prepared solution; $a^N = 10.23$, $a_o{}^H = 3.42$, $a_m{}^H = 1.10$, $a_{Bz}{}^H = 4.02$ G) along with that of **1a**$^{-}\cdot$, but both gave way to 4-nitrobenzaldehyde radical anion. When [**1a**$^{-}\cdot$] $\leq 10^{-3}$ M (see Table II), only the spectrum of [**1a**$^{-}\cdot$] was observed. This decayed following a first-order rate law and gave no detectable residual spectrum. (See Table II and Figure 1 for kinetic data.) It was not possible to observe the ESR spectrum of **1a**$^{-}\cdot$ in THF because decay was too rapid ($t_{1/2}$ < 120 s).

Reaction of 1a with Lithium Phenoxide. Compound **1a** (4 mg, 0.017 mmol) in 4.0 mL of Me_2SO was mixed with 2.0 mL of 0.73 M lithium phenoxide in Me_2SO (prepared from phenol and 1 equiv of MeLi in Me_2SO). A strong, easily identified spectrum of 4-nitrobenzaldehyde radical anion was observed after 70 min.

Products of the Cleavage of (4-Nitrophenyl)phenylmethyl Phenyl Ether Radical Anion, 1b$^{-}\cdot$. Compound **1b** (91.5 mg, 0.30 mmol) was treated with 6 mL of 0.025 M solution of TBNB$^{-}\cdot$ in Me_2SO. The red–violet reaction mixture was stirred for 6.5 min at ca. 25 °C and diluted with 200 mL of water. Workup with CH_2Cl_2 gave 142 mg of yellow solid. Addition of eicosane as a GC standard allowed analysis of the mixture as 4-nitrobenzophenone (0.147 mmol, 49%), **1b** (0.115 mmol, 38%), and (4-nitrophenyl)phenylmethane (0.030 mol, 10%). These were collected from GC, and their identity was confirmed by spectral comparison. IR analysis of the crude mixture of reaction products showed that 4-nitrobenzophenone was present prior to GC analysis. Phenol was extracted from the acidified aqueous extract in 36% yield.

If the initial ratio of TBNB$^{-}\cdot$ to **1b** was increased, the amount of 4-nitrobenzophenone produced decreased. A run in Me_2SO using a 2-fold excess of TBNB$^{-}\cdot$ produced a 75% yield of (4-nitrophenyl)-phenylmethane, 8% 4-nitrobenzophenone, and no detectable unreacted **1b** after 15 min.

For reactions in THF, quenching with $MeOH/H_2O$ in the absence of air gave only (4-nitrophenyl)phenylmethane. If instead O_2 was added, only 4-nitrobenzophenone was obtained.

Reaction of 1b with Lithium Phenoxide. The ether **1b** (15 mg, 0.05 mmol) in 0.5 mL of Me_2SO was stirred with lithium phenoxide (1.0 mL of 0.10 M) for 1.5 h at ca. 25 °C. Workup of the red–violet solution and GC analysis showed only **1b** and 4-nitrobenzophenone in a 3.5:1.0 ratio.

Cleavage of 1b$^{-}\cdot$ in the Presence of Lithium Phenoxide-d_5. Compound **1b** (61.0 mg, 0.20 mmol) in 1.0 mL of Me_2SO treated with lithium phenoxide-d_5 (1.0 mL of 0.81 M solution in Me_2SO) and TBNB$^{-}\cdot$ (2.0 mL of 0.083 M solution in Me_2SO) for 60 s at ca. 25 °C produced (4-dinitrophenyl)phenylmethane (0.36 mmol, 14%) and 4-nitrobenzophenone (0.36 mmol, 18%). Compound **1b**, recovered in 13% yield (26% by GC), contained no (<1%) deuterated phenoxy groups by negative ion mass spectrometry in the region m/e 93–98.

ESR Study of the Cleavage of 1b$^{-}\cdot$. Mixing Me_2SO solutions of TBNB$^{-}\cdot$ and **1b** gave **1b**$^{-}\cdot$ with hfsc's as shown in Table I. The signal decayed rapidly to noise level. No extra lines and no residual spectrum were observed. See Table IV and Figure 3 for kinetic data.

In THF, reaction of **1b** with TBNB$^{-}\cdot$Li$^+$ was very fast ($t_{1/2}$ max $\leq$ 60 s).

Products of the Decomposition of 4-Nitrophenyl Benzyl Ether Radical Anion, 2a$^{-}\cdot$. Compound **2a** (171.7 mg, 0.75 mmol) was sealed in an evacuated ampule with TBNB$^{-}\cdot$ (13 mL of 0.05 M solution in Me_2SO), kept in the dark at ca. 25 °C for 36 days, and worked up in CH_2Cl_2 (200 mL) and water (400 mL). After repeated water washing, the CH_2Cl_2 solution was dried and concentrated. GC analysis showed no detectable toluene. Complete evaporation gave 366 mg of a complex mixture (NMR) containing a small percentage of unreacted **2a**. GC analysis after standard addition showed only **2a** (9%) and TBNB. 1,2-Diphenylethane was specifically excluded (<1%). After extraction of TBNB with pentane, about 50% of the residue could be eluted from silica gel (up to 5% methanol in CH_2Cl_2). Of the eluted material, ca. 30% (15% yield) proved to be 4,4-bis(phenylmethoxy)azoxybenzene: mp 149–151 °C (methanol). ^1H NMR (200 MHz, $CDCl_3$) δ 8.26 (d, 2 H, J = 9 Hz), 8.23 (d, 2 H, J = 9 Hz), 7.40 (m, 10 H), 7.05 (d, 2 H, J = 9 Hz), 7.02 (d, 2 H, J = 9 Hz), 5.13 (s, 4 H). IR (KBr) 3020, 2910, 1592, 1498, 1455, 1381, 1248, 1155, 1026, 838, 732, 698 cm^{-1}. MS, m/e 410, 394, 381, 319, 303, 213, 199, 183, 108, *91*, 69, 65. Exact mass calcd for $C_{26}H_{22}N_2O_3$ 410.1630, found 410.1630. A small amount (7 mg) of an unidentified product, mp 164–168 °C, was also obtained. ^1H NMR (200 MHz, $CDCl_3$) δ 8.01 (s, 1 H), 7.60 (d, 2 H, J = 9 Hz), 7.50 (s, 1 H), 7.25 (m, 10 H), 7.02 (d, 2 H, J = 9 Hz), 6.90 (s, 1 H), 4.96 and 4.94 (overlapping s, 4 H), 1.41 (s, 6 H). MS, m/e 482.207, 406.171, 391, *315*, 243, 218, 196, 165, 150. Extraction of the acidified aqueous layer with CH_2Cl_2 gave 11 mg of brown oil which contained less than 2% of 4-nitrophenol (NMR and GC).

Treatment of **2a** (400 mg, 1.75 mmol in 4 mL THF) with TBNB$^{-}\cdot$ (4.0 mL of 0.44 M solution in THF) for 18 days in the dark at ca. 25 °C and workup as described above gave **2a** (76%) and 4,4-bis(phenylmethoxy)azoxybenzene (5%) along with small amounts of highly colored mixtures. No bibenzyl (<1%), toluene (<3%), or 4-nitrophenol (<2%) was detected.

ESR Study of the Cleavage of 2a$^{-}\cdot$. Mixing of Me_2SO solutions of **2a** and TBNB$^{-}\cdot$ gave easily identified solutions of **2a**$^{-}\cdot$. See Table I. With **2a** signal decay followed a second-order rate law (Table III and Figure 2). Reaction mixtures sealed in ampules under argon gave spectra of **2a**$^{-}\cdot$ which persisted for months although an interfering spectrum of the radical anion of 4-nitrobenzophenone eventually appeared in run 14. In THF, the ESR spectrum was not sufficiently well-resolved to allow unequivocal assignment to **2a**$^{-}\cdot$, however, with a 2-fold ratio of **2a** to TBNB$^{-}\cdot$, the intensity loss did follow a second-order rate law with $k = 5.2 \times 10^{-2}$ M^{-1} s^{-1} (r = 0.993, 12 points) and a maximum first-order component of 3×10^{-6} s^{-1}.

Decomposition of 2a$^{-}\cdot$ in the Presence of Lithium 4-Nitrophenoxide-*2,6*-d_2. Compound **2a** (22.9 mg, 0.10 mmol) was treated with lithium

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4-nitrophenoxide-*2,6-d*$_2$ (3 mL of 0.067 M solution in Me_2SO), $TBNB^{-}\cdot$ (2 mL of 0.025 M solution in Me_2SO), and 5.0 mL of Me_2SO. After 35 h at 22 °C, the spectral intensity of **2a**$^{-}\cdot$ had decreased by a factor of 5. The reaction mixture was then exposed to air and saturated with O_2. Recovered **2a** (65%) had <2% deuterium content (MS).

Attempted Identification of the Products from Cleavage of 1-(4-Nitrophenyl)ethyl Phenyl Ether, 1c$^{-}\cdot$, in Me_2SO. Compound **1c** (70.0 mg, 0.287 mmol), *n*-tetracosane (29.5 mg as internal standard), 6.0 mL of Me_2SO, and 4.0 mL of a 0.074 M solution of $TBNB^{-}\cdot Li^{+}$ in Me_2SO were mixed and allowed to stand at 24 °C for 5.6 h. A workup similar to those above showed only TBNB and tetracosane (GC) and <5% **1c**. Workup controls proved that neither 4-ethylnitrobenzene nor 2,3-bis(4-nitrophenyl)butane was present in the reaction mixture. Less volatile aromatic compounds were present (NMR) but were not identified.

ESR Study of the Decomposition of 4-Nitrophenyl Benzyl Thioether, 2g, in Me_2SO. Compound **2g** (7.0 mL of 2.8×10^{-2} M solution in Me_2SO) was treated with $TBNB^{-}\cdot$ (0.040 mL of 2.0×10^{-2} M solution in Me_2SO). A well-resolved ESR spectrum of **2g**$^{-}\cdot$ was observed (see Table I). After an initial period in which the intensity change followed neither first- nor second-order kinetics (ca. 0.5 h), the adherence to a second-order rate law was reasonably good for 2 h. After this time period, the signal remained essentially constant for 6 days.

Products of the Decomposition of 4-Nitrophenyl Diphenylmethyl Ether Radical Anion, 2b$^{-}\cdot$. Compound **2b** (305 mg, 1.00 mmol) was stirred with 20 mL of 0.029 M $TBNB^{-}\cdot$ solution in Me_2SO for 14.3 h at ca. 25 °C and the solution saturated with O_2. The Me_2SO solution was extracted with pentane (100 mL) and the pentane layer washed with water (100 mL), dried, and evaporated to give 228 mg of white solid (mainly TBNB and diphenylmethane). The water layers were extracted with CH_2Cl_2. This gave mainly (4-nitrophenyl)diphenylmethanol, **3**. Acidification and reextraction of the water layer gave more **3** along with 4-nitrophenol. Combined yields by GC analysis vs. $C_{24}H_{50}$ were **2b** (2%), diphenylmethane (18%), 1,1,2,2-tetraphenylethane (12%), **3** (58%), 4-nitrophenol (11%), diphenylmethanol (4%), and TBNB (100%). All components were isolated and identified by comparison with authentic samples. GC analyses of reaction mixtures similar to kinetic runs are listed in Table V.

Decomposition of 2b$^{-}\cdot$ in the Presence of Lithium 4-Nitrophenoxide-*2,6-d*$_2$. Compound **2b** (61.0 mg, 0.20 mmol) was treated with $TBNB^{-}\cdot$ (2.0 mL of 0.19 M in Me_2SO) and $LiOC_6H_2D_2NO_2$ (2.0 mL of 1.9 M in Me_2SO). After 0.5 h at ca. 25 °C, the reaction was worked up in water–CH_2Cl_2. The product yields were determined by GC vs. added standard. They were diphenylmethane (26%), 1,1,2,2-tetraphenylethane (11%), **3** (37%), and **2b** (24%). Mass spectral and NMR analyses of recovered **2b** showed no incorporation of deuterated phenoxide (<2%).

ESR Study of the Decomposition of 2b$^{-}\cdot$. **2b** and $TBNB^{-}\cdot$ in Me_2SO gave **2b**$^{-}\cdot$. See Table I. The decay of the signal intensity for **2b**$^{-}\cdot$ followed a second-order rate law and was eventually replaced by the spectrum of the radical anion of (4-nitrophenyl)diphenylmethylcarbinol, **3**$^{-}\cdot$, $a^{N} = 9.9$, $a_{o}^{H} = 3.30$, and $a_{m}^{H} = 1.04$ G (assignment verified by separate preparation).

In THF, the ESR spectrum was not sufficiently well resolved to be assigned unambiguously to **2b**$^{-}\cdot$ but decayed very slowly following a second-order rate law. Workup in the usual way after 40 h at ca. 25 °C gave mainly **2b** with some diphenylmethane and 1,1,2,2-tetraphenylethane. No **3** (<1%) was detected.

ESR Study of the Reaction of 2b with Dimsyllithium in the Presence of Diphenylmethane. Diphenylmethane (25.1 mg, 0.149 mmol) in 5.0 mL of Me_2SO was treated with 0.10 mL of 1.5 N MeLi in diethyl ether. After 4 h at ca. 25 °C, this was mixed with **2b** (0.149 mmol in 3.0 mL of Me_2SO). The spectrum of **2b**$^{-}\cdot$ appeared immediately but disappeared within 0.5 h and was replaced by the spectrum **3**$^{-}\cdot$. GC showed 1,1,2,2-tetraphenylethane, **3**, benzhydrol, **2b**, and diphenylmethane.

ESR Study of the Cleavage of 4-Nitrophenyl 1-Phenylethyl Ether Radical Anion, 2c$^{-}\cdot$. Potassium (60.2 mg, 1.54 mmol) was cut under hexane, placed in a small tube, blown dry with argon gas, and melted. This was treated with TBNB (290.3 mg, 1.04 mmol) in 1.50 mL of THF and the THF solution warmed to reflux for ca. 1 min. The red solution was separated from unreacted potassium and 0.10 mL added to 2.0 mL of Me_2SO and **2c** (9.1 mg, 0.037 mmol). Only the spectrum of **2c**$^{-}\cdot$ was visible (see Table I). The intensity decayed rather rapidly at first but slowed down by an amount greater than predicted by a second-order rate law. After 24 h the spectral intensity was essentially constant, showing at most a 20% decrease in intensity in 1.7×10^{6} s.

ESR Study of the Cleavage of 1-(4-Nitrophenyl)ethyl Phenyl Ether Radical Anion, 1c$^{-}\cdot$. The radical anion was prepared in the manner described for the potassium salt of **2c**$^{-}\cdot$ or by treating a THF solution of TBNB with methyllithium, evaporating most of the THF, and diluting with Me_2SO. A portion was added to a solution of **1c** in Me_2SO to give **1c**$^{-}\cdot$ (see Table I). Measurement of peak intensities was complicated by the unresolved splitting from the methyl group. Computer-generated partial spectra based on Lorentzian line shapes were used to model the relationship between line width and peak-to-peak intensities of selected spectral regions. The desired (peak-to-peak width)^2(peak-to-peak intensity) of the individual lines were then assumed proportional to concentration. This was done for several peaks in each run. The first-order rate constants calculated by using different peaks varied at most by 15%.

Reaction of Fluoradenide Ion with 4-Nitrophenyl Triphenylmethyl Ether, 2d. Fluoradene[33] (80 mg, 0.333 mmol) and **2d** (63.5 mg, 0.167 mmol) were dissolved in 20.0 mL of 0.035 N potassium *tert*-butoxide in *tert*-butyl alcohol by adding THF (3.0 mL) to improve solubility. The pink reaction mixture was stirred at 25 °C for 2.5 h and opened to air and the precipitate separated, giving 85.6 mg of white solid. Washing with ether gave 67.4 mg (84%) of bifluoradene identified through IR spectral comparison, mp 298–302 °C [lit.[33] mp 303–305 °C]; evaporation of an ether wash gave 17.4 mg (42%) of $\alpha,\alpha,\alpha,\alpha',\alpha'$-pentaphenyl-*p*-xylene identified by melting point, 232–236 °C [lit.[34] mp 233–234 °C], IR, NMR, and MS comparison with authentic material.

The filtrate was added to 200 mL of water and extracted with 150 mL of CH_2Cl_2. Evaporation of the dried solvent gave 37.5 mg of oily solid. The ether soluble yellow solid (30.5 mg, 35%) was identified as bis(triphenylmethyl)peroxide by melting point, mp 189–191 °C [lit.[35] mp 185–186 °C], and spectral properties.

The water layer was acidified with HCl. Extraction with CH_2Cl_2 gave 27.2 mg of oily solid shown by NMR and GC to be mostly 4-nitrophenol (estimated 75% recovery).

With 1 equiv of fluoradene, the pink color disappeared in ca. 30 min. The same products described above were obtained.

Solutions of fluoradene (0.0122 M) and **2d** (0.0094 M) in a 1:1 (v:v) mixture of THF/*tert*-butyl alcohol were mixed in an ESR cell with enough potassium *tert*-butoxide to make the final base concentration 0.028 M. A strong and persistent spectrum of triphenylmethyl radical was observed. No spectrum of **2d**$^{-}\cdot$ could be detected.

Reaction of 2,4,6-Trichlorophenyl Triphenylmethyl Ether, 4, with Fluoradenyl Anion. Fluoradene (12.3 mg, 0.051 mmol) and **4** (12.3 mg, 0.028 mmol) were treated with 3.0 mL of *tert*-butyl alcohol, 1.0 mL of THF, and 0.50 mL of a 0.78 N solution of potassium *tert*-butoxide in *tert*-butyl alcohol. The characteristic signal of the triphenylmethyl radical was observed immediately. A scaled-up run gave bifluoradene, $\alpha,\alpha,\alpha,\alpha',\alpha'$-pentaphenyl-*p*-xylene and 2,4,6-trichlorophenol (80% recovery) after 5.3 h.

Attempted Reaction of 2,4,6-Trichlorophenyl Diphenylmethyl Ether, 5, with Fluoradenyl Anion. Fluoradene (24.8 mg, 0.099 mmol) and **5** (71.8 mg, 0.198 mmol) were dissolved in 4.0 mL of 3/1, v/v, *tert*-butyl alcohol/THF. Potassium *tert*-butoxide (0.5 mL of 0.73 N) was added. No ESR signal could be detected within 5 h. After 24 h the solution was still deep red and no precipitate was observed. Fluoradene and **5** were present in 86% and 91% yields, respectively (NMR vs. added 4-methoxybenzophenone).

Reaction of Fluoradenyl Anion with 3-Nitrophenyl Triphenylmethyl Ether, 6. Fluoradene (22.8 mg, 0.095 mmol) and **6** (38.5 mg, 0.101 mmol) were dissolved in a 3/1, v/v, mixture of *tert*-butyl alcohol and THF which was 0.088 M in potassium *tert*-butoxide. The spectrum of **6**$^{-}\cdot$ was observed immediately ($a^{N} = 12.5$, $a_{o}^{H} = a_{p}^{H} = 3.3$, $a_{m}^{H} = 1.12$ G). The intensity of the spectrum increased slowly for the first 30 min after mixing. Irradiation with a medium-pressure Hanovia lamp (cutoff 350 nm) for 15 min gave the spectrum of triphenylmethyl radical, which decayed rapidly.

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