The Photochemistry of Methoxy-Substituted Benzyl Acetates and Benzyl Pivalates: Homolytic vs Heterolytic Cleavage

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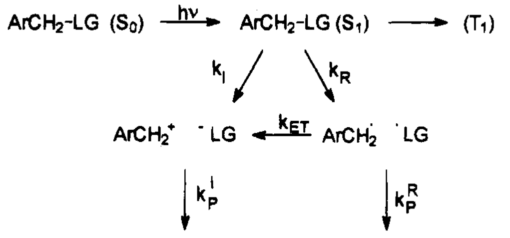
The multiple methoxy-substituted benzyl acetates (**3g−i**) and benzyl pivalates (**4g−i**) have been photolyzed in methanol solution. The products of these reactions are derived from two critical intermediates; the benzyl radical/acyloxy radical pair and the benzyl cation/carboxylate anion pair. As predicted by the *meta* effect, the yield of ion-derived product, the methyl ether in this case, was enhanced by the presence of the *m*-methoxy groups. The yield of ether, for the acetate esters, varied from 2% for the 4-methoxy-substituted ester to 66% for the 3,4,5-trimethoxy-substituted ester. In contrast, the yield of ether, for the pivalate esters, varied from <1% for the 4-methoxy-substituted ester to 20% for the 3,4,5-trimethoxy-substituted one. The *meta* effect does not explain these differences; electron transfer converting the radical pair to the ion pair is still an important pathway in the mechanism for ion formation. A quantitative analysis of the yield of the ethers was done in order to obtain the electron-transfer rate constants. This analysis revealed that the yield of the ethers was higher than expected based on previous results for other substituted benzyl acetates. A possible explanation for this discrepancy is that internal return of the radical pair to starting material for the acetate esters is more efficient than for the pivalate esters. Also, the esters **3k** and **3l**, were prepared to study the effect of electron-withdrawing groups in the *meta* position. For these esters, the benzylic cleavage reactions were inefficient and an isomerization reaction, the benzvalene rearrangement, was competitive.

Introduction

In recent years a large body of research has focused on the photogeneration of carbocations in solution and on the study of their reactivity by laser flash photolysis (LFP). This area of research has been the topic of an extensive review.[1] One of the reactions most commonly explored has been the "direct"[2] photoheterolysis of a carbon−heteroatom bond, for instance, in arylmethyl substrates with leaving groups (ArCH$_2$-LG). The products of photoheterolysis in nucleophilic solvents, like alcohols, are arylmethyl ethers and the process is therefore a photosolvolysis. Almost invariably accompanying these photosolvolyses products are others derived from arylmethyl radicals and these transients are also observed by LFP. Still in doubt, however, is the pathway involved in the formation of the ion pair, and two quite different mechanisms have been proposed as outlined in Scheme 1.

Scheme 1. General Mechanism for the Photolysis of Arylmethyl Substrates with Leaving Groups



The first of these, based on the pioneering work of Zimmerman,[3] proposed that the ion pair is formed by direct heterolytic cleavage. Product ratios are a result of competition between heterolytic cleavage (k_I for ion) and homolytic cleavage (k_R for radical) from the excited singlet state of the substrate. In some cases, triplet states undergo homolytic bond cleavage but for the leaving groups ($-O_2CR$) discussed in this work, the triplet is unreactive.[4,5] The second mechanism proposed exclusive homolytic cleavage from S$_1$ ($k_R \gg k_I$). The ion pair is formed by electron transfer from the radical pair. The critical competition is between electron transfer (k_{ET}) converting the radical pair to the ion pair and other reactions (k_P^R) converting the radical pair to product. Clearly, these proposals are mechanistic extremes and for some combination of substrate and solvent the ion pair could be generated both by heterolytic cleavage and by the electron transfer process of the radical pair. A useful probe for these mechanistic possibilities is the effect that substituents on the aromatic ring have on reactivity and product ratios.

To our knowledge there has been no direct observation by LFP of electron transfer resulting in ion pair formation. Clearly, the observation of radical pairs decaying and ion pairs appearing with the same rate constant would be proof of this electron-transfer pathway. In contrast to this possibility, in a very recent LFP study of diphenylmethyl chloride in acetonitrile, both the diphenylmethyl radical and the contact ion pair were observable within the time resolution (20 ps) of the instrument.[6] The absorption due to the radical did not decrease in intensity even after 4 ns. The ion pair was found to decay by two pathways, internal return to starting material, and diffusion to solvent separated ion pairs and free ions. Conversion of the ion pair to the radical pair by electron transfer was not observed; this

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[®] Abstract published in *Advance ACS Abstracts,* August 15, 1994.

[1] Das, P. K. *Chem Rev.* **1993,** *93,* 119.

[2] Direct is in quotes because the exact mechanism for forming the ion pair is not known but is assumed to be by heterolytic cleavage.

[3] Zimmerman, H. E.; Sandel, V. R. *J. Am. Chem. Soc.* **1963,** *85,* 915.

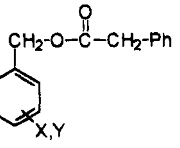
[4] DeCosta, D. P.; Pincock, J. A. *J. Am. Chem. Soc.* **1993,** *115,* 2180.

[5] Hilborn, J. W.; MacKnight, E.; Pincock, J. A.; Wedge, P. J. *J. Am. Chem. Soc.* **1994,** *116,* 3337.

[6] Peters, K. S.; Li, B. *J. Phys. Chem.* **1994,** *98,* 410.

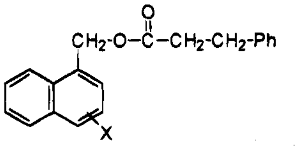
0022-3263/94/1959-5587$04.50/0

is not surprising because this process is endothermic by ~50 kcal/mol. These results are strongly suggestive of direct heterolytic cleavage, although the authors state: "The mechanism for the photochemical dissociation process producing the two transients is not revealed..." Similarly, many examples have been reported where both radical and ion pairs were observed simultaneously on the nanosecond time scale. Even if ion pairs were formed from radical pairs this time scale is too slow to observe the electron-transfer process which usually has a rate constant greater than 10^9 s^{-1}.



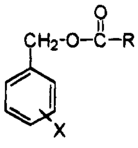
1

a, X = H, Y = H
b, X = 3-OCH$_3$, Y = H
c, X = 4-OCH$_3$, Y = H
d, X = 4-CH$_3$, Y = H
e, X = 4-CN, Y = H
f, X = 4-OCH$_2$CH$_3$, Y = H
g, X = 4-CO$_2$CH$_3$, Y = H
h, X = 4-OCH$_3$, Y = 5-OCH$_3$
i, X = 4-OCH$_3$, Y = 7-OCH$_3$
j, X = 4-OCH$_3$, Y = 8-OCH$_3$
k, X = F, Y = H



2

a, X = H
b, X = 3-OCH$_3$
c, X = 4-OCH$_3$



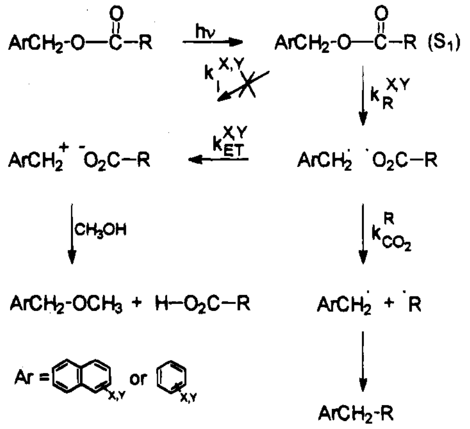
3a-l 4a-l

a, X = 4-CH$_3$
b, X = 4-CF$_3$
c, X = 4-CN
d, X = H
e, X = 3-OCH$_3$
f, X = 4-OCH$_3$
g, X = 3,4-(OCH$_3$)$_2$
h, X = 3,5-(OCH$_3$)$_2$
i, X = 3,4,5-(OCH$_3$)$_3$
j, X = 3-CH$_3$
k, X = 3-CN
l, X = 3-CF$_3$

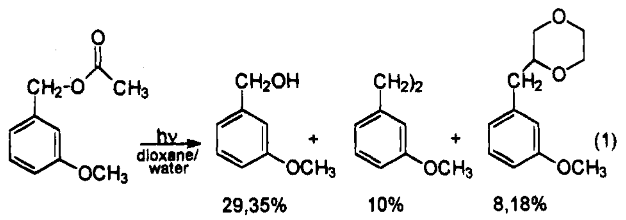
3, R = CH$_3$ **4**, R = C(CH$_3$)$_3$

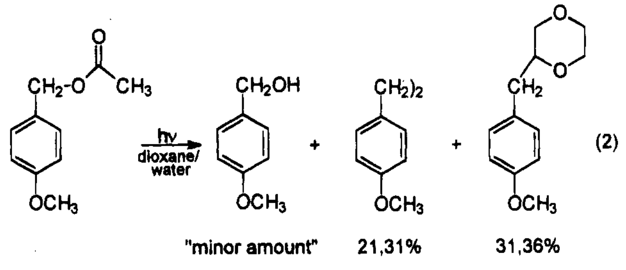
In contrast to the observations for diphenylmethyl chloride, our detailed results on the product distribution in the photolysis of 1-naphthylmethyl esters (**1a**–**k** and **2a**–**c**) and benzylic esters (**3a**–**f** and **4a**–**f**) can be explained by the homolytic cleavage/electron transfer pathway, Scheme 2. The electron-transfer rate constants obtained ranged from 0.01 × 10^{10} s^{-1} to 6 × 10^{10} s^{-1}. Direct heterolytic cleavage is of minimal importance. The estimated maximum efficiency of direct heterolytic cleavage is 10% for the 3-methoxy-substituted ester **4e**. The electron transfer rate constants, determined by product variation as a function of substituents (X,Y), were shown to fit Marcus theory in both the normal and inverted regions. The electron transfer rate varies with the oxidation potential of the arylmethyl radical which is being "clocked"[7] by the decarboxylation rate ($k^R_{CO_2}$) of the acyloxy radical. The oxidation potentials of the radicals as a function of the substituents (X,Y) correlated with σ^+.[8,9]

Scheme 2. Mechanism for the Photolysis of Arylmethyl Esters (1–4) in Methanol



The fact that the 3-methoxy-substituted esters exhibited the highest possibility of giving direct heterolytic cleavage agrees with Zimmerman's original observation on product yields for the photolysis of 3- and 4-methoxybenzyl acetate in aqueous dioxane.[10] The photolysis of 3-methoxybenzyl acetate gave 3-methoxybenzyl alcohol as the major product, eq 1; however, when 4-methoxybenzyl acetate was photolyzed, 4-methoxybenzyl alcohol was only a minor product; the major products were radical derived, eq 2.





Zimmerman had predicted these excited state results using charge density calculations from simple Hückel MO theory. The calculations showed that for a ground state benzylic compound an electron-donating substituent will increase the electron density at the benzylic carbon when it is substituted at the 4-position but in the excited state,

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(7) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.

(8) Sim, B. A.; Milne, P. H.; Griller, D.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1990**, *112*, 6635.

(9) Milne, P. H.; Wayner, D. D. M.; DeCosta, D. P.; Pincock, J. A. *Can. J. Chem.* **1992**, *70*, 121.

(10) The yields given in eqs 1 and 2 were determined by gravimetric analysis after chromatographic separation. This may, in part, explain the poor mass balance. Where there are two numbers, two separate determinations were made.

electron donation from an electron-donating substituent to the benzylic carbon is more efficient from the 3-position. Similarly, an electron-withdrawing substituent was predicted to be more effective in the 3-position. Therefore, when a benzylic compound is 3-methoxy-substituted, heterolytic cleavage is favored and the major products will be formed from ionic intermediates. The term "*meta* effect" has been coined for the ability of a substituent in the 3- or, *meta* position, to facilitate heterolytic cleavage. To further illustrate the *meta* effect, Zimmerman studied 3,5-dimethoxybenzyl acetate. In this case, the only product observed was the benzyl alcohol. Our conclusion is that although the *meta* effect is possibly increasing the contribution that k_I makes to ion pair formation for the 3-methoxy compound, the major pathway for ion formation in the photochemistry of arylmethyl esters is electron transfer.

Since Zimmerman's original report there have been many studies on reactions that support the *meta* effect, such as the photohydration of styrenes by McEwen *et al.*[11] and the acid-catalyzed photosolvolyses of benzyl alcohols by Wan *et al.*,[12] to name only two. However, a few benzylic systems that do not show the *meta* effect have also been studied. The work by Givens *et al.*[13] on benzyl phosphates and by McKenna *et al.*[14-17] on the photosolvolyses of benzyl ammonium salts are two examples.

From the flash photolysis results there is evidence that implies that ion pairs are generated directly by heterolytic cleavage in cases with good leaving groups. As well, product yields for the 3-methoxy-substituted esters indicated that this heterolytic pathway was becoming competitive with homolytic cleavage. Therefore, an examination of other methoxy-substituted esters seemed likely to be informative. The esters **3g–i** and **4g–i** were chosen for study. Clearly, the 3,5-dimethoxy derivatives (**3h, 4h**) where the *meta* effect would be enhanced are obvious choices. Again, the study of both the acetate (**3**) and pivalate (**4**) esters is necessary because the increase in the decarboxylation rate constant[18] of the acyloxy radical from 1×10^9 s^{-1} for the $CH_3CO_2^{\cdot}$ radical to 1.1×10^{10} s^{-1} for the $(CH_3)_3CCO_2^{\cdot}$ radical is a "clock" change that is necessary to monitor the electron-transfer rate.

The 3,4-dimethoxy derivatives **3g, 4g** were chosen as another useful probe of the mechanism. If the *meta* effect is important and the critical competition occurs between heterolytic and homolytic cleavage then the 3,4-dimethoxy-substituted esters **3g** and **4g** should behave very similarly to the 3-methoxy-substituted esters **3e** and **4e**, i.e., the additional 4-methoxy group would do little to change the dominant effect of the 3-methoxy group. However, if it is the competition between decarboxylation and electron transfer that is important then the 3,4-dimethoxy-substituted esters **3g** and **4g** should behave the same as the 4-methoxy-substituted esters **3f** and **4f** because the benzylic radicals for all of these esters would have very similar oxidation potentials, i.e., the additional 3-methoxy group would do little to change the dominant effect of the 4-methoxy group.

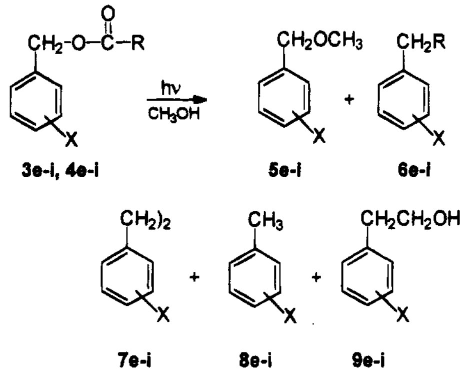
In addition, because the *meta* effect prediction is not exclusive to the methoxy group and because our previous work had only included *m*-methoxy, a study of other substituents seemed of interest. Therefore, a series of *meta*-substituted benzyl acetates **3j–l** was also studied.

The effect of *meta* substituents and multiple substituents in benzylic ester photochemistry has not been extensively explored. Wan *et al.*[19] have compared the reactivity of positional isomers of substituted benzyl acetates. A limited number of substituents (CH_3, F, Cl) in the three possible positions of benzyl acetate were examined. The esters were photosolvolyzed in 50% aqueous acetonitrile. The *ortho* isomer was found to be the most reactive, followed by the *meta* isomer. The *para* isomer was the least reactive. This effect was observed independent of the substituent. Their conclusion was that in S_1 substituent effects appear to follow an $o > m > p$ rule.

Wan *et al.*[20] have also studied the effect of multiple methoxy substitution on the photodehydroxylation of benzyl alcohols. They found that the effects of the methoxy groups were additive. The reactivity pattern of the disubstituted compounds follows the rule $o,o > o,m > m,m$.

Results and Discussion

Products and Yields on Irradiation of 3g–i and 4g–i. The esters **3g–i** and **4g–i** were photolyzed in methanol with a low pressure mercury lamp. As expected from previous results, five major benzylic products were formed as shown in eq 3. No attempt was made to isolate or quantify the low molecular weight carboxylic acids, acetic and pivalic, which were formed along with the ethers **5g–i**. Product yields are reported in Tables 1 and 2 along with those for **3e,f** and **4e,f** from previous work for comparison. The product yields were determined at less than 50% conversion of the starting ester. Calibrated GC or HPLC (for the dimers **7**) were used to determine these values. Authentic samples for calibrations were obtained either commercially, synthetically, or by isolation from the photolysis mixture in high conversion runs. Details are given in the Experimental Section.



(3)

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[11] McEwen, J.; Yates, K. *J. Phys Org. Chem.* **1991**, *4*, 193 and references therein.

[12] Wan, P.; Chak, B.; Krogh, E. *J. Photochem. Photobiol. A*, **1989**, 46, 49, and references therein.

[13] Givens, R. S.; Matuszewski, B.; Athey, P. S.; Stoner, R. M. *J. Am. Chem Soc.* **1990**, *112*, 6016.

[14] Appleton, D. C.; Bull, D. C.; Givens, R. S.; Lillis, V.; McKenna, J.; McKenna, J. M.; Thackeray, S.; Walley, A. R. *J. Chem. Soc. Perkin Trans. 2* **1980**, 77.

[15] Appleton, D. C.; Bull, D. C.; Givens, R. S.; Lillis, V.; McKenna, J. M.; McKenna, J. M.; Walley, A. R. *J. Chem. Soc., Chem Commun.* **1974**, 473.

[16] Lillis, V.; McKenna, J.; McKenna, J. M.; Smith, M. J.; Taylor, P. S. Williams J. H. *J. Chem. Soc. Perkin Trans 2* **1980**, 83.

[17] Lillis, V,; McKenna, J.; McKenna, J. M.; Smith, M. J.; Williams, J. H. *J. Chem. Soc., Chem Commun.* **1974**, 474.

[18] Hilborn, J. W.; Pincock, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 2683.

[19] Wan, P.; Chak, B.; Li, C. *Tetrahedron Lett.* **1986**, *27*, 2937.

[20] Wan, P; Chak, B. *J. Chem. Soc. Perkin Trans 2* **1986**, 1751.

Scheme 3. Mechanism for the Photolysis of Benzylic Esters 4 and 5

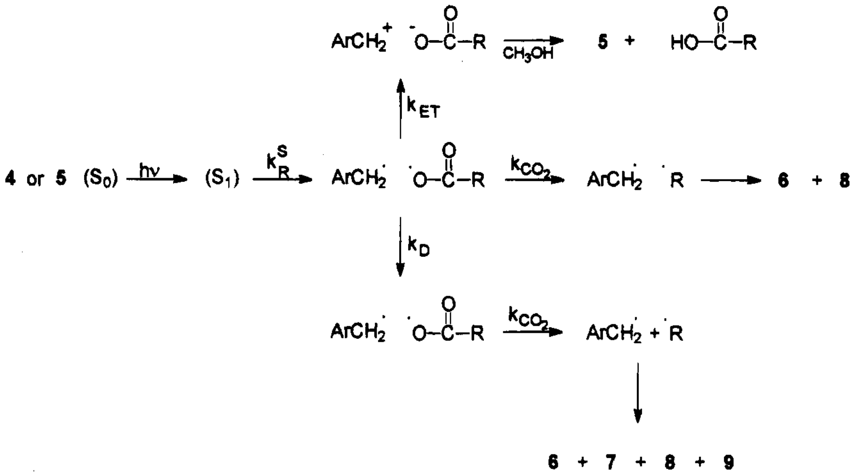


Table 1. **Product Yields[a] for the Photolysis of Esters 3 in Methanol**

ester **3** R = CH_3	ether **5**	coupled **6**	dimer[b] **7**	toluene **8**	alcohol **9**
3e, 3-OCH_3	32	14	38	<1	12
3f, 4-OCH_3	2	14	48	<1	25
3g, 3,4-$(OCH_3)_2$	43	7	28	<1	–
3h, 3,5-$(OCH_3)_2$	56	23	2	5	–
3i, 3,4,5-$(OCH_3)_3$	66	15	11	–	–

[a] The % yields reported are absolute yields based on consumed ester. Estimated error, ±2%, except for **3f**, ±0.1%. [b] Twice the molar yield.

Table 2. **Product Yields[a] for the Photolysis of Esters 4 in Methanol**

ester **4** R = $C(CH_3)_3$	ether **5**	coupled **6**	dimer[b] **7**	toluene **8**	alcohol **9**
4e, 3-OCH_3	10	46	20	17	–
4f, 4-OCH_3	–	48	23	13	4
4g, 3,4-$(OCH_3)_2$	7	25	36	11	–
4h, 3,5-$(OCH_3)_2$	14	44	10	23	
4i, 3,4,5-$(OCH_3)_3$	20	45	5	22	–

[a] The % yields reported are absolute yields based on consumed ester. Estimated error, ±2%. [b] Twice the molar yield.

The formation of the five benzylic products shown in eq 3 can be rationalized by the mechanism shown in Scheme 3. The ion pair is trapped by methanol to give the ether **5**. The remaining products are radical-derived. The benzylic radical forms **8** in a significant yield by in-cage disproportionation for R = $C(CH_3)_3$. These toluene products are only formed in minor amounts for the acetates where there is no readily available source of a hydrogen atom. The benzylic radical can also either couple with the alkyl radical ($R^\cdot$) to form **6**, the other in-cage product, or couple with itself to form **7**, the out-of-cage dimer. Finally, the benzylic radical can couple with the solvent to form **9**. We have discussed the details of these radical reactions previously.

Examination of the yields of these products in Tables 1 and 2 allows some qualitative conclusions to be made. A simple first approach is an examination of the ether yields because the ethers are the only products formed from the ionic intermediates. Focusing on Table 1, for the acetates, there seems to be a correlation between the ether yields and the methoxy substitution pattern. As predicted by the *meta* effect, the 3-methoxy- substituted ester (32%) as well as the 3,4-dimethoxy-substituted one (43%) gave a higher yield of ether product **5** from the ionic intermediate than the 4-methoxy-substituted ester (2%). The ether yield from the 3,5-dimethoxy-substituted ester (56%) was almost double that for a single *m*-methoxy group and was even greater for the 3,4,5-trimethoxy-substituted ester (66%). As predicted by the *meta* effect, the yield of product from the ionic intermediate is enhanced as methoxy groups are added to the aromatic ring.

An interesting result is the effect of a 4-methoxy group in the presence of a 3-methoxy group for the acetate esters. When the acetate ester is substituted with a 4-methoxy group only, very little ether product (2%) is formed. However, when there is a 3-methoxy group in combination with a 4-methoxy group, the latter seems to have a larger effect. The yield of the ether from the 3,4-dimethoxy-substituted ester is 43% whereas it is only 32% from the 3-methoxy-substituted ester. This is an increase of 9% in the yield of the ether, while a 4-methoxy group alone increases the ether yield by 2% relative to the unsubstituted ester. These substituents effects are not additive in a simple way.

The same trends are observed in Table 2 for the pivalate esters. As the number of methoxy groups is increased, the yield of ether is enhanced. If the available data were either only those in Table 1 or only those in Table 2, the conclusion would likely be made that *m*-methoxy groups enhance the efficiency of heterolytic cleavage. However, when the results in the two tables are compared, the yield of ether from the acetate esters (R = CH_3) is seen to be much higher than for the corresponding pivalate esters (R = $C(CH_3)_3$). Therefore, the *meta* effect, which is based only on excited state cleavage efficiencies, cannot completely explain the differences.

We have shown previously that the alkyl group (R) of the esters has virtually no effect on the photophysical properties of esters and therefore, any differences in ether yields as a function of R must be a consequence of processes that occur after excited-state bond cleavage. Because good estimates can be made for these rate constants, the results in Table 1 and 2 can be analyzed quantitatively.

Quantitative Mechanistic Scheme. We will begin the analysis by assuming that, for the pivalate esters, the ion pair, and thus the ether, is formed entirely by direct heterolytic cleavage. This is a reasonable assumption because decarboxylation of the $(CH_3)_3CCO_2^\cdot$ radical is rapid and electron transfer converting the radical pair to the ion pair will not compete effectively. Notice that

Table 3. Oxidation Potentials and Electron Transfer Rate Constants for Esters 3e–j

ester	yield difference of **5**,[a] %	k_{ET}[b] × 10^{-9}	E_{ox} (eV)
3e, 3-OCH_3	22	5.9	0.79[c]
3f, 4-OCH_3	2	0.43	0.26[c]
3g, 3,4-$(OCH_3)_2$	36	11.8	0.26[e]
3h, 3,5-$(OCH_3)_2$	42	15.2	0.77[d]
3i, 3,4,5-$(OCH_3)_3$	46	17.9	0.26[d]
3j, 3-CH_3	19	4.9	0.70[c]

[a] Obtained by subtracting the yield of **5** in Table 2 from that of **5** in Table 1. [b] Calculated from eq 4 with $k_{CO_2} = 1 \times 10^9$ s^{-1} and $k_D = 2 \times 10^{10}$ s^{-1}. [c] From ref 8. [d] This work, see Experimental Section. [e] Not measured but assumed equal to that of **3f** and **3i**.

the maximum yield of ether from this pathway occurs for the 3,4,5-trimethoxy-substituted compound **4i**, and it accounts for only 20% of the total product yield. The remainder of the products are obtained from the radical pair. In contrast, the ether yields for the acetate esters, where the decarboxylation rate of $CH_3CO_2^{\cdot}$ is slower, reflect both heterolytic cleavage and electron transfer. Therefore, the ether yields from the pivalate esters can be used to estimate what fraction of the yield of ether is formed by heterolytic cleavage from the acetate esters. After this subtraction, the remaining yield of ether for the acetates is the fraction formed by the electron transfer process (Table 3). This yield can then be used to determine k_{ET} using eq 4. The yield of ether **5** is simply expressed as a ratio of the possible pathways of reaction for the radical pair shown in Scheme 3. The only unknown in eq 4 is k_{ET} because k_{CO_2} (1×10^9 s^{-1}) is known and the value of k_D should be very similar to that

$$\text{yield of } \mathbf{5} = \frac{k_{\mathrm{ET}}}{k_{\mathrm{ET}} + k_{CO_2} + k_D} \qquad (4)$$

obtained from the study of esters **3a–f** and **4a–f** (2×10^{10} s^{-1}; due to an arithmetical error the value of 6×10^9 s^{-1} reported previously[5] was incorrect). The values of k_{ET} obtained in this way are given in Table 3, along with the known values[21] for the oxidation potentials of the substituted benzylic radicals in acetonitrile.

Previously, we have successfully analyzed electron transfer rate data for the conversion of the radical pair to the ion pair in arylmethyl esters by Marcus's[22] theory of electron transfer. The results were discussed briefly (vide supra) and are shown (solid circles) for the benzylic esters **3a–f** in Figure 1. We have now included the points (open circles) for **3g–i** on the same graph. The plot clearly shows that the multiple methoxy-substituted esters lie well above the line, meaning that the calculated rates of electron transfer are higher than predicted. The reason for this is that the difference in the yield of ether between the acetates and the pivalates, which is used to estimate the k_{ET} values, is greater than expected. There are several possible explanations for this observation. One possibility is that the rates of electron transfer for these methoxy-substituted benzylic radicals are actually higher than expected based on the other compounds. We have no explanation as to why this should be so.

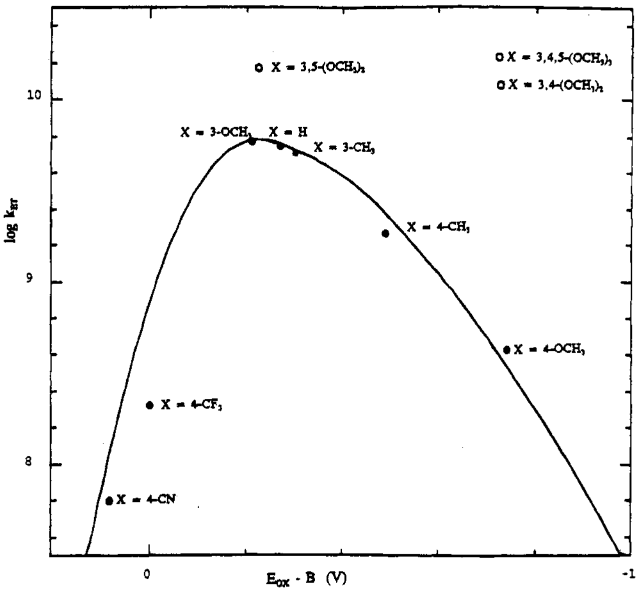
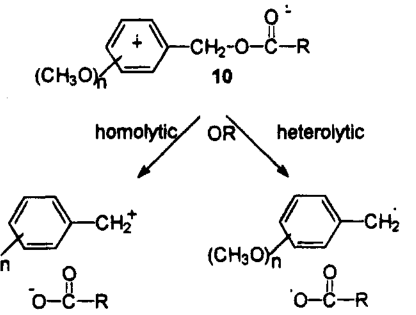


Figure 1. Plot of the rate of electron transfer (k_{ET}) for converting the radical pair to the ion pair as a function of the oxidation (E_{OX}) of the benzylic radical. The solid circles are for compounds **3a–f**, the open circles for **3g–i**, and the squares for **3j**.

A second possibility is that the yield of the ion pair from direct heterolytic cleavage is lower for the pivalate esters than for the acetate esters. Therefore, the ether yield attributed to electron transfer in the acetate photochemistry using our approximation would be too high. This is an unlikely possibility because, as was mentioned earlier, the singlet excited state behavior of the acetate esters **3** and the pivalate esters **4** was shown to be identical for compounds **3a–f** and **4a–f**. Unfortunately, the multiple methoxy-substituted compounds do not detectably fluoresce so we cannot compare the fluorescence quantum yields or lifetimes for compounds **3g–i** and **4g–i**.

A third possibility is that the rate of diffusional escape, k_D, of the radical pair is slower than expected for the multiple methoxy-substituted compounds. As can be seen from eq 4, this will result in a calculated yield of k_{ET} that is too high. Examination of Tables 1 and 2 indicate that this is a real possibility since the yield of diffusional escape product, the dimer **7**, is much lower for **3h**, **4h**, **3i**, and **4i** than for the other cases. A change in an order of magnitude of k_D from 2×10^{10} s^{-1} to 2×10^9 s^{-1} changes the calculated k_{ET} from 17.9×10^9 s^{-1} for **3i** to 2.6×10^9 s^{-1}. This is still not a sufficiently low value for this compound to fit on the curve in Figure 1.

A fourth possible explanation that we have examined is intramolecular electron transfer between the more easily oxidized methoxy-substituted rings and the ester carbonyl to form a charge transfer species **10**, eq 5. There



(5)

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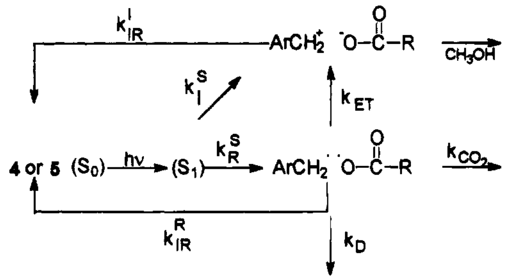
Scheme 4. Mechanism for the Photolysis of Benzylic Esters 4 and 5 Including the Internal Return Pathway



is literature precedence[23,24] for this process in arylmethyl esters of aromatic carboxylic acids ($ArCH_2O(CO)Ar$) where the ester functional group is more easily reduced than the aliphatic esters studied here. However, the presence of multiple methoxy groups would lower the oxidation potential of the ring and enhance this possibility. If **10** was formed preferentially for one alkyl group over another (i.e. ester **3** compared to ester **4**) and if **10** fragmented preferentially either homolytically or heterolytically as in eq 5, this would provide an additional pathway to form ion pairs or radical pairs, respectively. This new pathway would then perturb the product ratios from the normal excited state bond cleavage.

Normally, intramolecular electron transfer is detected by a decrease in the fluorescence quantum yield for the esters compared to related compounds that lack the ester functionality, for example, toluenes. The lack of fluorescence for esters **3g–i** and **4g–i** makes these experiments impossible. Because of this difficulty, methoxynaphthalenes were tested as model compounds. The oxidation potential of 1-methoxynaphthalene ($E_{1/2}$ = 1.38 V in acetonitrile vs SCE)[25a] is similar to that for a dimethoxy substituted benzene ($E_{1/2}$ = 1.45 V for 1,2-dimethoxybenzene in acetonitrile vs SCE)[25b] and the oxidation potential of 1,4-dimethoxynaphthalene ($E_{1/2}$ = 1.10 in acetonitrile vs SCE)[25c] is similar to that of a trimethoxy-substituted benzene ($E_{1/2}$ = 1.12 for 1,2,4-trimethoxybenzene in acetonitrile vs SCE).[25d] However, no quenching of the fluorescence was observed for either methoxynaphthalene compound in methanol solution containing up to 4 M ethyl acetate. Given that the lifetime of 1-methoxynaphthalene[26] is 10 ns, the rate constant for quenching must be less than 10^6 M^{-1} s^{-1}. This is orders of magnitude smaller than the rate constants for the other reaction pathways.

When comparing the acetate and pivalate esters, differences in their excited state properties have been ruled out as a reason for the large differences in the yield of the ether. This means that differences in the rates of ground state processes following the bond cleavage must be responsible. One possibility is the intervention of internal return of either the radical pair (k_{IR}^{R}) or the ion pair (k_{IR}^{I}) to the starting ester, as shown in Scheme 4. If ion pair return is important, the yield of the ether will drop relative to the yield expected from the bond cleavage processes. However, it is not obvious why this process should be faster for R = $C(CH_3)_3$ than for R = CH_3. The alternate possibility is that internal return in the radical pair is more efficient for the acetate esters. This is a real possibility because the lifetime of the radical pair will be longer for the $CH_3CO_2^{\cdot}$ than for the $(CH_3)_3CCO_2^{\cdot}$ radical. The lifetime is decreased for the latter because it decarboxylates 1 order of magnitude more rapidly. This internal return would therefore amplify the importance of the direct heterolytic cleavage (k_I^S) for the acetates (**3g–i**) and increase the yield of the ether in the photosolvolyses of these esters. The inclusion of this process in the kinetic scheme complicates the analysis so that the individual rate constants for electron transfer are more difficult to evaluate. However, a quantitative analysis indicates that if a large percentage (>75%) of the radical pairs react by internal return and if k_D decreases for the multiple methoxy compounds (*vide supra*), then the model gives a more reasonable value for k_{ET}. Internal return in benzylic ester photochemistry has been observed before by examining ^{18}O scrambling between the ester carbonyl and alcohol oxygen atoms.[27,28] A study of the efficiency of internal return as a function of substituents on the aromatic ring for both photochemical and thermal reactivity of esters is currently in progress in our laboratory. We hope that these results will determine whether this proposal is correct or not.

Table 4. Product Yields[a] for the Photolysis of Esters 3j and 4j in Methanol

ester	ether **5j**	coupling **6j**	dimer[b] **7j**	toluene **8j**	alcohol **9j**
3j	26	18	17	2	nd
4j	7	45	24	10	nd

[a] Estimated error, ±2%. [b] Twice the molar yield.

Finally, note that for the acetates **3a–f**, where the k_I^S route is only of minor importance, this internal return from the radical pair only decreases the quantum yield of ester disappearance but does not alter the product partitioning through k_{ET}, k_{CO_2}, and k_D. The kinetic analyses for these cases should still be correct.

Photolysis of Ester 3j,k,l. In order to further explore the effect of *meta* substituents, the *meta*-substituted esters **3j–l** were prepared and studied. These *meta* substituents were chosen so that the oxidation potentials of the incipient benzylic radicals would span a wide range. This is necessary to probe the competition between the electron transfer and heterolytic cleavage mechanisms for ion formation.

Esters **3j** and **4j** were studied first. They gave the expected products when photolyzed in methanol. The yields were quantified and are shown in Table 4. When the esters **3k** and **3l** were photolyzed in methanol the products as well as the ester isomerized. For instance, on irradiation of the 3-cyano-substituted ester **3k**, products with the cyano group in both the 3- and 4- positions were formed along with the 4-cyano-substituted ester. We were unable to obtain reliable results on the primary product distribution for the 3-cyano-substituted ester because of this complication. The mechanism for these positional isomerizations on the aromatic ring is presumed to be the known benzvalene rearrangement.[29] This reaction, which is quite inefficient (Φ = 0.05 for benzene-1,3,5-d_3),[30] was competitive with the reaction pathways

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that formed the benzylic cleavage products. This had not been a problem with other substituents, but the electron-withdrawing groups make the esters **3k** and **3l** quite unreactive to benzylic cleavage. A study of a series of *meta*-substituted esters where the resulting benzylic radical has a range of oxidation potentials will not be possible because data for the two most convenient substituents that raise the oxidation potential of the benzylic radical, trifluoromethyl, and cyano, cannot be obtained. However, the substituent dependence of the benzvalene rearrangement reactions is of interest and is being investigated further.

Aside from the methoxy substituents, the only other *meta* substituent to be studied is the methyl group. A value of k_{ET} was calculated for this ester using eq 4 and is shown in Table 3. If this point (closed square) is added to the Marcus curve for esters, Figure 1, good agreement with the values for the *para*-substituted esters results.

Experimental Section

General Procedure. Proton (^1H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were obtained in $CDCl_3$ on an AC 250 F NMR spectrometer in automation mode. Chemical shifts are reported in parts per million (δ) relative to tetramethylsilane (0.00) as an internal standard. Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

Infrared spectra were obtained on a Nicolet 205 FTIR spectrometer and the frequencies are reported in wavenumbers (cm^{-1}). Ultraviolet (UV) spectra were obtained in methanol solution in 1 cm quartz cuvettes on a Varian Cary 219 spectrometer. Wavelength maxima (λ_{max}) are reported in nanometers. GC/MS analyses were done on a Hewlett-Packard 5890A GC and a 5970 mass selective detector. The column used was a 25 m × 0.2 mm 5% phenyl methyl silicone on fused silica with a film thickness of 0.25 μm. Masses are reported in units of mass over charge (m/z). Intensities are reported as a percent of the base peak intensity. The molecular ion is indicated by $M^{+\cdot}$. GC/FID analyses were performed using a Hewlett-Packard 5890A gas chromatograph with an HP 7673 automatic injector and HP 3396A integrator. A 1 m glass column packed with 10% Fluorad FC-431 and 1% H_3PO_4 on Chromosorb W HP 80/100 mesh was used. HPLC analyses were obtained with a Waters 6000 solvent delivery system and a Waters U6K injector under isocratic conditions with a flow rate of 2 mL/min using a Brownlee Lab Spheri-10 10 μL reverse phase column (25 cm × 0.46 cm) with a Waters Model 450 variable wavelength detector. UV detection for monitoring the reaction was at 254 nm. Combustion analyses were carried out by Canadian Microanalytical Service Ltd., Delta, BC, Canada. Silica gel T-6145 plates from Sigma were used for thin layer chromatography (TLC). Silica gel, 60 Å (70–230 mesh), was used for normal column chromatography. The following starting materials were purchased from the Aldrich Chemical Co.: 3,5-dimethoxybenzoic acid, 3,4,5-trimethoxybenzaldehyde, and 3-cyanobenzaldehyde.

Fluorescence Measurements. Fluorescence measurements were done using a Perkin-Elmer MPF 66 fluorescence spectrometer at 25 °C. Corrected spectra were obtained. All samples were degassed by three freeze-pump-thaw cycles. 1-Methoxynaphthalene was purchased from the Aldrich Chemical Co. 1,4-Dimethoxynaphthalene was available in our laboratory. Distilled ethyl acetate was used for the quenching studies.

Syntheses of the Benzyl Alcohols. The preparation of the esters 3 and 4 required the corresponding benzyl alcohols. The alcohols, 3-(trifluoromethyl)benzyl alcohol and 3-methylbenzyl alcohol, were purchased from the Aldrich Chemical Co. The other alcohols were synthesized using the following procedures:

3,5-Dimethoxybenzyl alcohol was prepared by reducing the corresponding carboxylic acid with 1 M borane/THF solution in dry THF. A standard workup gave 8.5 g (51 mmol, 89%) of the crude alcohol. The alcohol was purified by bulb-to-bulb distillation. The ^1H NMR agreed with the literature[31] spectrum. **3,5-Dimethoxybenzyl alcohol**: ^1H NMR δ 6.6 (s, 2H), 6.45 (s, 1H), 4.72 (s, 2H), 3.85 (s, 6H), 2.0 (s, 1H).

The remaining alcohols were prepared by sodium borohydride reductions, in methanol, of the corresponding aldehydes. The alcohols were purified by bulb-to-bulb distillation. The ^1H NMR spectra of the pure alcohols were compared to previously reported spectra: 3,4-dimethoxybenzyl alcohol,[32] 3,4,5-trimethoxybenzyl alcohol,[33] 3-cyanobenzyl alcohol.[34]

Synthesis of Substituted Benzyl Acetates and Benzyl Pivalates (3 and 4). The acid chloride (0.022 mol) in 30 mL of dry benzene was added to a solution of the benzyl alcohol (0.02 mol) and 1 mL of pyridine in 50 mL of dry benzene. The solution was stirred overnight at room temperature. Water was added (50 mL) and the two layers were separated. The benzene layer was washed twice with 10% aqueous HCl, once with 5% aqueous NaOH, and finally with water. The organic layer was dried ($MgSO_4$), filtered, and evaporated under reduced pressure to give the crude ester. The esters were purified by either chromatography or bulb-to-bulb distillation.

3,4-Dimethoxybenzyl acetate (3g): ^1H NMR 6.96–6.83 (m, 3H), 5.04 (s, 2H), 3.89 (s, 3H), 3.88 (s, 3H), 2.09 (s, 3H); ^{13}C NMR δ 170.9, 149.1, 149.0, 128.4, 121.3, 111.8, 111.0, 66.4, 55.88, 55.86, 21.1; IR (neat) 3000, 2946, 2833, 1736, 1518, 1263, 1237, 1161, 1140, 1028 cm^{-1}; GC/MS m/z 210 ($M^{+\cdot}$, 58), 168 (31), 152 (12), 151 (100), 137 (14), 135 (12), 107 (23), 79 (12), 77 (12), 65 (12), 51 (12); UV (CH_3OH) λ_{max} 276 (ϵ 2400). Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 62.36; H, 6.75.

3,5-Dimethoxybenzyl acetate (3h): ^1H NMR δ 6.50 (s, 2H), 6.41 (s, 1H), 5.04 (s, 2H), 3.79 (s, 6H), 2.11 (s, 3H); ^{13}C NMR δ 170.7, 160.9, 138.2, 106.0, 100.1, 66.2, 55.3, 20.9; IR (neat) 2910, 2904, 2840, 1769, 1609, 1465, 1242, 1154, 1070, 834 cm^{-1}; GC/MS m/z 210 ($M^{+\cdot}$, 49), 169 (11), 168 (100), 167 (40), 151 (24), 139 (98), 124 (18), 108 (12), 107 (12), 91 (24), 79 (19), 78 (21), 77 (39), 65 (25), 63 (19); UV (CH_3OH) λ_{max} 278 (ϵ 2100). Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 62.57; H, 6.65.

3,4,5-Trimethoxybenzyl acetate (3i): ^1H NMR δ 6.47 (s, 2H), 4.89 (s, 2H), 3.73 (s, 6H), 3.69 (s, 3H), 1.97 (s, 3H); ^{13}C NMR δ 170.7, 153.3, 137.9, 131.6, 105.6, 66.5, 60.7, 56.1, 21.0; IR (neat) 2998, 2841, 1739, 1592, 1508, 1462, 1423, 1236, 1128, 1009 cm^{-1}; GC/MS m/z 240 ($M^{+\cdot}$, 86), 198 (52), 155 (13), 138 (13), 123 (25), 95 (25), 77 (18), 52 (13); UV (CH_3OH) λ_{max} 265 (ϵ 730). Anal. Calcd for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71. Found: C, 59.94; H, 6.68.

3-Methylbenzyl acetate (3j): ^1H NMR δ 7.24–7.08 (m, 4H), 5.04 (s, 2H), 2.32 (s, 3H), 2.06 (s, 3H); ^{13}C NMR δ 170.8, 138.2, 136.0, 129.06, 129.03, 128.5, 125.4, 66.4, 21.3, 21.0; IR (neat) 3026, 2954–2923, 1740, 1490, 1460, 1360, 1229, 1028 cm^{-1}; GC/MS m/z 164 ($M^{+\cdot}$, 41), 123 (10), 122 (100), 107 (50), 106 (10), 105 (76), 104 (38), 103 (38), 93 (25), 91 (40), 79 (32), 78 (47), 77 (49), 65 (24), 63 (19), 51 (20); UV (CH_3OH) λ_{max} 261 (ϵ 260).

3-Cyanobenzyl acetate (3k): ^1H NMR δ 7.67–7.46 (m, 4H), 5.14 (s, 2H), 2.14 (s, 3H); ^{13}C NMR δ 170.5, 137.6, 132.6, 131.8, 131.4, 129.5, 118.5, 112.7, 64.8, 20.9; IR (neat) 3075, 2950, 2232, 1746, 1380, 1227, 688 cm^{-1}; GC/MS m/z 175 ($M^{+\cdot}$, 28), 134 (10), 133 (100), 132 (24), 116 (81), 115 (25), 104 (38), 102 (15), 89 (40), 77 (13), 76 (17), 75 (16), 63 (23), 62 (10), 51 (21); UV (CH_3OH) λ_{max} 269 (ϵ 630). Anal. Calcd for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.07; H, 5.16; N, 7.81.

3-(Trifluoromethyl)benzyl acetate (3l): ^1H NMR δ 7.62–7.44 (m, 4H), 5.15 (s, 2H), 2.12 (s, 3H); ^{13}C NMR δ 170.6, 137.0,

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131.4, 129.0, 124.9, 124.8, 65.3, 20.8; IR (neat) 3080, 2960, 1751, 1450, 1390, 1331, 1239, 1165, 1125, 1075, 1050, 800, 710 cm^{-1}; GC/MS *m/z* 218 (M^{+}, 16), 176 (100), 159 (75), 158 (31), 145 (25), 137 (11), 127 (49), 119 (15), 109 (38), 107 (38), 89 (19), 77 (13), 75 (17), 69 (16), 51 (19); UV (CH$_3$OH) λ_{max} 259 (ϵ 500).

3,4-Dimethoxybenzyl pivalate (4g): ^{1}H NMR δ 6.93–6.82 (m, 3H), 5.05 (s, 2H), 3.88 (s, 3H), 3.87 (s, 3H), 1.22 (s, 9H); ^{13}C NMR δ 178.3, 148.88, 148.81, 129.0, 120.6, 111.2, 110.9, 66.0, 55.84, 55.80, 38.8, 27.2; IR (neat) 2970–2875, 2838, 1727, 1519, 1464, 1278, 1268, 1239, 1159, 1148, 1030 cm^{-1}; GC/MS *m/z* 252 (M^{+}, 15), 151 (100); UV (CH$_3$OH) λ_{max} 276 (ϵ 2900). Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.57; H, 7.95.

3,5-Dimethoxybenzyl pivalate (4h): ^{1}H NMR δ 6.47 (s, 2H), 6.39 (s,1H), 5.05 (s, 2H), 3.78 (s, 6H), 1.24 (s, 9H); ^{13}C NMR δ 178.2, 161.0, 138.8, 105.3, 99.8, 65.8, 55.3, 38.8, 27.2; IR (neat) 2938, 2840, 1729, 1610, 1478, 1343, 1035, 833 cm^{-1}; GC/MS *m/z* 252 (M^{+}, 41), 168 (24), 167 (100), 151 (79), 91 (22), 78 (19), 77 (24), 65 (19), 57 (98); UV (CH$_3$OH) λ_{max} 278 (ϵ 1500). Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.65; H, 7.93.

3,4,5-Trimethoxybenzyl pivalate (4i): ^{1}H NMR δ 6.58 (s, 2H), 5.05 (s, 2H), 3.84 (s, 6H), 3.83 (s, 3H), 1.24 (s, 9H); ^{13}C NMR δ 177.4, 152.7, 137.1, 131.7, 104.0, 65.4, 60.4, 55.3, 38.1, 26.6; IR (neat) 2970–2908, 2640, 1728, 1592, 1509, 1462, 1239, 1152, 1128 cm^{-1}; GC/MS *m/z* 282 (M^{+}, 27), 197 (13), 182 (8), 181 (100), 57 (27); UV (CH$_3$OH) λ_{max} 264 (ϵ 710). Anal. Calcd for $C_{15}H_{22}O_5$: C, 63.81; H, 7.85. Found: C, 64.05; H, 7.93.

3-Methylbenzyl pivalate (4j): ^{1}H NMR δ 7.19–7.10 (m, 4H), 5.05 (s, 2H), 2.33 (s, 3H), 1.24 (s, 9H); ^{13}C NMR δ 178.2, 138.0, 136.4, 128.7, 128.48, 128.45, 66.0, 38.7, 27.2, 21.3 (CH$_3$); IR (neat) 3028, 2973–2872, 1735, 1490, 1459, 1395, 1282, 1148 cm^{-1}; GC/MS *m/z* 206 (M^{+}, 12), 106 (12), 105 (98), 103 (11), 91 (12), 79 (12), 78 (11), 57 (100); UV (CH$_3$OH) λ_{max} 268 (ϵ 130). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.60; H, 8.64.

Preparative Photolyses. The photolyses of the benzyl esters were carried out as follows. A solution was prepared consisting of 1–2 g of the ester dissolved in 100 mL of distilled methanol. The solution was placed in a quartz tube and purged with nitrogen for 15 min before and during the irradiation. The light source was a Rayonet photochemical reactor using 16 × 75W 253.7 nm lamps. The progress of the reaction was monitored by HPLC and the reaction was stopped when the ester was >90% consumed. The products of the photolyses were separated by column chromatography and identified by spectroscopic methods.

Characterization of Ethers 5. The ethers, 5g–j, were prepared by reaction of the corresponding alcohols with NaH in dry DMSO followed by addition of CH$_3$I. Standard workup gave the crude ethers which were purified by chromatography or bulb-to-bulb distillation.

3,4-Dimethoxybenzyl methyl ether (5g): ^{1}H NMR δ 6.89–6.78 (m, 3H), 4.38 (s, 2H), 3.89 (s, 3H), 3.88 (s, 3H), 3.35 (s, 3H); ^{13}C NMR δ 149.0, 148.6, 130.7, 120.3, 111.0, 110.8, 74.6, 57.9, 55.9, 55.8; GC/MS *m/z* 182 (M^{+}, 43), 181 (11), 152 (13), 151 (100), 108 (11), 107 (13), 77 (11), 65 (12), 51 (11).

3,5-Dimethoxybenzyl methyl ether (5h): ^{1}H NMR δ 6.49 (s, 2H), 6.38 (s, 1H), 4.39 (s, 2H), 3.77 (s, 6H), 3.37 (s, 3H); ^{13}C NMR δ 160.9, 140.6, 105.3, 99.7, 74.6, 58.0, 55.3; GC/MS *m/z* 182 (M^{+}, 25), 152 (100), 91 (20), 77 (24).

3,4,5-Trimethoxybenzyl methyl ether (5i): ^{1}H NMR δ 6.57 (s, 2H), 4.39 (s, 2H), 3.86 (s, 6H), 3.83 (s, 3H), 3.40 (s, 3H); ^{13}C NMR δ 153.3, 137.3, 133.9, 104.5, 74.9, 60.9, 58.2, 56.1; GC/MS *m/z* 212 (M^{+}, 90), 197 (11), 182 (42), 181 (100), 169 (22), 167 (14), 154 (13), 151 (14), 148 (14).

Methyl 3-Methylbenzyl ether (5j): ^{1}H NMR δ 7.22–7.04 (m, 4H), 4.37 (s, 2H), 3.34 (s, 3H), 3.00 (s, 3H); ^{13}C NMR δ 138.3, 138.0, 128.6, 128.5, 128.4, 124.9, 74.8, 58.0, 21.4; GC/MS *m/z* 136 (M^{+}, 42), 135 (36), 121 (76), 106 (37), 105 (100), 104 (43), 103 (22), 91 (87), 79 (39), 78 (25), 65 (35), 63 (25), 51 (35).

Characterization of Toluenes 8. The toluenes were prepared by reduction of the aldehyde by the Huang-Minlon modification[35] of the Wolff–Kishner reaction. The crude products were purified by silica gel chromatography or by bulb-to-bulb distillation. Toluene **8j** was purchased from the Aldrich Chemical Co.

3,4-Dimethoxytoluene (8g): H NMR δ 6.78–6.68 (m, 3H), 3.90 (s, 3H), 3.88 (s, 3H), 2.29 (s, 3H); ^{13}C NMR δ 148.7, 146.8, 130.4, 120.8, 112.4, 111.2, 55.9, 21.0; GC/MS *m/z* 152 (M^{+}, 100), 109 (49), 107 (13), 94 (22), 91 (33), 81 (25), 79 (33), 78 (13), 77 (44), 66 (32), 65 (32), 63 (14), 53 (16), 52 (12), 51 (25).

3,5-Dimethoxytoluene (8h): ^{1}H NMR δ 6.34 (d, 2H, *J* = 2.60 Hz), 6.29 (t, 1H, *J* = 2.2 Hz), 3.78 (s, 6H) 2.30 (s, 3H); ^{13}C NMR δ 160.7, 140.2, 107.1, 97.6, 55.2, 21.8; GC/MS *m/z* 152 (M^{+}, 100), 123 (75), 121 (16), 109 (24), 92 (19), 91 (38), 77 (512), 66 (19), 65 (19).

3,4,5-Trimethoxytoluene (8i): ^{1}H NMR δ 6.42 (s, 2H), 3.88 (s, 9H), 2.22 (s, 3H); ^{13}C NMR δ 153.0, 135.8, 133.6, 106.0, 60.8, 55.9, 21.8; GC/MS *m/z* 182 (M^{+}, 82), 167 (100), 139 (59), 124 (44), 121 (10), 108 (48), 106 (48), 91 (12), 79 (30), 77 (21), 66 (11), 65 (26), 53 (82), 52 (19).

Characterization of Photoproducts 6 and 7. The photoproducts **6** and **7** were isolated from preparative photolyses mixtures by silica gel chromatography, with the exception of **6j** (R = CH$_3$) which was purchased from the Aldrich Chemical Co.

4-Ethyl-1,2-dimethoxybenzene (6g, R = CH$_3$): GC/MS *m/z* 166 (M^{+}, 51), 152 (10), 151 (100), 108 (12), 107 (10), 95 (20), 91 (20), 79 (12), 77 (17), 65 (10), 51 (12).

1,2-Dimethoxy-4-neopentylbenzene (6g, R = C(CH$_3$)$_3$): ^{1}H NMR δ 6.79–6.76 (m, 4H), 3.86 (s, 3H), 3.85 (s, 3H), 2.43 (s, 2H), 0.90 (s, 9H); ^{13}C NMR δ 148.2, 147.3, 132.4, 122.5, 114.0, 110.7, 55.8, 49.9, 31.8, 29.4; GC/MS *m/z* 208 (M^{+}, 25), 152 (16), 151 (100).

1-Ethyl-3,5-dimethoxybenzene (6h, R = CH$_3$): Spectra of this compound were not run because insufficient quantity of the pure compound was isolated. The toluene **8h** was used for quantification by GC/FID. A correction was made for the fact that the toluene contains one fewer carbon atoms. A GC/MS of **6h** was obtained from the photolysis mixture. GC/MS *m/z* 166 (M^{+}, 100), 165 (17), 137 (16), 121 (32), 109 (32), 108 (16), 105 (13), 91 (44), 79 (22), 78 (16), 77 (33), 65 (26), 63 (15), 53 (13), 51 (17).

1,3-Dimethoxy-5-neopentylbenzene (6h, R=C(CH$_3$)$_3$): ^{1}H NMR δ 6.33 (t, 1H, *J* = 2.25 Hz), 6.29 (d, 2H, *J* = 2.27 Hz), 3.77 (s, 6H), 2.43 (s, 2H), 0.92 (s, 9H); ^{13}C NMR δ 160.1, 142.1, 108.8, 97.7, 55.2, 50.6, 29.6; GC/MS *m/z* 208 (M^{+}, 27), 152 (100), 137 (6), 121 (6), 91 (8), 77 (8), 57.2 (31).

5-Ethyl-1,2,3-trimethoxybenzene (6i, R = CH$_3$): ^{1}H NMR δ 6.42 (s, 2H), 3.85 (s, 6H), 3.82 (s, 3H), 2.60 (q, 2H, *J* = 7.63 Hz), 1.24 (t, 3H, *J* = 7.63 Hz); ^{13}C NMR δ 153.0, 140.0, 135.9, 105.9, 60.8, 56.0, 29.3, 15.7; GC/MS *m/z* 196 (M^{+}, 74), 181 (100), 153 (25), 138 (22), 123 (15), 121 (19), 93 (12), 91 (14), 79 (13), 77 (18), 67 (18), 65 (13), 53 (12).

1,2,3-Trimethoxy-5-neopentylbenzene (6i, R = C(CH$_3$)$_3$): ^{1}H NMR δ 6.33 (s, 2H), 3.84 (s, 9H), 2.44 (s, 2H), 0.93 (s, 9H); ^{13}C NMR δ 152.4, 136.2, 135.5, 107.5, 60.8, 56.0, 31.8, 29.5; GC/MS *m/z* 238 (M^{+}, 15), 182 (14), 181 (100), 57 (50).

1-Methyl-3-neopentylbenzene (6j, R = C(CH$_3$)$_3$): ^{1}H NMR δ 7.24–6.91 (m, 4H), 2.45 (s, 2H), 2.33 (s, 3H), 0.90 (s, 9H); ^{13}C NMR δ 139.7, 137.0, 131.3, 127.45, 126.4, 50.1, 31.7, 29.4, 21.5; GC/MS *m/z* 162 (M^{+}, 13), 106 (98), 105 (47), 103 (10), 91 (42), 79 (13), 78 (10), 77 (21), 57 (100).

3,3′,4,4′-Tetramethoxybibenzyl (7g): ^{1}H NMR δ 6.76–6.65 (m, 3H), 3.84 (s, 3H), 3.82 (s, 3H), 2.83 (s, 2H); ^{13}C NMR δ 148.7, 147.2, 134.4, 120.3, 111.9, 111.1, 55.9, 55.7, 37.7; GC/MS *m/z* 302 (M^{+}, 47), 152 (11), 151 (100).

3,3′,5,5′-Tetramethoxybibenzyl (7h): ^{1}H NMR δ 6.35 (s, 2H), 6.32 (s, 1H), 3.76 (s, 6H), 2.84 (s, 2H); ^{13}C NMR δ 160.7, 144.1, 106.4, 97.9, 55.2, 38.0; GC/MS *m/z* 302 (M^{+}, 99), 152 (13), 151 (100), 91 (10), 77 (12).

3,3′,4,4′,5,5′-Hexamethoxybibenzyl (7i): ^{1}H NMR δ 6.37 (s, 2H), 3.82 (s, 9H), 2.85 (s, 2H); ^{13}C NMR δ 153.0, 137.4, 136.1, 105.4, 60.9, 56.0, 38.5; GC/MS *m/z* 362 (M^{+}, 37), 181 (100).

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3,3′-Dimethylbibenzyl (7j): ^{1}H NMR δ 7.24–7.00 (m, 4H), 2.86 (s, 2H), 2.33 (s, 3H); ^{13}C NMR δ 141.9, 137.9, 129.2, 128.2, 126.6, 125.4, 38.0, 21.4; GC/MS *m/z* 210 (M^+, 23), 106 (11), 105 (100), 79 (20), 77 (23).

Quantitative Photolyses. Photolyses were done to quantify the amount of photoproducts present in the reaction mixture. The procedure followed was the same as that described in Preparative Photolyses, except the solutions were prepared with 100–200 mg of the ester and analyses were done with less than 50% of the ester consumed. The yields reported in Tables 1 and 2 are absolute yields based on consumed ester. Standard solutions of each photoproduct were prepared to determine the yields of the photoproducts for the photolysis reaction. The photolyses samples and the standards were analyzed by GC/FID and the integrated areas for the standards containing a known amount of photoproduct were compared to the integrated areas of the photoproducts. The photoproducts **7g–i** were not volatile enough for GC analysis and thus were analyzed by HPLC. This was done in the same manner as above. The peak heights in a sample of the reaction mixture were compared to the peak heights of a standard solution of the photoproduct.

Oxidation Potential Measurements. Oxidation potentials for the 3,5-dimethoxybenzyl radical and the 3,4,5-trimethoxybenzyl radical were measured. This required the corresponding substituted toluene. The oxidation potentials were measured by modulated photolysis cyclic voltammetry. The details of this technique have been previously reported by Wayner *et al.*[21] The measured potentials are given in Table 3.

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