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Reaction of Benzyl and Naphthylmethyl Esters with Arene Radical Anions

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The reactions of four esters, naphth-1-ylmethyl acetate, naphth-1-ylmethyl benzoate, benzyl acetate, and benzyl benzoate, with the salts of radical anions of fluoranthene and biphenyl have been studied. When ester radical anion formation is energetically possible, CH_2–O bond cleavage follows rapidly. The resultant $ArCH_2$ radical is reduced under the reaction conditions. The $ArCH_2$ anion thus produced can react with the ester both as a nucleophile and as a base to promote a variety of side reactions. In most cases, these processes compete with the initial reduction and cleavage.

Our interest in the cleavage of radical anions had previously led us to study the reactions of ethers having the structure $ArCH_2OAr'$ (either Ar or Ar′ = naphthyl) with the radical anion salts of fluoranthene and biphenyl ($FL^{-\bullet}$ and $BP^{-\bullet}$) to produce $ArCH_3$ and $ArCH_2CH_2Ar$.[1] Even with the less potent of these two one-electron donors, $FL^{-\bullet}$, electron transfer to the naphthyl moiety was viable and this was followed by CH_2–O bond scission. We anticipated a similar sequence for the related esters, $ArCH_2O(C{=}O)R$. RCO_2^- was expected to be a better leaving group than $Ar'O^-$, allowing us to use the ester cleavage to test some hypotheses from our earlier work.[2] As it turned out, the unexpected diversity of the reaction products obtained from the reaction of the esters **1a–d** with $FL^{-\bullet}$ and $BP^{-\bullet}$ and the associated mechanistic uncertainty have temporarily redirected our effort toward a simple attempt to rationalize the observed reaction outcomes.

The reaction of esters with arene radical anions appears not to have been studied extensively, although there is a wealth of literature describing reactions with alkali metals. In hydroxylic solvents, aliphatic esters are generally reduced via the Bouveault–Blanc reaction[3] to alcohols having the same number of carbon atoms. In benzene or ether the outcome is more likely to be acyloin condensation[4] and this is also favored in ammonia.[5] An acyloin-type sequence has been observed when alkyl benzoates react with lithium and a catalytic amount of 4,4′-di-*tert*-butylbiphenyl.[6] The reaction involves the radical anion of the substituted biphenyl as an electron-transfer agent and initially formed product is converted to bibenzyl, an outcome not observed with other alkali metals. The acyloin condensation has been extensively utilized for the synthesis of ring compounds.[7] It is generally agreed that all of these reactions proceed via the radical anions of the esters.[8] In addition to the foregoing transformations in which the alkyl–oxygen bond remains intact, there are also reports of one-electron reductions in which it is broken. This was true for electrochemical reduction of a series of 4-carbomethoxybenzyl esters[9] and for photochemical generation of certain radical anions which cleaved to nonbenzylic radicals.[10,11] Even for dissolving metal reductions of certain completely aliphatic esters, yields of up to 90% of alkyl–oxygen bond cleavage products have been observed using K/Na alloy in THF with *tert*-butylamine and crown ether.[12] Masnovi[13] has compared the products from radical anions of benzyl benzoate produced in ethanol by radiolysis to products from alkali metal reduction in the same solvent. The radiolysis-generated intermediate gives exclusively alkyl–oxygen scission, whereas the chemically-generated species, if formed under these conditions, reacts by other paths.

Results and Discussion

Cleavage by One-Electron Donors in THF. Arylmethyl acetates and benzoates were treated with solutions of radical anion salts in tetrahydrofuran (THF). The observed products are generalized in Scheme I and the mole percentages of these products are given in Table I. With the exception of benzoate and acetate salts which were not isolated, the entries in Table I are believed to include all of the significant reaction products as observable by NMR and GC analysis of the reaction mixtures.

The most readily interpretable data are those for **1b** and **1c**. Particularly when treated with $BP^{-\bullet}$, it is clear that reductive cleavage has occurred. Toluene is a major product (runs 14, 15, 16, 19, and 20) but arylmethyl phenyl ketones **4b** and **4c** are also observed. The amount of alcohol **5** produced approximately matches the amount of ketone. These results are explained by the simple mechanistic interpretation of eqs 1–4. In the case of ethers, $ArCH_2^\bullet$ was reduced by $FL^{-\bullet}$ to give $ArCH_2^-$ which led to

$$1 + FL^{-\bullet} \text{ or } BP^{-\bullet} \rightarrow 1^{-\bullet} \qquad (1)$$

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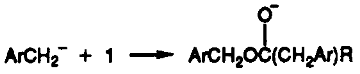
$$1^{-\bullet} \rightarrow ArCH_2^{\bullet} + RCO_2^{-} \qquad (2)$$

$$ArCH_2^{\bullet} + FL^{-\bullet} \text{ or } BP^{-\bullet} \rightarrow ArCH_2^{-} \qquad (3)$$

$$ArCH_2^{-} + HR' \rightarrow \mathbf{2} + R'^{-} \qquad (4)$$

$ArCH_3$. Although the agent involved in protonation of $ArCH_2^-$ (HR) was uncertain in those cases, the fact that equimolar amounts of ether and $FL^{-\bullet}$ gave only a 50% yield of $ArCH_3$ and left 50% of starting ether unreacted strongly supported this sequence. The reduction potential of benzyl radical has been measured by Wayner and Griller to be −1.78 V vs $Ag/AgNO_3$ (−1.45 V vs SCE)[14] which would, indeed, demand that $ArCH_2^{\bullet}$ be reduced to $ArCH_2^-$ when it is formed in the presence of any of the radical anions involved in either the present study of esters or the former study of ethers.

The logical pathway for the formation of **4** is shown in eq 5. An alternative path would involve coupling between



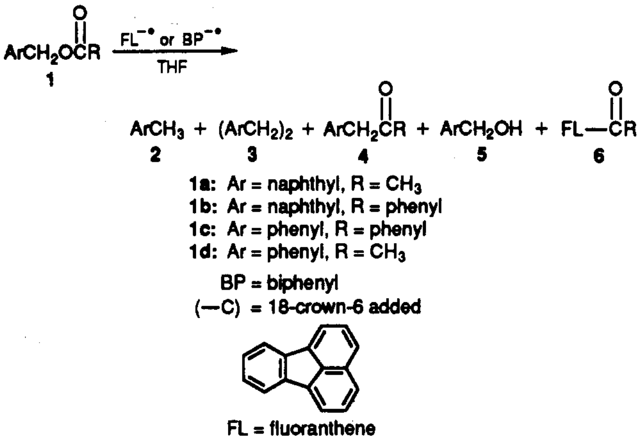
$$ArCH_2^- + \mathbf{1} \longrightarrow ArCH_2O\overset{O^-}{\overset{|}{C}}(CH_2Ar)R \qquad (5)$$

4

the ester radical anion and the benzyl radical. However, the latter seems untenable if it is considered that the radical anions of the esters **1a–d** are more powerful reducing agents than $FL^{-\bullet}$ which itself is capable of reducing $ArCH_2^{\bullet}$. (The reduction potential of fluoranthene is −1.78 vs SCE in DMF.[15]) The reduction potential of these esters is not known, but $E_{1/2}$ for acetophenone is −1.99 V vs SCE[16] and the reduction potentials of esters **1a–d** are certain to be more negative.

In all runs for **1b** and **1c**, it would appear that some of the benzylic anion produced in eq 3 reacts to give ketone **4** via eq 5. Once formed, deprotonation of either ketone **4b** or **4c** by subsequently formed benzylic anion would be an energetically favored outcome. If it is assumed that benzylic anion produced by the sequence of eqs 1–3 deprotonates **4** faster than it adds to the ester, the product distribution in the $BP^{-\bullet}$ runs is nicely accommodated. One equivalent of benzylic anion produces ketone and each newly-produced equivalent of ketone protonates a second benzylic anion. The enolate ion produced in the latter process is presumably unreactive. In run 20, the amount of toluene exceeds that of **4**, possibly indicating that some other proton source competes for the benzylic anion. For runs 14–16, the amount of methylnaphthalene is roughly twice that of ketone, possibly because of a somewhat faster reaction sequence for **1b** as discussed later. It will be noted that in all of the reactions of **1b** and **1c** with $BP^{-\bullet}$ small amounts of dimer **3** were detected, substantiating the involvement of benzylic radicals as intermediates in the formation of benzylic anions. The yield of dimer was somewhat unreproducible and this is believed to be related to mixing efficiency. Electron transfer from $BP^{-\bullet}$ to ester is energetically favorable and, therefore, very fast. Dimer formation is believed to be the fate of benzylic radicals formed in a $BP^{-\bullet}$ depleted zone. This phenomenon was not investigated in detail.

Scheme I



1a: Ar = naphthyl, R = CH_3
1b: Ar = naphthyl, R = phenyl
1c: Ar = phenyl, R = phenyl
1d: Ar = phenyl, R = CH_3
BP = biphenyl
(—C) = 18-crown-6 added
FL = fluoranthene

For the reaction of **1b** and **1c** with $FL^{-\bullet}$, runs 11–13 and 17–18, it will be noted that the amount of ketone is smaller than that for the $BP^{-\bullet}$ runs and that there is usually somewhat more **5** than **4**. Again this is particularly evident in the crown ether reactions. In run 17 an additional product, **6**, was detected. This could be produced either from benzoylation of FL^{2-} or by coupling of $\mathbf{1c}^{-\bullet}$ with $FL^{-\bullet}$. Such processes account for some of the excess **5** which would be a necessary byproduct.

In the case of the reaction of **1a** and **1d** with $BP^{-\bullet}$ and $FL^{-\bullet}$, the ester itself presents a viable proton source to the benzylic anion. Interestingly, products from ester deprotonation do not appear to be very significant in the $BP^{-\bullet}$-promoted reactions of **1a**, runs 9 and 10, which give the highest yields of reductive cleavage products. The yield of **4** is also reduced. It is clearly predictable and demonstrated below that $\mathbf{1a}^{-\bullet}$ should dissociate more rapidly than either $\mathbf{1b}^{-\bullet}$ or $\mathbf{1c}^{-\bullet}$ and thus, in the case where the reducing reagent is $BP^{-\bullet}$, the sequence of eqs 1 and 2 apparently consumes the ester so rapidly that the reaction of ester with benzylic anion does not compete. When $BP\text{–}C^{-\bullet}$ is used, run 10, the dimer **3** becomes the major product. This was observed for $BP^{-\bullet}$, itself in reacting with $ArCH_2OAr$ ethers and was interpreted in terms of a drop of $BP^{-\bullet}$ solution reacting so rapidly as to develop locally high concentrations of radicals which then dimerized. The same seems a likely explanation for run 10.

Proton removal from the acetyl methyl group becomes a viable option in the case of **1d** where reductive cleavage by $FL^{-\bullet}$ is small to undetectable (runs 22–24). The absence of reductive cleavage is the reasonable consequence of an anticipated highly negative reduction potential for **1d** which lacks both naphthyl and benzoyl moieties. With $\mathbf{1d}^{-\bullet}$ inaccessible, the reaction produces only base-promoted Claisen condensation products **7d** and **5** in equal amounts. This requires that there be an alternate path though which $FL^{-\bullet}$ can generate a basic/nucleophilic species when $ArCH_2^-$ formation is slow. The stoichiometry of this process seems likely to require 2 equiv of $FL^{-\bullet}$ to produce one base/nucleophile as expected for disproportionation to the fluoranthene dianion FL^{2-}. Surprisingly, if the reaction temperature is lowered to −55 °C as in runs 5 and 6, even **1a** avoids reductive cleavage by $FL^{-\bullet}$ both in the presence and absence of crown ether. Apparently under these circumstances, the formation and cleavage of $\mathbf{1a}^{-\bullet}$ are slowed relative to the disproportionation to and protonation of FL^{2-}. This explanation seems reasonable in view of the fact that the second reduction potential of fluoranthene is less negative than the first reduction

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Table I. Products of Reactions of Ester 1a–d with One-Electron Donors in THF at 25 °C

		mol %					
run no.	**1**, [**1**]; D, [$D^{-\bullet}$], M × 10^{-2}	**1**	**2**	**3**	**4**	**5**	note
1	**1a**, 9.8; FL, 12	3 ± 1	35 ± 2	<0.2	12 ± 2	38 ± 2	*a*
2	**1a**, 5.5; FL, 14	<0.2	52 ± 2	<0.2	8 ± 2	40 ± 2	
3	**1a**, 4.6; FL-C, 8.3	<0.2	51 ± 3	~0.5	<0.02	34 ± 2	*b*
4	**1a**, 7.5; FL-C, 8.2	<0.2	43 ± 3	<0.1	<0.01	37 ± 2	*b*
5	**1a**, 5.1; FL-C, 7.9	21 ± 2	~0.5	~1	<0.01	61 ± 4	*b, c*
6	**1a**, 6.3; FL, 12.8	64 ± 2	2 ± 1	<0.2	<0.1	32 ± 2	*b, c*
7	**1a**, 12.6; FL, 12.9	24 ± 2	24 ± 2	<0.2	9 ± 1	32 ± 2	*a*
8	**1a**, 8.1; FL, 122	<0.2	48 ± 2	<0.2	15 ± 2	33 ± 2	*a*
9	**1a**, 7.4; BP, 14.5	<0.2	77 ± 2	<0.2	4 ± 1	18 ± 2	*d*
10	**1a**, 6.1; BP-C, 26	<0.2	24 ± 2	30 ± 2	<0.01	16 ± 2	*d*
11	**1b**, 7.5; FL, 7.5	24 ± 2	23 ± 2	4 ± 2	20 ± 2	25 ± 3	
12	**1b**, 6.3; FL-C, 11.7	2 ± 1	52 ± 4	~0.1	14 ± 1	31 ± 4	
13	**1b**, 5.1; FL-C, 10.4	2 ± 1	54 ± 4	~0.1	12 ± 2	32 ± 4	
14	**1b**, 5.1; BP, 6.7	2 ± 1	53 ± 4	~0.1	23 ± 2	23 ± 2	
15	**1b**, 5.9; BP, 11.7	<0.2	55 ± 4	4 ± 2	18 ± 2	19 ± 2	
16	**1b**, 6.0; BP-C, 12.0	<0.2	50 ± 30	15 ± 15	8 ± 2	13 ± 2	*e*
17	**1c**, 9.3; FL, 19	23 ± 2	21 ± 1	<0.2	18 ± 2	38 ± 3	*f*
18	**1c**, 5.9; FL-C, 7.5	24 ± 2	41 ± 4	<0.2	11 ± 2	24 ± 3	*f*
19	**1c**, 9.3; BP, 19	2 ± 1	32 ± 3	2 ± 1	31 ± 3	31 ± 3	
20	**1c**, 9.8; BP-C, 20	<1	41 ± 5	2.5 ± 1	27 ± 2	27 ± 2	
21	**1d**, 21.1; FL, 22.5	3 ± 1	<0.2	<0.2	<0.2	51 ± 2	*g*
22	**1d**, 16.5; FL, 16.4	15 ± 2	<0.2	<0.2	<0.2	40 ± 2	*g*
23	**1d**, 10.2; FL, 20.4	<0.2	<0.2	<0.2	<0.2	50 ± 3	*g*
24	**1d**, 12.1; FL-C, 11.7	63 ± 4	2 ± 1	<0.2	<0.2	23 ± 4	*g*
25	**1d**, 8.9; BP, 17.7	32 ± 3	31 ± 3	<0.2	<0.2	37 ± 3	
26	**1d**, 6.3; BP-C, 12.6	9 ± 2	55 ± 3	<0.2	<0.2	27 ± 3	*g*

[a] Amounts of naphthylmethyl acetoacetate (NMA) ranging from 2 to 14 mol % were observed in these runs. [b] NMA amounts from 15 to 19% were observed, except for run 6 where the amount was 2%. [c] Reaction was run at −55 °C. [d] No NMA (<0.2%) was observed in these runs. [e] Difficulty was encountered in obtaining consistent ratios of **2** and **3** under these conditions. Differences in mixing procedures are suspected. The yields of **4** and **5** were fairly consistent however. [f] 5 ± 2% and 16 ± 3% of **6** was found in runs 16 and 17, respectively. No measurable amount of **6** (<1%) could be detected in run 18. [g] Benzyl acetoacetate (BA) was found to be 46 ± 4% in runs 21–23 and 11 ± 3% in runs 24 and 26.

potential of naphthalene.[17] Thus there should be a higher concentration of FL^{2-} than of $\mathbf{1a}^{-\bullet}$. The fact that $FL^{-\bullet}$ solutions in THF are stable for time periods much longer than those for the reaction of this study would seem to rule out involvement of solvent and suggests that FL^{2-} is directly responsible for destruction of part of the starting ester, possibly by several different routes. While Claisen condensation is dominant for **1d**, this does not account for all of the **5** formed from **1a**. In runs 1–4 and 7, one-half to one-third of the **5** formed is not matched by a product containing the acyl moiety and for run 6 which was carried out at −55 °C, most of the ester conversion to **5** is unexplained. Because for the reaction of **1c** (run 17) benzoylated fluoranthene, **6**, was identified, it seem possible that acylated fluoranthene could be formed from **1a**; however this was not detected.

A curious change in product distribution occurs for **1a** when crown ether is included in that the ketone **4** is no longer obtained, even in trace amounts (runs 3–5). While crown ether does slightly reduce the yield of **4** in the reactions of **1b** and **1c** (runs 12, 13, and 18), it does not exhibit the dramatic effect of completely eliminating **4** for reactions involving these substrates.

Apparently, the benzylic anion when present as an ion pair with K^+ functions both as a nucleophile to give the tetrahedral intermediate of eq 5 and as a base (eq 4) which, when HR′ = **1a** or **1d**, leads to Claisen condensation products. When crown ether complexes the potassium ion or when the reaction is carried out at low temperature, conditions known to discourage ion pairing in THF both for carbanions[18] and radical anions,[19] only the base-promoted process occurs and formation of **4** is eliminated. For reactions of **1b** and **1c**, the base-promoted reaction of the ester itself is not possible and therefore **4** is formed both with and without crown ether. The somewhat reduced yields of **4** from these substrates in the presence of crown ether could reflect a less competitive rate for eq 5 relative to formation of enolate from **4** when ion pairing is reduced.

Cleavage in Pulse Radiolysis. Masnovi[13] has measured cleavage rate constants for a number of ester radical anions, including $\mathbf{1c}^{-\bullet}$ and $\mathbf{1d}^{-\bullet}$, by pulse radiolysis. His reported rate constant were $4.8 \times 10^4\ s^{-1}$ for $\mathbf{1c}^{-\bullet}$ and $1.4 \times 10^6\ s^{-1}$ for $\mathbf{1d}^{-\bullet}$ in ethanol at 22 °C. Product studies showed **3** and **2** along with the products from coupling of benzyl radicals with solvent-derived intermediates. Under conditions where we were able to duplicate Masnovi's rate constant for $\mathbf{1c}^{-\bullet}$ (ethanol), we observed $5.6 \times 10^5\ s^{-1}$ as the first-order rate constant for dissociation of $\mathbf{1b}^{-\bullet}$. The spectrum of this transient is displayed in Figure 1. The absorbance in the 450-nm region is the same as observed by Masnovi for several benzoate esters and the decay of this absorbance was used to determine the rate constant. Masnovi also observed absorbance for benzoate ester radical anions (e.g., ethyl benzoate) at 310 nm and Figure 1 shows a transient absorbance in this region for $\mathbf{1b}^{-\bullet}$. At times of >5 μs after the pulse, the spectrum of $\mathbf{1b}^{-\bullet}$ has decayed, leaving the known spectrum of 1-naphthylmethyl radical (maxima at 340 and 365 nm),[20] which then fades in typical slow, second-order fashion.

We also attempted to study the decay of $\mathbf{1a}^{-\bullet}$ by pulse radiolysis in ethanol but could find no evidence for any

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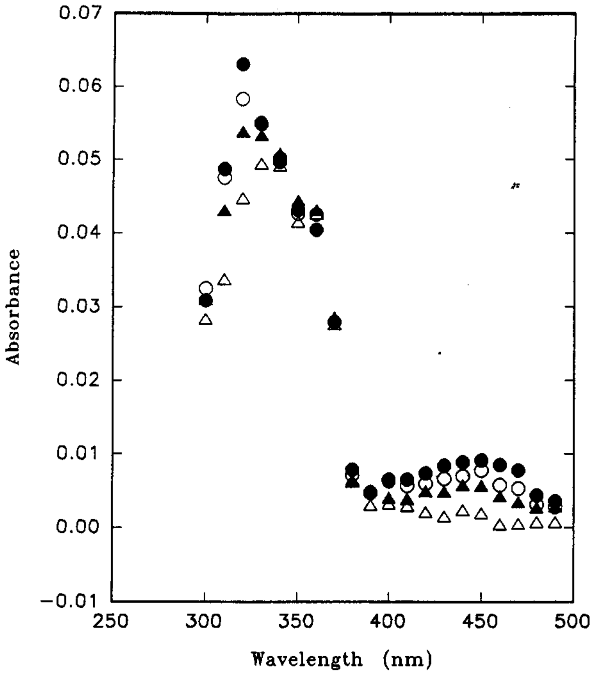

Figure 1. Pulse radiolysis of **1b** in ethanol: (●) 0.2 μs; (○) 0.65 μs; (▲) 1.35 μs; (△) 5.22 μs.

transient other than the naphthylmethyl radical. The absorption for this transient was, within the limits of our measurement parameters, fully established within the pulse. We could thus be certain that the rate constant for dissociation of **1a**$^{-\bullet}$ was greater than 5×10^6 s^{-1}.

Pulse radiolysis measurements in ethanol are not necessarily legitimate references for estimating cleavage rate constants for the radical anions of these esters in THF. In addition to the solvent difference, the radiolysis experiment probably generates free ions, whereas our THF solution intermediates are almost certainly ion pairs. Nevertheless, it seems likely that the order of cleavage rates observed in the radiolysis experiments, **1a**$^{-\bullet}$ > **1d**$^{-\bullet}$ > **1b**$^{-\bullet}$ > **1b**$^{-\bullet}$, is maintained. This information demonstrates that if the equilibrium amount of **1d**$^{-\bullet}$ formed in our reactions was comparable to that of **1b**$^{-\bullet}$ or **1c**$^{-\bullet}$, it would almost certainly undergo cleavage. It seems likely that the unreactivity of **1d** with FL$^{-\bullet}$ reflects the fact that neither the phenyl ring nor the acetyl group is a sufficiently accessible electrophore with this reductant. Probably when **1a** reacts with FL$^{-\bullet}$, it is the naphthyl group which houses the electron whereas with **1b** it is the benzoyl moiety. This interpretation is supported by the fact that naphthylmethyl phenyl ethers react readily with FL$^{-\bullet}$.[1] The high yield of reductive cleavage products obtained with **1a** and BP$^{-\bullet}$ is very likely a result of the rapid cleavage of **1a**$^{-\bullet}$ being coupled to the energetically favored electron transfer from BP$^{-\bullet}$ to **1a**. In this case, product formation is so fast that the various possible proton-transfer reactions cannot compete significantly.

Although both radical anions **1a**$^{-\bullet}$ and **1d**$^{-\bullet}$ dissociate very rapidly, it would appear that **1a**$^{-\bullet}$ is the faster. In addition to the fact that its dissociation rate is outside of the range of pulse-radiolysis measurement, previous indirect estimates of the rate constants for dissociation of radical anions of naphthylmethyl phenyl ethers, wherein the phenoxide leaving group should be inferior to acetate formed from **1a**$^{-\bullet}$, suggest that the rate constant for dissociation of **1a**$^{-\bullet}$ is likely to be several powers of ten larger than the upper limit of the present pulse radiolysis experiments.

Summary

Arylmethyl acetates and benzoates react with arene radical anion salts to give reductive cleavage of the CH_2–O bond provided that the arene radical anion, the ester, and the reaction conditions are chosen so as to permit the necessary endergonic electron transfer. BP$^{-\bullet}$ will reduce all of the esters of this study. FL$^{-\bullet}$ will work when benzoyl or naphthyl groups are part of the ester, but not with only acetyl and phenyl. Once formed, the ester radical anions cleave rapidly to give arylmethyl radicals which are, in most cases, reduced by residual arene radical anions in the reaction mixture to give arylmethyl anions. These anions then act as bases and nucleophiles in reactions with the starting esters. Base-promoted reactions appear to be favored by the presence of crown ether. When the reactants are such that both reduction and cleavage are fast, base- and nucleophile-promoted reactions of the starting ester may not compete with reductive cleavage. But in such circumstances, local high concentrations of radicals and/or depleted levels of reductant may lead to radical dimerization.

Experimental Section

Solvents and Reagents. Tetrahydrofuran was distilled from a solution of sodium benzophenone ketyl and collected under argon just prior to use. Reactants and reagents not mentioned below were commercial samples shown to be of greater than 98% purity by gas chromatographic analysis.

Methods. All the melting points were determined on a Fisher-Johns melting point apparatus and are uncorrcted. Gas chromatographic analyses were performed on a Varian 3700 gas chromatograph with flame ionization detector connected to a HP 3390A integrator. The column was 3% OV-101 on Partisorb. ^{1}H NMR spectra were taken on Varian EM-390 (90 MHz) and GEMINI-200 (200 MHz) NMR spectrometers and $CDCl_3$ was used as the solvent. All reported chemical shifts are in δ units from TMS (tetramethylsilane). GC-MS data were taken using a SUPERCAP "High Temperature", Al-clad fused silica bonded methyl silicone column (15 m × 0.25 mm i.d., 0.1-μm film).

Preparation of Naphth-1-ylmethyl Acetate (1a). This compound was made by a modification of the procedure of MacLachlan.[21] 1-(Chloromethyl)naphthalene (5.3 g, 30.1 mmol) in 10 mL of DMF was treated with sodium acetate (3.0 g, 36.0 mmol) in 10 mL of DMF and the mixture was stirred at 60 °C for 4 h. When the reaction was complete by TLC, the reaction mixture was dissolved in 100 mL of CH_2Cl_2 and washed with H_2O (3 × 50 mL). Drying and evaporation of the CH_2Cl_2 gave crude product as a clear liquid. Distillation under reduced pressure (90 °C/1 Torr) [lit.[21] 80 °C/0.5 Torr] gave 4.5 g (75%) of pure product. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.1 (s, 3 H), 5.6 (s, 2 H), 7.2–8.1 (m, 7 H).

Preparation of Naphth-1-ylmethyl Benzoate (1b). This compound was made by a modification of the procedure of Hyde.[22] Naphth-1-ylmethanol (1.58 g, 10.9 mmol) was dissolved in 4 mL of pyridine. To this solution was added benzoyl chloride (1.55 g, 11.0 mmol). When the temperature dropped to 25 °C, the reaction mixture was heated for 2 min until all solid had dissolved. The solution was poured into 17 mL of H_2O, with vigorous stirring, and the mixture was extracted with CH_2Cl_2 (3 × 30 mL). The

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CH_2Cl_2 was washed with 5% Na_2CO_3 (3 × 20 mL) and H_2O (3 × 20 mL). Drying and evaporation of CH_2Cl_2 gave a clear oil which was purified by column chromatography (solvent hexane); 1.5 g (57%) of pure product was obtained. The product was distilled under reduced pressure (lit.[22] 230–234 °C/15 mm). ^1H NMR (200 MHz, $CDCl_3$): δ 5.85 (s, 2 H), 7.2–8.2 (m, 12 H). MS: *m/e* 262, 141, 105, 77.

General Procedure for Cleavage Reactions of Esters. Cleavage reactions were carried out by treating esters with a THF solution of the potassium salt of fluoranthene radical anion or of biphenyl radical anion in THF. All solutions were prepared and the cleavage reactions were carried out under an atmosphere of pure argon using an Ace-Burlich inert atmosphere system. Solutions were transferred using gas-tight syringes. For crown-ether mediated reactions, the radical anion solutions were combined with a THF solution of the ether and allowed to stir for 1 h before use. Reactions were allowed to proceed for 10 min to 24 h at 25 °C. For workup, reaction mixtures were poured into 100 mL of H_2O, acidified with 1% HCl to pH 2–3, and extracted with a mixture of 100 mL of pentane and 40 mL of CH_2Cl_2 (5:2). For crown-ether reactions, 3 × 50 mL washes with 17% KCl followed by 2 × 30 mL water washes were added to the procedure. After drying and evaporating the solvent, the remaining mixture was subjected to GC, GC-MS, and ^1H NMR analysis. In the case of benzyl benzoate and acetate, the reaction mixture was analyzed by GC before the solvent was evaporated. In all cases, the NMR spectra of the reaction mixtures showed no significant signals which were not accounted for by the products listed in Table I. Amounts determined by ^1H NMR and by GC were in reasonable agreement. Examples of specific reactions are given below.

Reaction of Naphth-1-ylmethyl Acetate (1a) with Fluoranthene Radical Anion. Naphth-1-ylmethyl acetate (294.7 mg, 1.474 mmol) was dissolved in 5 mL of THF under argon. To this solution was added 10 mL of 0.184 M fluoranthene radical anion. Ten minutes later, 3 mL of this reaction mixture was removed and worked up using the general procedure described above. Thirty minutes later, another 3 mL of this reaction mixture was taken out and worked up as before. The remaining solution was allowed to stir for 24 h and worked up using the general procedure. 1-Methylnaphthalene, 1,2-bis(1-naphthyl)ethane, naphth-1-ylmethanol, and unreacted ester were confirmed by comparison with standard compounds. Naphth-1-ylmethyl methyl ketone was identified by GC-MS (*m/e*, 184, *141*, 115). The methyl and methylene protons in its NMR spectrum appeared at δ 2.1 (s, 3 H) and 4.1 (s, 2 H), respectively [lit.[23] (60 MHz, CCl_4) δ 1.83 (s, 3 H), 3.82 (s, 2 H)]. The presence of naphth-1-ylmethyl acetoacetate is suggested by ^1H NMR peaks at δ 2.2 (s, 3 H), 3.5 (s, 2 H), and 5.6 (s, 2 H). The following reaction mixture compositions were determined by gas chromatography:

	mol %		
	10 min	30 min	24 h
unreacted ester	3 ± 1	3 ± 1	0
1-methylnaphthalene	35 ± 2	35 ± 2	35 ± 2
1,2-bis(1-naphthyl)ethane	<0.2	<0.2	<0.2
naphth-1-ylmethyl methyl ketone	12 ± 2	12 ± 2	13 ± 2
naphth-1-ylmethanol	38 ± 2	39 ± 2	38 ± 2
naphth-1-ylmethyl acetoacetate	12 [illegible] 2	11 ± 2	14 ± 2

Reaction of Naphth-1-ylmethyl Benzoate (1b) with Fluoranthene Radical Anion. Naphth-1-ylmethyl benzoate (117.5 mg, 0.45 mmol) was dissolved in 5 mL of THF under argon. To this solution was added 0.94 mL of fluoranthene radical anion solution in THF (K salt) (0.45 mmol). The reaction mixture was allowed to stir for 24 h at room temperature and worked up using the general procedure described above. 1-Methylnaphthalene, 1,2-bis(1-naphthyl)ethane, naphth-1-ylmethanol, and unreacted ester were confirmed by comparison with standard compounds. Naphth-1-ylmethyl phenyl ketone was determined by GC-MS (*m/e* 246, 141, *105*, 77) [lit.[23] *m/e* 246, 215, 202, 141, 115, 105]. The methylene protons appeared in its NMR spectrum at δ 4.75 (s, 2 H) [lit.[23] (60 MHz, CCl_4) δ 4.72 (s, 2 H)]. The following yields were determined by gas chromatography:

	mol %
unreacted ester	24 ± 2
1-methylnaphthalene	23 ± 2
1,2-bis(1-naphthyl)ethane	4 ± 2
naphth-1-ylmethyl phenyl ketone	20 ± 2
naphth-1-ylmethanol	25 ± 3

Reaction of Benzyl Benzoate (1c) with Fluoranthene Radical Anion. Benzyl benzoate (226.1 mg, 1.1 mmol) was dissolved in 5 mL of THF under argon. To this solution was added 6.5 mL of a solution of fluoranthene radical anion (K salt) in THF (2.2 mmol). The reaction mixture was allowed to stir for 3 h at room temperature and worked up by using the general procedure described above. Toluene, bibenzyl, benzyl alcohol, and unreacted ester were confirmed by comparison with standard compounds. Benzyl phenyl ketone was identified by GC-MS (*m/e* 196, *105*, 91, 77) and the methylene protons in its NMR spectrum appeared at δ 4.3 (s, 2 H).[24] Fluoranthyl phenyl ketone was suggested by MS analysis: *m/e 306*, 229, 201, 105, 77. Its precise structure is not known. The following yields were determined by gas chromatography:

	mol %
unreacted ester	21 ± 2
toluene	20 ± 1
bibenzyl	<0.1
benzyl phenyl ketone	17 ± 2
benzyl alcohol	35 ± 2
F1-COPh	7 ± 3

Reaction of Benzyl Acetate (1d) with Fluoranthene Radical Anion. Benzyl acetate (197.8 mg, 1.3 mmol) was dissolved in 5 mL of THF under argon. To this solution was added 8.0 mL of a THF solution of fluoranthene radical anion (K salt) (2.6 mmol). The reaction mixture was allowed to stir for 3 h at room temperature and worked up by using the general procedure described above. Benzyl alcohol and benzyl acetoacetate were obtained. Benzyl acetoacetate was confirmed by comparison with an authentic sample. GC-MS: *m/e* 192, 107, *91*. ^1H NMR: δ 2.2 (s, 3 H), 3.5 (s, 2 H), 5.2 (s, 2 H).

Pulse Radiolysis. Pulse radiolysis was carried out at the Center for Fast Kinetics Research using a system described previously.[13] Solutions were normally 2 mM and were bubbled with argon gas for at least 0.5 h before use. Pulses of 4 MeV electrons of 50–500 ns were employed.

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