Photochemistry of Substituted Benzyl Acetates and Benzyl Pivalates: A Reinvestigation of Substituent Effects

J. W. Hilborn, E. MacKnight, J. A. Pincock,* and P. J. Wedge

Contribution from the Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada

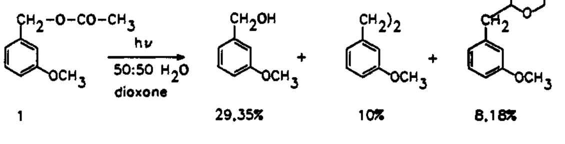
Received December 2, 1993®

Abstract: The photosolvolysis reactions, in methanol, of six substituted benzyl acetates (**7a–f**) and benzyl pivalates (**8a–f**) were studied. Five major benzylic products were formed from two critical intermediates. The ethers (**9**) were formed from the ion pair, **15**, and all of the other products (**10–14**) were formed from the radical pair, **16**. Quenching studies showed that only excited singlet state reactivity was important. The product yields were found to be highly substituent dependent. For instance, for the acetate esters, the yield of ether (**9**) varied from 2% for X = 4-OCH_3 to 32% for X = 3-OCH_3. Most of the differences in the yields could be attributed to ground state processes that occur after bond cleavage. The important competition is between electron transfer, converting the radical pair to the ion pair, and decarboxylation of $RCO_2^\bullet$. The rates of electron transfer are shown to fit Marcus theory in both the normal and inverted regions. Direct heterolytic cleavage to form the ion pair is of minimal importance.

Introduction

Photochemical cleavage reactions of arylmethyl compounds with leaving groups ($ArCH_2$–LG) have attracted considerable interest both for mechanistic reasons and for their synthetic potential particularly in functional group protection chemistry. A comprehensive review of this material up to the early 1980's has been written.[1] A general mechanism is shown in Scheme 1. In most cases, products result from both the intermediate arylmethyl–leaving group radical pair [$ArCH_2^\bullet$ •LG] and the ion pair [$ArCH_2^+$ $^-$LG]. The former could be either a singlet or triplet state. Typical hydrogen atom abstraction and coupling products are obtained from the radical pair. The ion pair, on the other hand, can often be trapped by nucleophilic solvents (water, alcohols), and therefore, the process is a photosolvolysis. Many factors, some of which are still not well understood, control the competition between the pathways for formation of these critical intermediates. One of these is substituent effects on the aromatic ring, and two quite different mechanistic proposals have been advanced for the case where the leaving group is an ester (O–(CO)–R).

The first of these is founded on a much cited fundamental paper by Zimmerman[2] on the photolysis of 3- and 4-methoxybenzyl acetate in aqueous dioxane (eqs 1 and 2, respectively).[3]



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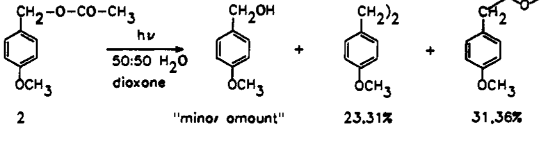

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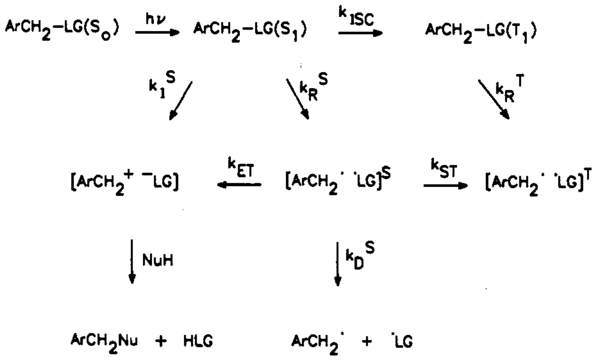
Scheme 1. General Mechanism for the Photolysis of Arylmethyl Compounds with Leaving Groups



As shown, the 3-methoxy isomer, **1**, gave a higher yield of the alcohol that results from trapping of the cation by water than did the 4-methoxy isomer, **2**. The benzyl dimer that is formed by out-of-cage coupling of benzylic radicals was a major component of the radical-derived products. Moreover, the quantum yield for product formation was higher for the 3-methoxy case. These observations, which are contrary to ground state expectations, were rationalized by changes in charge density (as calculated by simple Hückel MO theory) that occur on excitation. In the excited state, a methoxy group is predicted to be a better electron donor from the 3-position (i.e. *meta*) than from the 4-position. A general mechanism for a photosolvolysis reaction is shown in Scheme 2. Zimmerman's mechanism assumed that the yield of the ion pair was determined by the efficiency of direct heterolytic cleavage of the carbon–oxygen bond of the ester in the excited singlet state, i.e. the ratio of k_I^S/k_R^S controlled product distribution. The term "*meta* effect" was adopted for this proposal. The electron-transfer pathway converting the radical pair to the ion pair was not considered. Since then, there have been other observations of photochemical cation generation, for instance, in the photohydration of styrenes[4] and the acid-catalyzed photosolvolysis of benzyl alcohols[5] that support this idea. Other

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® Abstract published in *Advance ACS Abstracts*, March 15, 1994.

(1) Cristol, S. J.; Bindel, T. H. *Organic Photochemistry*; Marcel Dekker: New York, 1983; Vol. 6, p 327.

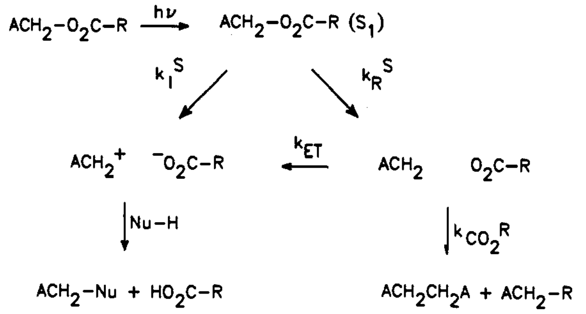
(2) Zimmerman, H. E.; Sandel, V. R. *J. Am. Chem. Soc.* **1963**, 85, 915.

(3) 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.

(4) McEwen, J.; Yates, K. *J. Phys. Org. Chem.* **1991**, 4, 193 and references therein.

(5) Wan, P.; Chak, B.; Krogh, E. *J. Photochem. Photobiol., A* **1989**, 46, 49 and references therein.

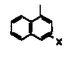
Scheme 2. General Mechanism for the Photosolvolysis of Arylmethyl Esters



reactions, such as the photosolvolysis of benzyl phosphates,[6] show an order of reactivity that reflects ground state substituent effects.

The second mechanistic proposal is based on our results[7-9] for the photolysis in methanol of the set of 11 substituted 1-naphthylmethyl esters of phenylacetic acid, **3** (eq 3). The ethers, **4**,

$$\underset{3}{ACH_2\text{-}O_2C\text{-}R} \xrightarrow[CH_3OH]{h\nu} \underset{4}{ACH_2\text{-}OCH_3} + \underset{5}{H\text{-}O_2C\text{-}R} + \underset{6}{ACH_2\text{-}R} \quad (3)$$

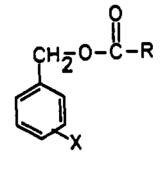
A =


and phenylacetic acid, **5**, result from trapping of the ion pair by the solvent, methanol, whereas the hydrocarbons, **6**, result from radical coupling after loss of carbon dioxide. For these substrates the yield of ether from the 3-methoxy compound was lower than that for the 4-methoxy compound, i.e. no *meta* effect. Note also that the major product from the radical pair resulted from in-cage coupling. The yield of out-of-cage dimers was usually less than 5%. The variation in yield as a function of the substituents, X, could, however, be explained by the general mechanism in Scheme 2 with the assumption that $k_R{}^S \gg k_I{}^S$, i.e. only homolytic, not heterolytic, cleavage of the carbon–oxygen bond of the ester occurs from the excited singlet state. (The triplet state was shown to be unreactive by sensitization studies.) The steps that control the yield of the products are electron transfer, conversion of the radical pair to the ion pair, and decarboxylation of the acyloxy radical with rate constants k_{ET} and k_{CO_2}, respectively. Systematic variation of X changes the oxidation potential of the 1-naphthylmethyl radical and hence the rate constant for electron transfer.[7,8] The values of k_{ET} as a function of X were found to follow Marcus theory in both the normal and inverted regions. Systematic variation in R changed the rate of decarboxylation.[9] Moreover, both k_{ET} and k_{CO_2} were greater than 5×10^9 s^{-1} which meant that diffusional escape from the solvent cage was slow relative to these in-cage processes.

These two mechanistic proposals, of course, represent the extreme cases. In the first, product yields are determined only by initial excited state behavior, i.e. competition occurs between $k_I{}^S$ and $k_R{}^S$. In the second, product yields are independent of excited state behavior and instead are determined by processes that occur after bond cleavage, i.e. $k_R \gg k_I$ for all substrates. The competition is between k_{ET} and k_{CO_2}, processes that occur for a ground state intermediate after the excited state chemistry is complete. Obviously, there may be cases where neither of these extremes apply and product yields would then be determined, in a complex way, by competition in rate processes at more than one place in Scheme 2.

Because of the differences in both product yields and mechanistic conclusions between the benzyl esters (eqs 1 and 2) and the 1-naphthylmethyl esters (eq 3), a reinvestigation of the former seemed necessary. There are several reasons for this. First, only a very limited number of substituents, namely 3-methoxy, 4-methoxy, and 3,5-dimethoxy, were examined. The importance of the electron-transfer pathway (k_{ET}) can only be assessed if a set of substituents spanning a wide range in oxidation potential of the arylmethyl radical are examined. Second, only acetate esters were studied. Variation in the acid part of the ester is a useful probe of the importance of the decarboxylation step (k_{CO_2}). Third, the multiplicity of the reactive excited state for the benzylic esters was not determined. For 1-naphthylmethyl esters, the triplet state is known to be unreactive[8,10,11] so that triplet radical pairs do not need to be considered as intermediates. The higher energy (~330 kJ/mol) of the triplet state of benzene derivatives means that there is now sufficient excitation energy to allow cleavage of the carbon–oxygen bond of esters (BDE = ~280 kJ/mol for benzyl acetate[12]). The formation of triplet radical pairs from the triplet excited state would enhance the yield of products derived from the benzylic radical because electron transfer converting a triplet radical pair to an ion pair is spin forbidden and, therefore, should be slow. Finally, product yields were determined gravimetrically by isolation after column chromatography and cannot be expected to be quantitative, particularly for volatile products.

With these ideas in mind, we have prepared and studied the photochemistry in methanol of the set of benzyl esters, **7a–f** and **8a–f**. The substituents were chosen to span the range of the σ^+



7a-f, 8a-f

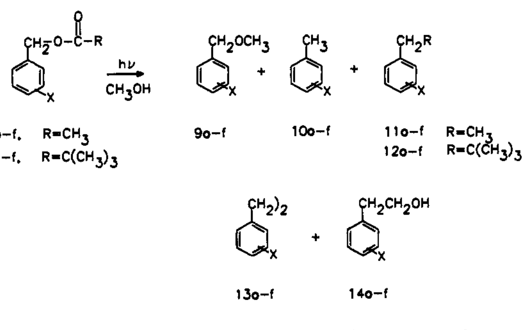
a, X = 4-OCH$_3$
b, X = 4-CH$_3$
c, X = H
d, X = 3-OCH$_3$
e, X = 4-CF$_3$
f, X = 4-CN

7, R = CH$_3$
8, R = C(CH$_3$)$_3$

scale from −0.65 for **a** to 0.66 for **f** and, also to compare 3- and 4-methoxy substituents as a test of the *meta* effect. The choice of **7** (acetate) and **8** (pivalate) was made to probe the importance of the decarboxylation process since k_{CO_2} changes by an order of magnitude from 1×10^9 s^{-1} for $CH_3CO_2{}^\bullet$ to 11×10^9 s^{-1} for $(CH_3)_3CCO_2{}^\bullet$.[9]

Results and Discussion

Products and Yields on Direct Irradiation of 7 and 8. The photolysis in methanol of **7a–f** and **8a–f** gave five major benzylic products as shown in eq 4. No attempt was made to isolate or quantify the low molecular weight carboxylic acids, acetic (from **7**) and pivalic (from **8**), which were formed along with **9**. The yields for these photoproducts are reported in Table 1. Calibrated GC or HPLC (for the dimers **13**) was used to determine these



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

[7] DeCosta, D. P.; Pincock, J. A. *J. Am. Chem. Soc.* **1989**, 111, 8948.

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

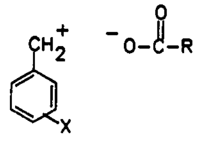
[9] Hilborn, J. W.; Pincock, J. A. *J. Am. Chem. Soc.* **1991**, 113, 2683.

Table 1. Product Yields[a] for the Photolysis of Esters **7** and **8** in Methanol

esters, **7** + **8**	%**9**	%**10**	%**11**/**12**[b]	%**13**	%**14**	total %
7a, X = 4-OCH_3	1.7[c]	nd	14	48	25	89
8a	nd[d]	13	48	24	4	89
7b, X = 4-CH_3	8[c]	2	14	52	21	97
8b	nd	14	53	31	0	98
7c, X = H	26	nd	19	23	26	94
8c	5	14	45	18	6	88
7d, X = 3-OCH_3	32	nd	14	38	12	96
8d	10	17	46	20	nd	93
7e, X = 4-CF_3	1.0[c]	14	24	17		56
8e	nd	38	34	13		85
7f, X = CN	0.3[c]	5	16	67	5	95
8f	nd	16	43	32	nd	91

[a] The numbers represent the yield of the benzylic fragment based on the amount of reacted starting material. Therefore the molar yield of the dimer **13** is multiplied by 2. The estimated error based on reproducibility of injections and multiple runs is about ±2%. However, note footnote *c*. [b] This is the product that results from coupling after decarboxylation. For the acetate esters (**7**), the product is **11**, and for the pivalate esters (**8**), the product is **12**. [c] The yield of the methyl ether from the acetate esters is important for analyzing the results. For cases where this yield is low, analyses were more carefully done and the estimated error is ±0.2%. [d] Not determined (nd) but <0.5%.

values. Authentic samples for calibrations were obtained either commercially, synthetically, or by isolation from photolysis mixtures in high-conversion runs. Details are given in the Experimental Section. Dark samples of the esters in methanol showed no significant conversion to products. At conversions below 50%, product yields were shown to be independent of percent conversion. At very high conversions, the mass balance dropped to 75–80% because of slow photodegradation of the products. This is not surprising because the starting ester and the photoproducts have the same chromophore and at high conversion most of the light is being absorbed by the products.



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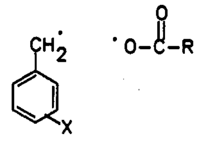

16

As expected, the products formed can be readily rationalized by the intermediate ion pair **15** and the radical pair **16**. The ion pair is trapped by the solvent to give methyl ether **9**. In agreement with Zimmerman's observations[2] (eqs 1 and 2), the yield of this ether is higher for the 3-methoxy (32%) than for the 4-methoxy isomer (1.7%). It is important to notice that the yield of this ether drops substantially for the pivalate esters (R = $C(CH_3)_3$) relative to the corresponding acetate esters (R = CH_3). Now, for 3-methoxy, the yield of ether is only 10%. Therefore, for the 3-methoxy pivalate ester (**8d**), this 10% represents the maximum yield of heterolytic cleavage; homolytic cleavage from S_1 dominates heterolytic cleavage by at least a factor of 10. As expected, and as we will demonstrate clearly below, the excited singlet state behaviors of the acetate and the pivalate esters are essentially the same. The enhanced yield of ion-derived products from the 3-methoxybenzyl acetate (**7d**) must be a consequence of processes that occur after excited state bond cleavage. The obvious difference (Scheme 2) is the increased rate of decarboxylation (k_{CO_2}) for the $(CH_3)_3CCO_2^\bullet$ radical relative to $CH_3CO_2^\bullet$. As a confirmation that this observation was not a function of the solvent methanol, the yield of 3-methoxybenzyl alcohol was determined on photolysis of **7d** and **8d** in 50% aqueous dioxane, the solvent used in the initial study by Zimmerman.[2] The yield dropped even more dramatically from 62% for **7d** to 11% for **8d**.

Because the rest of the products **10–14** are all derived from the benzylic radical, the fate of the radical pair **16** is clearly more complicated. Again, in agreement with Zimmerman's earlier observations, the dimer **13** ($ArCH_2CH_2Ar$) is a major product, particularly for the acetate esters. Thus, out-of-cage dimerization of benzylic radicals is a dominant process in contrast to the observations for 1-naphthylmethyl esters (eq 3). In fact, the 2-arylethanol product **14** ($ArCH_2CH_2OH$) is also an out-of-cage coupling product, benzylic radicals combining with solvent-derived $^\bullet CH_2OH$ radicals. For most acetates (except **7c**, X = H, and **7d**, X = 3-OCH_3, where the ion pair **15** is a more important intermediate), the sum of the yields for these two out-of-cage products, **13** and **14**, is over 70%. Clearly, diffusional escape from the solvent cage is of major importance. The pathway for formation of the hydroxymethyl radicals is not certain, but arguments can be advanced that reaction of methanol with methyl radicals provides the major route.

First, the rate constant obtained by laser flash photolysis,[13] for hydrogen atom abstraction from ethyl ether by the ((4-methoxyphenyl)acyl)oxy radical ($ArCO_2^\bullet$), is $<10^6$ M^{-1} s^{-1}. Decarboxylation will be preferred to hydrogen atom abstraction from the solvent because the decarboxylation rate[9] of $CH_3CO_2^\bullet$ (10^9 s^{-1}) is 3 orders of magnitude faster than the hydrogen atom abstraction. Second, a rate constant for diffusional escape of the radical pair of 6×10^9 s^{-1} can be calculated using the simple diffusional escape[14] equation assuming 6-Å spheres in a solvent like methanol of viscosity 5.5 mP. Third, benzylic radicals do not efficiently abstract hydrogen atoms from methanol; dimerization dominates.[15] This observation is explained by the fact that the hydrogen atom abstraction process from methanol by a benzylic radical is endothermic by ~29 kJ/mol as calculated from bond dissociation energies.[12] Therefore, the logical conclusion is that most of the acetyloxy radicals decarboxylate after diffusion from the solvent cage. The methyl radical then abstracts a hydrogen atom from methanol (exothermic by ~50 kJ/mol) to form $^\bullet CH_2OH$. The benzylic radical either dimerizes to **13** or couples with $^\bullet CH_2OH$ to form **14**. The ratio of these two processes is substituent dependent (see Table 1) since dimerization is more favorable for benzylic radicals with electron withdrawing groups. We have no good explanation for this last observation.

For the radical pair derived from the pivalate esters, out-of-cage radical reactions are less important. Now, decarboxylation occurs with a rate constant[9] of 1.1×10^{10} s^{-1}, which is faster than diffusional escape. Also, the ratio of dimerization of the benzylic radicals to form **13**, relative to solvent coupling to form **14**, favors **13**. This is a result of the fact that the *tert*-butyl radical probably abstracts hydrogen atoms from the solvent at a slower rate than does the methyl radical. The hydrogen abstraction by the *tert*-butyl radical is now exothermic[12] by only ~6 kJ/mol. For this reason, as well as for steric reasons, the hydrogen abstraction should be slow.

The products from the in-cage radical pair are the toluene **10** and the coupling product **11** (R = CH_3) or **12** (R = $C(CH_3)_3$). For the pivalate esters, the ratio of coupling to disproportionation (**12**/**10**), is 3.2 ± 0.4 and is essentially substituent independent (ignoring the 4-CF_3 case, **8e**, which has a very different and unexplained value of 0.9). For the acetate esters, disproportionation is impossible and coupling to ethylbenzene, **11** (R = CH_3), is the only in-cage product derived from the radical pair.

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(10) Arnold, B.; Donald, L.; Jurgens, A.; Pincock, J. A. *Can. J. Chem.* **1985**, 63, 3140.

(11) Matuszewski, B.; Givens, R. S.; Neywick, C. V. *J. Am. Chem. Soc.* **1973**, 95, 1973.

(12) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, 33, 493.

(13) Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, 110, 2877, 2886.

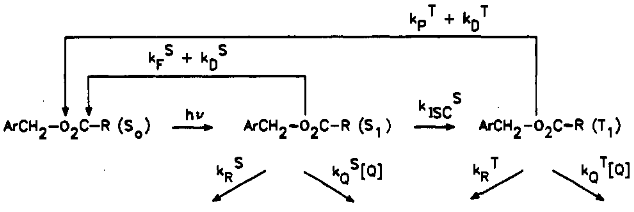
(14) Gardiner, W. C. *Rates and Mechanisms of Chemical Reactions*; Benjamin: New York, 1969; p 168.

(15) Langler, R. F.; Marini, Z.; Pincock, J. A. *Can. J. Chem.* **1978**, 56, 903.

Before putting these ideas on a more quantitative mechanistic basis, the multiplicity of the reactive excited state will be discussed.

Multiplicity of the Reactive Excited State. Product yields in these photocleavage reactions are well known[1] to depend on the multiplicity (singlet versus triplet) of the reactive excited state. Triplet states give triplet radical pairs so that the only possible products are derived from radical intermediates. Usually out-of-cage processes dominate since in-cage coupling reactions are spin forbidden. For reactive singlet states both radical pairs and ion pairs can be formed and in this case in-cage products are spin allowed. The major differences in the yields of out-of-cage products for the 1-naphthylmethyl esters (eq 3) when compared to the benzylic esters (eq 4 and Table 1) suggested that triplet states might be involved for the latter. In terms of analyzing substituent effects on the relative yield of products derived from the ion pair versus the radical pair in direct irradiations, the importance of triplet reactivity is critical. This is so because if, for one substituent, triplet state reactivity is a major pathway, whereas for another it is not, the yield of products derived from ionic intermediates is likely to be higher for the latter. This observation would not then necessarily be a result of the substituent enhancing the process that forms the ionic intermediate. In order to test this possibility, either triplet sensitization or quenching experiments are necessary.

Scheme 3. Possible Excited State Pathways for a Benzylic Ester in the Presence of a Quencher



The difficulty in doing these experiments is exemplified by Cristol's[16,17] detailed studies on substituted benzyl chlorides. The triplet energies of these substrates are high, and triplet sensitizers of high enough triplet energy to allow unambiguous exothermic triplet energy transfer are not available. Another potential problem is electron-transfer sensitization, as has been demonstrated for 1-naphthylmethyl iodide.[18] Moreover, sensitizers such as ketones are good hydrogen atom abstractors in their n,π* triplet excited state and are incompatible with methanol as the solvent. Because of these problems, selective quenching of the triplet state by the diene, 2,3-dimethylbutadiene, was chosen as the preferred method. The basic idea is shown in Scheme 3, where the rate constants are defined as follows: $k_R{}^S$, reaction of the singlet; $k_Q{}^S$, quenching of the singlet by quencher Q; $k_D{}^S$, radiationless decay of the singlet; $k_{ISC}{}^S$, intersystem crossing of singlet to triplet; $k_R{}^T$, reaction of the triplet; $k_Q{}^T$, quenching of the triplet by quencher Q; $k_P{}^T$, phosphorescence of the triplet; $k_D{}^T$, radiationless decay of the triplet. The concentration of quencher used to selectively quench the triplet state and not the singlet state was determined by eqs 5 and 6, where %S and %T are the percentages of the excited state quenched in each case.

$$\%S = 100k_Q{}^S[Q]/(k_Q{}^S[Q] + 1/\tau_S) \qquad (5)$$

$$\%T = 100k_Q{}^T[Q]/(k_Q{}^T[Q] + 1/\tau_T) \qquad (6)$$

In order to confirm that only the triplet state was being quenched, lifetimes and k_Q values were measured and are reported for 7 and 8 in Table 2. Quantum yields of fluorescence are also given. For comparison, values of the singlet excited state properties for the corresponding benzyl alcohol, **17**, were also measured. The singlet lifetimes and quantum yields of fluorescence are essentially identical for the acetate (**7**) and pivalate (**8**) esters. As expected, and as we have observed previously,[9] changes in the carboxylic acid part of the ester have little effect on the excited state properties of the aromatic chromophore. For this reason, we have only determined triplet values, τ_T and $k_Q{}^T$, by laser flash photolysis (LFP) for the acetate esters (**7**).

Table 2. Photophysical Properties of Esters 7 and 8 in Methanol

ester	$\tau_s \sim 10^9$ [a] (s^{-1})	ϕ_F [b]	$k_Q{}^S \times 10^{-9}$ [c]	$\tau_T \times 10^6$ [d] (s^{-1})	$k_Q{}^T \times 10^{-9}$ [e]
7a, X = 4-OCH_3	6	0.17	2.3	3	8
8a	6	0.16			
17a	7	0.17			
7b, X = 4-CH_3	22	0.12	2.9	0.4	4
8b	23	0.11			
17b	25	0.15			
7c, X = H	12	0.04	nd[f]	nd[g]	
8c	14	0.03			
17c	21	0.07			
7d, X = 3-OCH_3	<1	<0.01	>3	0.8	3
8d	<1	<0.01			
17d	7	0.16			
7e, X = 4-CF_3	8	0.11	nd[h]	nd[h]	nd[h]
8e	7	0.11			
10e	13	0.09			
7f, X = CN	11	0.10	11	>3	>3
8f	10	0.10			
17f	11	0.10			

[a] By single photon counting of fluorescence. [b] By comparison with a value of 0.13 for toluene in methanol. [c] By Stern–Volmer quenching studies of fluorescence spectra. [d] By triplet–triplet absorption using laser flash photolysis. [e] By Stern–Volmer quenching studies of triplet–triplet absorption. [f] Not determined, see text. [g] No triplet–triplet absorption observable. [h] Not determined.

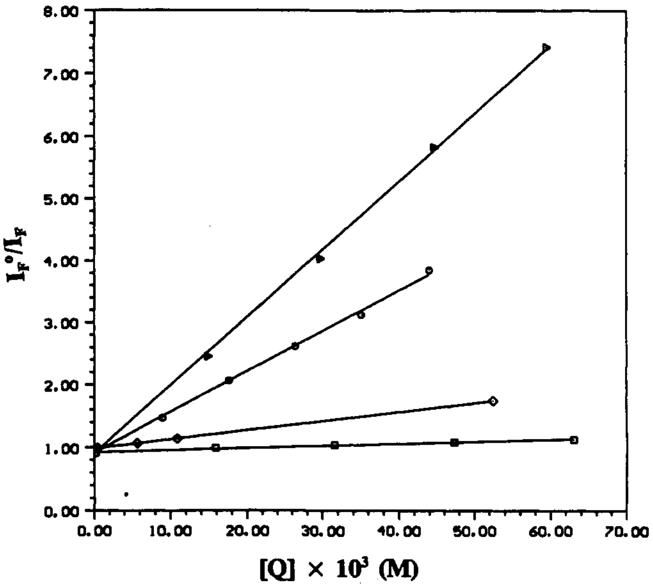
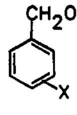


Figure 1. Stern–Volmer quenching plots of the fluorescence intensity of the esters **8a** (◇), **8b** (○), **8c** (□), and **8f** (△) by 2,3-dimethyl-1,3-butadiene.



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The $k_Q{}^S$ values for the pivalate esters (**8**) were determined from the Stern–Volmer plots of $I_F{}^0/I_F$ versus diene concentrations shown in Figure 1. For the 3-methoxy isomer, **8d**, the singlet lifetime is so short (<1 ns) that even at 0.1 M diene concentration

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(16) Cristol, S. J.; Bindel, T. H. *J. Org. Chem.* **1980**, 45, 951.

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the value of I_F^0/I_F is only 1.3. The slope of this plot is therefore difficult to determine reliably. For the unsubstituted case, absorption measurements indicate that the long wavelength tail of the absorption band of the diene was competing for light absorption with the weak π,π^* absorption of the aromatic ring. At lower concentrations of the diene, this competitive absorption disappeared but then no quenching of the fluorescence was observed. Tests with other substituted dienes (piperylene, cyclohexadiene) indicated that this effect was minimized for 2,3-dimethylbutadiene probably because the adjacent methyl groups distort the geometry of the diene from planarity to some extent. This competitive absorption was not a problem for the substituted aromatics which have higher extinction coefficients at longer wavelengths. Combining the singlet lifetimes (τ_S) with the Stern–Volmer slopes ($k_Q{}^S\tau_S$) gave the $k_Q{}^S$ values shown in Table 2. Quenching of the excited singlet states of substituted naphthalene rings by dienes has been reported previously[19,20] and is very efficient. The same is true for these substituted benzenes. In agreement with the naphthalene work, there is an electron-transfer component to this quenching with the diene as the donor and the aromatic as the acceptor. The rate constant for quenching (11×10^9 M^{-1} s^{-1}) approaches the diffusional limit[21] in methanol (18×10^9 M^{-1} s^{-1}) for the most easily reduced substrate, the 4-cyano case, **8f**.

The values of τ_T and $k_Q{}^T$ were determined by laser flash photolysis.[22] Excitation of the substituted benzyl acetates at 266 nm in methanol gave a strong absorption in the 300–350-nm range and a weaker band around 400 nm. The band at 400 nm was quenched by both oxygen and 2,3-dimethylbutadiene and was assigned to the triplet–triplet absorption of the acetate. The shorter wavelength band is probably a combination of the triplet and benzylic radical since this absorption decreases in intensity with the 400-nm band, but persisted after the latter disappeared. Interestingly, this band for the radical still appeared even after all the triplets had been quenched by added diene. This suggests that the radical is generated from the singlet state. The signal for the triplet–triplet absorption was in general weak. Moreover, the strong fluorescence from the acetates and the absorption by the benzylic radical make the measurements for the triplet decay difficult. The values reported in Table 2 for τ_T and $k_Q{}^T$ should best be considered semiquantitative. Nevertheless, they do provide the necessary information for doing selective quenching studies. As expected, the τ_T values are in the millisecond range, 3 orders of magnitude longer than the τ_S values. The $k_Q{}^T$ values are close to the diffusional limit, in agreement with the exothermic nature of this process.

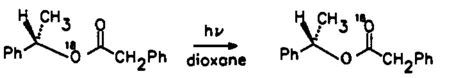
The values for product yields for the photolysis of a selected set of the esters **7** and **8** in the presence of 2,3-dimethylbutadiene are reported in Table 3 along with those for unquenched direct irradiations. The results in Table 3 show that the direct and quenched irradiations gave essentially the same values for the product yields in almost all cases; therefore, triplet excited states and triplet radical pairs can be ignored. The exception is the decreased yield of the arylmethyl dimers, **13**; presumably some of the out-of-cage arylmethyl radicals are reacting with the diene quencher. This comparison of product mixtures in direct and triplet quenched reactions is the classic "fingerprint" method.[23]

Quantitative Mechanistic Scheme. Putting the results for product yields in Table 1 along with the conclusion that only the excited singlet state S_1 is reactive requires a mechanism as outlined in Scheme 4. The process labeled k_D represents diffusion from the solvent cage before decarboxylation. Diffusion from the solvent cage after decarboxylation should not compete with in-cage coupling to **12** or with disproportionation to **10** for R = $C(CH_3)_3$. For R = CH_3, diffusion from the solvent cage is probably faster than decarboxylation (*vide supra*). Two potentially important steps are missing from this scheme: internal return of either the radical pair **16** or the ion pair **15** to the starting ester **7** or **8**. The importance of these processes can be determined by selective labeling of the alcohol oxygen of the ester with ^{18}O followed by monitoring of the scrambling of this label to the carbonyl oxygen as a function of percent conversion to products. This is a process that could have a major influence on product yields if, for instance, internal return occurs from the ion pair **15** and if the efficiency of this process is substituent dependent. The result would be a decrease in the yield of products derived from the ion pair independent of the pathway and efficiency of its formation.

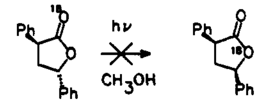
Table 3. Product Yields for the Esters **7** and **8** in Methanol with the Quencher, 2,3-Dimethylbutadiene

ester	[Q] × 10^3 (mol/L)	%T	%S	**9**	**10**	**11/12**	**13**	**14**
7a, X = 4-OCH_3	0			2	1	14	48	25
	1.0	96	0.5	2	1	13	20	30
8a, X = 4-OCH_3	0				13	48	23	4
	1.0	96	0.5		10	35	20	6
7b, X = 4-CH_3	0			8	2	14	52	21
	2.0	76	11	7	2	11	54	14
7d, X = 3-OCH_3	0			32	1	14	38	
	6.6	94	<2	31	1	13	18	
8d, X = 3-OCH_3	0			10	17	46	20	
	6.6	94	<2	15	13	46	19	
7f, X = 4-CN	0			2	5	16	67	5
	1.2	92	13	5	5	19	49	7

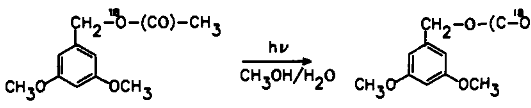
There are literature reports of ^{18}O exchange in ester photochemistry as outlined in eqs 7,[24] 8,[24] and 9.[25] For eq 7, after 50% conversion of the ester to products, the label was 35% scrambled, but the chiral center had maintained its configuration. For eq 8, after 53% conversion, there was neither ^{18}O scrambling nor *trans* to *cis* isomerization. For eq 9, after 48% conversion, the label was 68% scrambled. On the basis of these results, Givens[24] suggested that the observed ^{18}O scrambling does not occur through a fragmentation/recombination pathway but rather through a concerted 1,3-migration of the benzylic carbon from the alcohol oxygen to the carbonyl oxygen of the ester. For the lactone in eq 8, this process is geometrically impossible so neither ^{18}O exchange nor isomerization results. For the ester in eq 7, exchange is possible by this concerted mechanism but racemization is not. In effect, the conclusion reached is that the exchange process only contributes to excited state decay and to a decreased quantum yield of product formation. It does not complicate the reactivity



(7)



(8)



(9)

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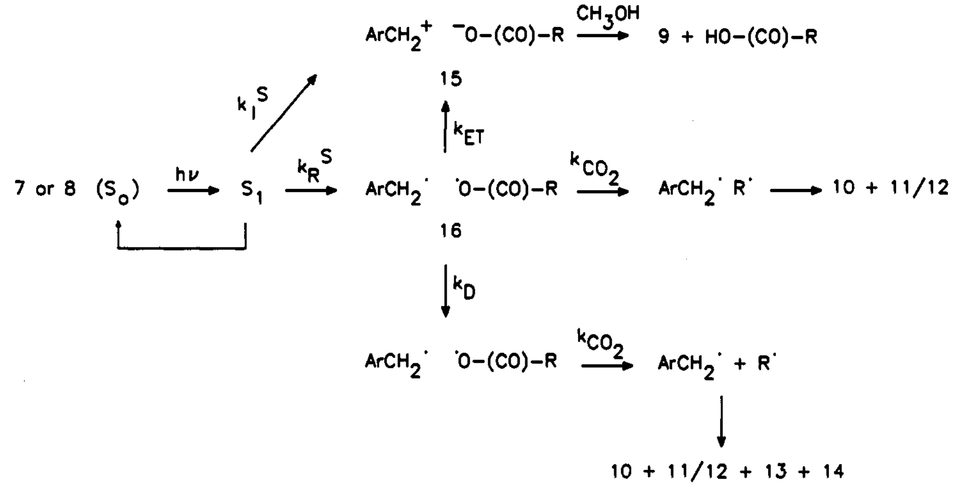
Scheme 4. Possible Reaction Pathways for Formation of the Products **9–14** from the Esters **7** and **8**



of either the radical or the ion pairs. We are currently testing this tentative conclusion in more detail and particularly as a function of substituents.[26]

Assuming that internal return does not interfere with the distribution of products derived from either the radical or the ion pair, Scheme 4 can be used to obtain rate constants for the reactivity of the various species involved by using the product yields in Table 1.

As a starting point for this discussion, we will assume that the total yield of the methyl ethers (**9**) formed by photolysis of the pivalate esters (**8**) results from direct heterolytic cleavage of the C–O bond in the excited singlet state (k_I^S). This process is maximized for the 3-methoxy compound, **8d**, at 10%, drops to 5% for the unsubstituted compound, **8c**, but is undetected (<0.5%) for the other substituted compounds. These observations are consistent with the prediction[2] of the "*meta* effect" for enhanced excited state heterolytic cleavage with the electron donating substituent at the *meta* position. However, it is important to emphasize that this process is only a minor component in the overall mechanism. The singlet excited state behaviors for the acetates and pivalates, as determined by fluorescence quantum yields and singlet lifetimes, are essentially identical (Table 2). This is expected since the alkyl group is remote from the benzylic chromophore. Therefore the efficiency of direct heterolytic cleavage for the acetates should parallel that for the pivalates and also be maximized for the 3-methoxy case. The higher yield of the ether obtained for photolysis of the acetates must result from the intervention of another process, and the only possibility in Scheme 4 is the formation of the ion pair by electron transfer (k_{ET}) from the initially formed radical pair. We will return to a quantitative analysis of this process later.

Because the yields of the ion pairs and thus the ion-derived products are so low for the pivalate esters, these substrates serve as good probes for the reactivity of the radical pair. The two competing pathways are decarboxylation and diffusional escape from the solvent cage (k_{CO_2} and k_D in Scheme 4). Also, for the pivalates, the yield of the methanol incorporated alcohol, **14** ($ArCH_2CH_2OH$), is negligibly low for most cases. This observation is consistent with the expected reactivity of $(CH_3)_3CCO_2^{\bullet}$ because neither this radical nor the $(CH_3)_3C^{\bullet}$ radical will be capable of rapid hydrogen atom abstraction from the solvent, methanol (*vide supra*). Because the rate of decarboxylation of the $(CH_3)_3CCO_2^{\bullet}$ radical has been determined previously, it can be used as a "radical clock"[27] for diffusional escape. This is not straightforward, however, since the radical disproportionation product, **10** ($ArCH_3$), and the radical coupling product, **12** ($ArCH_2$–R, R = $C(CH_3)_3$), will be formed either from in-cage radical pairs or from a reencounter of out-of-cage radical pairs. Fortunately, a reasonable assumption can be made that, once the radical pair has separated by diffusion, reencounters leading to disproportionation, **10**, and coupling, **12**, should occur at the same rate as reencounters leading to the dimer, **13** ($ArCH_2CH_2Ar$). This is true because the concentration of the two radicals, $ArCH_2^{\bullet}$ and $(CH_3)_3C^{\bullet}$, will be the same; eq 10 then applies. This equation

$$\text{yield}(\mathbf{10} + \mathbf{12})/\text{yield}(\mathbf{13}) = (k_{CO_2} + k_D/2)/(k_D/2) \qquad (10)$$

$$k_D = 2k_{CO_2}/[(\text{yield}(\mathbf{10} + \mathbf{12})/\text{yield}(\mathbf{13})) - 1] \qquad (11)$$

simply states that **10** and **12** are formed by two routes and that half of the out-of-cage radicals form **10** and **12**, and the other half, **13**. Rearranging eq 10 gives eq 11. Because k_{CO_2} (11 × 10^9 s^{-1}) is known, k_D can be evaluated from product yield data for each substrate. For the six compounds (**8a–f**) studied, a value of (6 ± 1) × 10^9 s^{-1} is obtained, which is in very good agreement with the value of 5.6 × 10^9 s^{-1} calculated from the simple diffusional separation equation[14] (*vide supra*). The conclusion to be reached from the pivalate chemistry is that greater than 90% of the reactivity can be rationalized by homolytic cleavage of S_1 to form a radical pair followed by competition between two pathways, in-cage decarboxylation and diffusional escape.

For the acetates, **7**, the electron-transfer pathway is clearly more important since the ether derived from the ion pair is now formed in higher yield (up to 32% for the 3-methoxy case). Some of the yield of the ether, 10% for the 3-methoxy compound and 5% for the unsubstituted one, is formed by direct heterolytic cleavage. Therefore, the remaining 22% and 21% (for the 3-methoxy and unsubstituted compounds, respectively) are formed by the electron-transfer pathway. The rate constant for electron transfer, k_{ET}, can be determined according to the mechanism in Scheme 4 by eq 12, where the yield of **9** (after subtracting the

$$\text{yield}(\mathbf{9}) = k_{ET}/(k_{ET} + k_{CO_2} + k_D) \qquad (12)$$

$$k_{ET} = (k_{CO_2} + k_D)/[(1/\text{yield}(\mathbf{9})) - 1] \qquad (13)$$

amount of **9** formed by direct heterolytic cleavage) is simply expressed as a ratio of the possible pathways of reaction for the radical pair. Rearranging eq 12 gives eq 13. Because k_{CO_2} (1 × 10^9 s^{-1}) is known from previous results and k_D should be very similar to that obtained from the pivalate results (6 × 10^9 s^{-1}), the only unknown in eq 13 is k_{ET}. It is important to understand that k_{CO_2} and k_D are serving as "radical clocks"[27] for k_{ET}. Any error in these values will be transferred to k_{ET}, but only as a scaling factor and not by changing their relative magnitudes. We

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Table 4. Values of k_{ET} and E_{ox} for the Radical Pair Generated in the Photolysis of Esters, **7**

ester	yield of **9** (%)	$k_{ET} \times 10^9$ (s^{-1})	E_{ox} (V)
7a, X = 4-OCH_3	1.7[a]	0.12 ± 0.01	0.26
7b, X = 4-CH_3	8.0[a]	0.61 ± 0.02	0.51
7c, X = H	26[b]	1.8 ± 0.4 (2.5 ± 0.3)[c]	0.73
7d, X = 3-OCH_3	32[b]	2.0 ± 0.5 (3.3 ± 0.3)[c]	0.79
8e, X = 4-CF_3	1.0[a]	0.071 ± 0.015	1.00[d]
8f, X = 4-CN	0.3[a]	0.021 ± 0.014	1.08

[a] Error estimated at ±0.2%. [b] Error estimated at ±2%. [c] Calculated assuming that the total yield of ion pairs (which form ether **9**) is formed by electron transfer in the radical pair. See text. [d] Not determined but obtained from the $\rho\sigma^+$ plot using $\sigma^+ = 0.54$ and the literature value[28] of $\rho = 0.475\ V/\sigma^+$.

have made what we think are very good estimates for the "clock" rate constants so that the scaling factor is unlikely to be greater than a factor of 2. The values of k_{ET} obtained this way are given in Table 4 along with the known values[28] for the oxidation potentials of the substituted benzylic radicals in acetonitrile. Because the yield of **9** is very low for most cases, considerable care has been taken to insure that these values are as reliable as possible. Multiple samples, multiple GC injections, and multiple standards were used. For the values below 10%, the estimated error is about ±0.2%. For the 4-cyano case, the value is just above detection limits but still measurably greater than zero.

Previously,[7,8] we have successfully analyzed electron-transfer rate data for the conversion of the radical pair to the ion pair in the photochemistry of 1-naphthylmethyl esters (eq 3) by Marcus' theory[29] of electron transfer. This required fitting the k_{ET} values to eqs 14, 15, and 16. The fitting parameters are the following:

$$k_{ET} = \sum_{j=0}^{\infty} F_j V^2 \frac{(4\pi^3)^{1/2}}{(h^2 \lambda_S k_B T)^{1/2}} \exp\left(-\frac{(jh\nu_V + \Delta G_{ET} + \lambda_S)^2}{4\lambda_S k_B T}\right) \tag{14}$$

$$F_j = \frac{e^{-S} S^j}{j!} \tag{15}$$

$$S = \frac{\lambda_V}{h\nu_V} \tag{16}$$

ν_V, the vibrational modes that are important in the vibrational electronic coupling; λ_S, the solvent reorganization energy; λ_V, the nuclear reorganization energy; and V, the matrix coupling term. The fit also requires values of ΔG_{ET} (as a function of substituents) as given by eq 17, where F is the Faraday constant, E_{OX} is the

$$\Delta G_{ET} = F(E_{ox} + E_{RED}) + A + e^2/Dr_{12} \tag{17}$$

oxidation potential of the substituted benzylic radical in acetonitrile (Table 4), E_{RED} is the reduction potential of the acyloxy radical, and A is an unknown factor that corrects for the fact that the measured values of E_{OX} are in acetonitrile but the photochemistry was done in methanol. As before, we assume that this value is independent of substituents on the aryl ring so that eq 17 simplifies to eq 18 where B replaces all the constant terms in eq 17.

$$\Delta G_{ET} = FE_{ox} + B \tag{18}$$

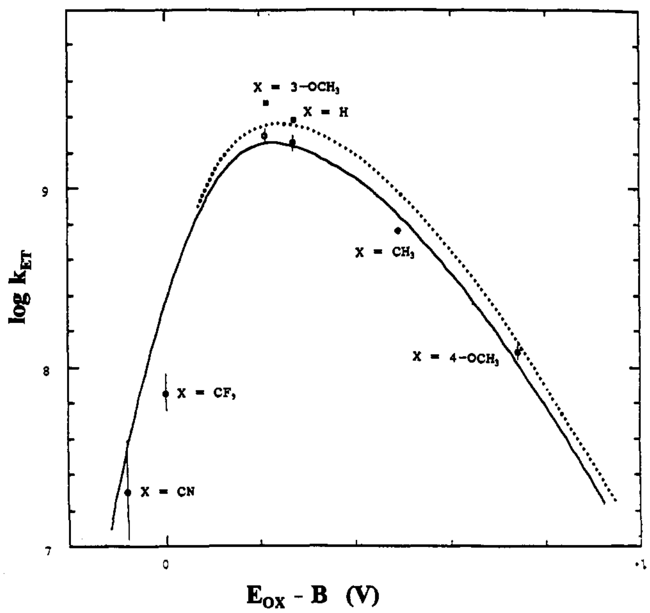

Figure 2. Plot of the rate of electron transfer (k_{ET}) for converting the radical pair **16** to the ion pair **15** as a function of the oxidation potential (E_{OX}) of the benzylic radical. The fits are to eqs 14 and 18. The solid line has $\lambda_V = 0.1$ eV, $\lambda_S = 0.2$ eV, $V = 2.2\ cm^{-1}$, and $B = -1$ V; the dashed line is the same except $V = 2.6\ cm^{-1}$. The difference is the method of calculating k_{ET} for X = H and X = OCH_3. The circles are obtained by assuming that some of the ether **9** is derived from direct heterolytic cleavage, the squares that all of the ether **9** is by the electron-transfer pathway. See text.

The data in Table 4, fitted to eqs 14 and 18, are plotted in Figure 2.[30] A value of 1500 cm^{-1} was assigned to λ_V which is typical of both carbon–carbon skeletal vibrations in the arylmethyl species and the carbonyl stretch in the carboxylate anion.[31] The other parameters obtained were $V = 2.2\ cm^{-1}$, $\lambda_V = 0.1$ eV, $\lambda_S = 0.2$ eV, and B = −1.0 V.

This plot is qualitatively similar to that obtained previously for the radical pair to ion pair process for 1-naphthylmethyl esters.[7,8] The quantitative differences will be discussed below. The plot clearly shows that the electron-transfer process is slow for electron withdrawing groups (X = 4-CN, X = 4-CF_3), resulting in very low yields of the methyl ether that would be formed from the ion pair. The electron-transfer rate is a maximum for the 3-methoxy and the H cases and then decreases in the inverted region as the process becomes thermodynamically more favorable for electron donating groups (X = 4-CH_3, X = 4-OCH_3). The reason for the high yield of the ion-derived product for the 3-methoxy esters is mainly a result of the increased rate of electron transfer relative to those of the other substituents, particularly, for historical reasons,[2] 4-methoxy.

To arrive at the data plotted in Figure 2, we assumed that some of the ether (**9**) was formed by a pathway of direct heterolytic cleavage of the excited singlet state to the ion pair. The importance of this pathway was estimated by the results for the photochemistry of the pivalates (**8**). If the assumption is made instead that all of the ether (**9**) is formed by the electron-transfer pathway for all substrates (i.e. $k_R \gg k_I$), then different values of k_{ET} are obtained for the 3-methoxy and H substituted radical pairs. These slightly larger values of k_{ET} are shown in Table 4 (and are also plotted, with solid squares, in Figure 2). Although the fitting of the data is now slightly worse, only a slight increase in V from 2.2 to 2.6 cm^{-1} is required to make the two fits very comparable (dashed line in Figure 2). The decision as to which of these

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mechanisms is preferred is therefore not possible with the present data, but the major conclusion is clear. Homolytic cleavage of the carbon–oxygen bond in the excited singlet state of the ester is the major photochemical pathway and rationalizes greater than 90% of the product yield data even for the 3-methoxy case. For the other substituted esters, greater than 95% of the reaction proceeds by this mechanism. The substituents have little effect on the efficiency of direct heterolytic cleavage; the "*meta* effect" is minimal.

Returning to the quantitative aspects of the fit of the data to the electron transfer (eq 14), the major difference between the results for the 1-naphthylmethyl–(phenylacetyl)oxy radical pair (NaphthylCH_2• •O–(CO)CH_2Ph)[7,8] and the present results for the benzylic–acetyloxy radical pair (PhCH_2• •O–(CO)–CH_3) is the very large decrease in the rate of electron transfer for the latter. The maximum rate in Figure 2 is 1.8×10^9 s^{-1} for the 3-methoxy compound as compared to a maximum of 5.5×10^{10} s^{-1} for the 4-methyl substituent in the 1-naphthylmethyl case. The total reorganization energy, λ, of 0.3 eV for the benzylic substrates is similar to but smaller than the value of 0.5 eV determined previously for the 1-naphthylmethyl compounds. This lower value for a reorganization energy should increase the rate of electron transfer for the benzylic radical pairs. Therefore, the large decrease in the rate of electron transfer must be due entirely to the large drop in the value of the matrix coupling term V from 12.4 to 2.2 cm^{-1}. Because this term is well-known to be distance dependent,[32,33] this observation suggests that the radical pair is further separated for the benzylic radical pairs before electron transfer takes place, perhaps because diffusion is more rapid for the smaller radical pair species. Whatever the reasons for this decreased value, the consequences are obvious. Electron transfer in the radical pair is slow enough so that it no longer dominates diffusional escape (k_D), particularly for the acetates, or decarboxylation (k_{CO_2}), particularly for the pivalates. Therefore, overall, ion pairs are much less important reaction intermediates.

The reorganization energy values are also very different for the benzylic radical pair ($\lambda_V = 0.1$ eV and $\lambda_S = 0.2$ eV) when compared to those for the 1-naphthylmethyl case ($\lambda_V = 0.1$ eV and $\lambda_S = 0.5$ eV). The asymmetry in the Marcus "parabola" in the inverted region requires inclusion of nuclear reorganization, λ_V. The value obtained, for λ_V, of 0.1 eV is small but reasonable on the basis of the fact that the electron is being transferred from a nonbonding MO of the benzylic radical to, at least superficially, a nonbonding MO on the acetyloxy radical. We have tried to estimate λ_V[8] by MO calculations of the bond length and angle changes required for converting the radical pair (PhCH_2• •O_2-CCH_3) to the ion pair (PhCH_2^+ $^-O_2$CCH_3) and obtained a value of about 0.2 eV. This value can be attributed entirely to the change from an asymmetric structure (unequal C–O bond lengths) in the acyloxy radical to a symmetric one for the acetate anion (equal C–O bond lengths). In fact, we were surprised a value of zero for λ_V was obtained previously. The solvent reorganization energy, λ_S, of 0.2 eV seems small since typical values of 0.5 eV are obtained for electron transfer over short distances.[7,8,32,33] However, the only literature precedent for charge separation electron transfer in radical pairs is our own,[7,8] so comparative discussions are difficult.

Conclusion

The photolysis of 3-methoxybenzyl acetate (**7d**) in aqueous dioxane[2] has often been cited as a fundamental example of substituents directing formation of ionic intermediates in photochemical reactions. Our more detailed reinvestigation of substituent effects in these reactions has demonstrated that this pathway is, at the most, a minor one. The major pathway for generation of ionic intermediates is by electron transfer from the initially formed radical pairs. The implications that these results have for other examples of photochemical generation of ionic intermediates should be seriously considered.

Experimental Section

General Procedure. Proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were obtained in $CDCl_3$ on a 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 spectrophotometer, and 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 5890 A GC 5970 with a mass selective detector. The column used was a 25-m × 0.2-mm 5% phenylmethyl 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 $M^{•+}$.

GC/FID analyses were obtained on a Hewlett Packard 5890 A gas chromatograph using a Hewlett Packard 7673 automatic injector with a Hewlett Packard 7673 A controller and a Hewlett Packard 3396 A integrator. A 1-m glass column was used with 10% Fluorad FC-431 and 1% H_3PO_4 on Chromosorb W HP 80/100 mesh. The detector used was a flame ionization detector.

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 × 0.46 cm) with a Waters Model 450 variable wavelength detector. UV detection for monitoring the reactions 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), purchased from the Aldrich Chemical Co., was used for normal column chromatography.

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. Fluorescence quantum yields were determined by comparison with a fluorescence quantum yield of 0.13 for toluene in methanol.[21] Singlet state energies were determined by the position of the 0,0 band using the overlap between the emission and excitation spectra. Singlet lifetimes were measured using a PRA single photon counting apparatus with a hydrogen flash lamp of pulse width about 1 ns.

Syntheses of the Benzyl Alcohols (17a–f). The preparation of the esters **7** and **8** required the corresponding benzyl alcohols. The alcohols **17** were either purchased from the Aldrich Chemical Co. or, for **17b,f**, prepared by the following methods:

4-Methylbenzyl Alcohol (17b). 4-Methylbenzoic acid was reduced with $LiAlH_4$ in diethyl ether. To 28.4 g (0.75 mol) of $LiAlH_4$ in 1 L of diethyl ether was added 40.0 g (0.29 mol) of 4-methylbenzoic acid in 300 mL of THF. The addition was continued so that the ether was at a constant reflux. After the addition was complete, the solution was allowed to stir for 3 h and water (300 mL) followed by 30% aqueous H_2SO_4 (300 mL) was added. The solution was filtered, the ether layer was separated and dried, and the solvent was removed to give 29.4 g (0.24 mol, 83%) of 4-methylbenzyl alcohol. The crude alcohol was recrystallized from heptane, mp 59-61 °C (lit.[34] 61–62 °C). The ^{1}H NMR of the purified alcohol was identical to that found in the literature.[35]

4-Cyanobenzyl Alcohol (17f). To a solution of 3.14 g (0.024 mol) of 4-cyanobenzaldehyde in 40 mL of ethanol was slowly added 0.30 g (0.008 mol) of sodium borohydride. The solution was kept at room temperature, and the reaction was stirred for 3 h. Water (50 mL) was then added to destroy any excess sodium borohydride. The aqueous layer was extracted twice with CH_2Cl_2 (2 × 40 mL), the organic layers were combined and dried with $MgSO_4$, and the solvent was removed under reduced pressure

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[32] Gould, I. R.; Moody, R.; Farid, S. *J. Am. Chem. Soc.* **1988**, 110, 7242 and references therein.

[33] Closs, G. L.; Calcaterra, L. T.; Green, N. J.; Penfield, K. W.; Miller, J. R. *J. Phys. Chem.* **1986**, 90, 3673.

[34] *CRC Handbook of Chemistry and Physics*, 70th ed.; Weast, R. C., Ed.; Chemical Rubber Corp.: Boca Raton, FL, 1989–1990; p C-147.

[35] *Aldrich Library of NMR Spectra*, 2nd ed.; Pouchert, C. J., Ed.; Aldrich Chemical Co. Inc: Milwaukee, WI, Vol. 1, 1983; p 936-C.

to give the impure alcohol. Column chromatography of the crude alcohol gave the pure compound as a colorless solid, mp 131–133 °C (lit.[36] 133–134 °C).

General Method for the Preparation of Esters 7 and 8. The corresponding acid chloride (0.02 mol) in 30 mL of dry benzene was added to a solution of the corresponding benzyl alcohol (0.02 mol) and 1 mL of pyridine in 50 mL of dry benzene. The solution was stirred overnight at room temperature. Then 50 mL of water was added 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 column chromatography followed by distillation. The yields were 40–80%.

4-Methoxybenzyl Acetate (7a): bp 92–95 °C at 0.5 mmHg (lit.[37] 180–181 °C at 30 mmHg); UV (CH_3OH) λ_{max} 273.5 (ϵ 1520), 280 (1320) (lit.[38]); ^{1}H NMR δ 7.28 (d, 2H, J = 8.6 Hz), 6.87 (d, 2H, J = 8.7 Hz), 5.02 (s, 2H, CH_2—O), 3.77 (s, 3H, CH_3—O), 2.05 (s, 3H, CH_3C=O); ^{13}C NMR δ 170.8 (C=O), 159.5 (C), 130.0 (CH), 127.9 (C), 113.8 (CH), 66.0 (CH_2—O), 55.2 (CH_3—O), 21.0 (CH_3); IR (neat) 3000, 2960, 2900, 2820, 1745 (C=O), 1620, 1590, 1470, 1380, 1360, 1300, 1250, 1175, 1030, 960, 820 cm^{-1}; GC/MS 180 ($M^{\cdot+}$, 48), 138 (24), 122 (11), 121 (100), 120 (42), 92 (11), 91 (37), 78 (20), 77 (33).

4-Methylbenzyl Acetate (7b): bp 65–67 °C at 0.5 mmHg (lit.[37] 137–138 °C at 30 mmHg); UV (CH_3OH) λ_{max} 253 (ϵ 230), 259 (270), 268 (180), 269 (220); ^{1}H NMR δ 7.25 (d, 2H, J = 8.0 Hz), 7.17 (d, 2H, J = 7.9 Hz), 5.06 (s, 2H, CH_2—O), 2.35 (s, 3H), 2.08 (s, 3H, CH_3C=O); ^{13}C NMR δ 170.8 (C=O), 138.0 (C), 132.8 (C), 129.1 (CH), 128.3 (CH), 66.2 (CH_2-O), 21.1 (CH_3C=O), 21.0 (CH_3); IR (neat) 3040, 3020, 2960, 2920, 1750 (C=O), 1520, 1380, 1360, 1240, 1020, 800 cm^{-1}; GC/MS 164 (M^{+}, 38), 122 (76), 107 (59), 105 (100), 104 (63), 103 (39), 93 (17), 91 (36), 79 (32), 78 (59), 77 (59), 65 (29), 63 (18), 51 (25).

Benzyl Acetate (7c). This compound, purchased from the Aldrich Chemical Co., was distilled under reduced pressure and chromatographed through silica gel before use. The ^{1}H NMR, ^{13}C NMR, UV, and IR spectra were identical to those in the literature.[39–42]

3-Methoxybenzyl Acetate (7d): bp 86–89 °C at 0.5 mmHg (lit.[37] 165–167 °C at 30 mmHg); UV (CH_3OH) λ_{max} 271 (ϵ 1930), 277 (1750); ^{1}H NMR δ 7.27 (t, 1H, J = 7.9 Hz), 6.94–6.85 (m, 3H), 5.07 (s, 2H, CH_2—O), 3.80 (s, 3H, CH_3—O), 2.10 (s, 3H, CH_3); ^{13}C NMR δ 170.8 (C=O), 159.6 (C), 137.3 (C), 129.6 (CH), 120.3 (CH), 113.6 (CH), 66.1 (CH_2—O), 55.2 (CH_3—O), 21.0 (CH_3); IR (neat) 3000, 2940, 1750 (C=O), 1610, 1590, 1490, 1460, 1380, 1360, 1290, 1250, 1155, 1040, 775, 735, 685 cm^{-1}; GC/MS 180 ($M^{\cdot+}$, 47), 139 (12), 138 (100), 121 (41), 109 (48), 107 (21), 92 (12), 91 (49), 78 (24), 77 (46), 65 (20).

4-(Trifluoromethyl)benzyl Acetate (7e): bp 75–78 °C at 2 mmHg (lit.[37] 126–127°C at 30 mmHg); UV (CH_3OH) λ_{max} 254 (ϵ 411), 259 (490), 265 (379); ^{1}H NMR δ 7.63 (d, 2H, J = 8.2 Hz), 7.47 (d, 2H, J = 8.2 Hz), 5.16 (s, 2H), 2.13 (s, 3H); ^{13}C NMR δ 170.7 (C=O), 140.0 (C), 130.0 (q, C, J_{CF} = 37.0 Hz), 128.2 (CH), 125.6 (q, CH, J_{CF} = 3.82 Hz), 124.0 (q, CF_3, J_{CF} = 272 Hz), 65.3 (CH_2—O), 20.9 (CH_3); IR (neat) 2950, 1740 (C=O), 1617, 1450, 1375, 1360, 1320, 1220, 1160, 1120, 1060, 1040, 1012, 830, 820 cm^{-1}; GC/MS 218 ($M^{\cdot+}$, 25), 199 (15), 176 (100), 159 (94), 158 (30), 145 (23), 127 (47), 119 (14), 109 (47), 108 (13), 107 (96), 95 (10), 89 (18), 77 (13), 75 (15), 63 (16), 51 (16).

4-Cyanobenzyl Acetate (7f): mp 64–65 °C (lit.[37] 64–65 °C); UV (CH_3OH) λ_{max} 265 (ϵ 760), 270 (800), 276 (750); ^{1}H NMR δ 7.67 (d, 2H, J = 8.2 Hz), 7.46 (d, 2H, J = 7.9 Hz), 5.16 (s, 2H, CH_2—O), 2.14 (s, 3H, CH_3); ^{13}C NMR δ 170.4 (C=O), 141.2 (C), 132.3 (CH), 128.3 (CH), 118.5 (CN), 112.0 (*C*-CN), 65.0 (CH_2—O), 20.8 (CH_3); IR (Nujol) 3100, 2260, 1750 (C=O), 1630, 1380, 1300, 1265, 1065, 940, 835 cm^{-1}; GC/MS 175 ($M^{\cdot+}$, 37), 134 (11), 133 (100), 132 (20), 116 (81), 115 (40), 114 (10), 89 (33), 77 (12), 76 (11), 75 (12), 63 (20).

4-Methoxybenzyl 2,2-Dimethylpropanoate (8a): bp 85–87 °C at 1.5 mmHg; UV (CH_3OH) λ_{max} 272 (ϵ 1900), 278 (1700), ^{1}H NMR δ 7.27 (d, 2H, J = 8.6 Hz), 6.88 (d, 2H, J = 8.6 Hz), 5.03 (s, 2H, CH_2—O), 3.79 (s, 3H, CH_3—O), 1.20 (s, 9H, $C(CH_3)_3$); ^{13}C NMR δ 178.4 (C=O), 159.3 (C), 129.5 (CH), 128.5 (C), 113.8 (CH), 65.8 (CH_2—O), 55.2 (CH_3—O), 38.7 ($\mathit{C}(CH_3)_3$), 27.1 ($C(\mathit{C}H_3)_3$); IR (neat) 3000, 2980, 2940, 2880, 2840, 1740 (C=O), 1630, 1530, 1280, 1260, 1150, 1040, 820 cm^{-1}; GC/MS 222 ($M^{\cdot+}$, 14), 122 (12), 121 (100). Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 69.92; H, 8.00.

4-Methylbenzyl 2,2-Dimethylpropanoate (8b): bp 72–75 °C at 1.5 mmHg; UV (CH_3OH) λ_{max} 254 (ϵ 215), 260 (265), 264 (210), 268 (180); ^{1}H NMR δ 7.22 (d, 2H, J = 7.9 Hz), 7.15 (d, 2H, J = 7.9 Hz), 5.06 (s, 2H, CH_2—O), 2.34 (s, 3H), 1.21 (s, 9H, $C(CH_3)_3$); ^{13}C NMR δ 178.3 (C=O), 137.6 (C), 133.4 (C), 129.1 (CH), 127.8 (CH), 66.0 (CH_2—O), 38.7 ($\mathit{C}(CH_3)_3$), 27.2 ($C(\mathit{C}H_3)_3$), 21.2 (CH_3); IR (neat) 3040, 3020, 2960, 2920, 1735 (C=O), 1485, 1440, 1430, 1280, 1155, 1030, 795, 760 cm^{-1}; GC/MS 206 ($M^{\cdot+}$, 23), 107 (10), 106 (37), 105 (100), 91 (16), 79 (23), 78 (19), 77 (39), 57 (99). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.80, H, 8.60.

Benzyl 2,2-Dimethylpropanoate (8c): bp 63–65 °C at 1.5 mmHg (lit.[43] 67-70 °C at 2 mmHg); UV (CH_3OH) λ_{max} 246 (ϵ 158), 252 (198), 256 (158), 262 (99); ^{1}H NMR δ 7.30 (s, 5H), 5.08 (s, 2H, CH_2—O), 1.21 (s, 9H, $C(CH_3)_3$); ^{13}C NMR δ 178.2 (C=O), 136.4 (C), 128.4 (CH), 127.6 (CH), 66.0 (CH_2—O), 38.8 ($\mathit{C}(CH_3)_3$, 27.2 ($C(\mathit{C}H_3)_3$); IR (neat) 3050, 3020, 2960, 1735 (C=O), 1480, 1460, 1280, 1150, 1025, 740, 725, 690 cm^{-1}; GC/MS 192 ($M^{\cdot+}$, 5), 91 (98), 65 (24), 57 (100), 51 (11).

3-Methoxybenzyl 2,2-Dimethylpropanoate (8d): bp 80–82 °C at 1.5 mmHg; UV (CH_3OH) λ_{max} 271 (ϵ 1930), 277 (1740); ^{1}H NMR δ 7.25 (t, 1H, J = 7.9 Hz), 6.91–6.81 (m, 3H), 5.08 (s, 2H, CH_2—O), 3.78 (s, 3H, CH_3—O), 1.23 (s, 9H, $C(CH_3)_3$); ^{13}C NMR δ 178.2 (C=O), 159.6 (C), 138.0 (C), 129.5 (CH), 119.7 (CH), 113.3 (CH), 113.0 (CH), 65.8 (CH_2—O), 55.1 (CH_3—O), 38.8 ($\mathit{C}(CH_3)_3$, 27.2 ($C(\mathit{C}H_3)_3$); IR (neat) 3000, 2980, 2910, 2880, 2830, 1735 (C=O), 1625, 1600, 1500, 1480, 1280, 1160, 1040, 770, 680 cm^{-1}; GC/MS 222 ($M^{\cdot+}$, 79), 138 (98), 137 (37), 136 (39), 122 (24), 121 (100), 109 (37), 107 (11), 91 (65), 78 (48), 77 (48), 65 (32), 57 (99). Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 69.91; H, 7.84.

4-(Trifluoromethyl)benzyl 2,2-Dimethylpropanoate (8e): bp 84–86 °C at 22 mmHg; UV (CH_3OH) λ_{max} 253 (ϵ 419), 259 (503), 265 (398); ^{1}H NMR δ 7.61 (d, 2H, J = 8.1 Hz), 7.45 (d, 2H, J = 8.1 Hz), 5.16 (s, 2H), 1.25 (s, 9H); ^{13}C NMR δ 178.2 (C=O), 140.6 (C), 130.0 (q, C, J_{CF} = 34 Hz), 127.7 (CH), 125.5 (q, CH, J_{CF} = 3.82 Hz), 124.0 (q, CF_3, J_{CF} = 272 Hz), 65.1 (CH_2), 38.9 (C), 27.2 (CH_3); IR (neat) 2970, 2865, 1730 (C=O), 1618, 1478, 1458, 1418, 1396, 1365, 1322, 1280, 1140, 1062, 1015, 820 cm^{-1}; GC/MS 260 ($M^{\cdot+}$, 3), 159 (47), 109 (18), 85 (12), 57 (100).

4-Cyanobenzyl 2,2-Dimethylpropanoate (8f): bp 76–78 °C at 1.5 mmHg; UV (CH_3OH) λ_{max} 265 (ϵ 775), 270 (850), 277 (750); ^{1}H NMR δ 7.65 (d, 2H, J = 8.2 Hz), 7.44 (d, 2H, J = 7.9 Hz), 5.15 (s, 2H, CH_2—O), 1.25 (s, 9H, $C(CH_3)_3$); ^{13}C NMR δ 177.9 (C=O), 141.7 (C), 132.3 (CH), 127.8 (CH), 118.5 (CN), 111.7 (*C*-CN), 64.8 (CH_2—O), 38.8 ($\mathit{C}(CH_3)_3$), 27.1 ($C(\mathit{C}H_3)_3$); IR (neat) 2980, 2940, 2900, 2880, 2220, 1740 (C=O), 1620, 1485, 1460, 1400, 1370, 1280, 1150, 820 cm^{-1}; GC/MS 217 ($M^{\cdot+}$, 5), 116 (33), 89 (13), 85 (14), 57 (100). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.77; H, 6.76; N, 6.49.

Preparative Photolyses. For each ester, a solution of 1–2 g in 100 mL of methanol was purged with nitrogen and then irradiated in a Rayonet photochemical reactor using 16 lamps (75 W, 253.7 nm). The progress of the reaction was monitored by HPLC, and the reaction was stopped when the ester was >90% consumed. The products of the photolysis were separated by column chromatography and identified by spectroscopic methods.

Characterization and Preparation of the Photoproducts 9–14. Many of the products were commercially available. Those that were not available were either isolated from the photolysis mixture or synthesized by a literature procedure.

The methyl ethers (**9a–f**) were prepared from the corresponding benzyl alcohols using the following general procedure: To a well-stirred solution of 0.015 mol of the alcohol in 30 mL of DMSO was added 0.6 g (0.025 mol) of sodium hydride. The hydride was washed with hexane and then dried in the oven for 2 min. The solution was stirred for 10 min, then 5.7 mL (0.092 mol) of iodomethane was added, and the mixture was stirred for 2 h. Water (50 mL) was added, and the aqueous layer was

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(36) *Dictionary of Organic Compounds*, 5th ed.; Buckingham, J., Ed.; Chapman and Hall: London, 1982; Vol. 3, p H-02315.

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(38) *(38) Sadtler Handbook of Ultraviolet Spectra*; Simons, W. W., Ed.; Sadtler Research Laboratories Inc: Philadelphia, PA, 1979; Part 2, #2839.

(39) Reference 35, Vol. 2, p 270-C.

(40) Johnston, L. J.; Jankowski, W. C. *Carbon-13 NMR Spectra*; Wiley: New York, 1972, p 345.

(41) *(41)* Reference 38, #2832.

(42) *(42) Aldrich Library of Infrared Spectra*, 1st ed.; Pouchard, C. J., Ed.; Aldrich Chemical Co. Inc: Milwaukee, WI, Part 2, 1981; p 1018-C.

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then extracted twice with CH_2Cl_2 (2 × 25 mL). The organic layer was washed with water (NaCl sat) and dried with $MgSO_4$. The solvent was removed under reduced pressure to give the crude ethers which were further purified by distillation. The ^1H NMR spectra of **9a-d,f** were identical to those in the literature.[44]

4-(Trifluoromethyl)benzyl Methyl Ether (9e): bp 65 °C at 2 mmHg; ^1H NMR δ 7.61 (d, 2H, J = 8.3 Hz), 7.44 (d, 2H, J = 8.1 Hz), 4.51 (s, 2H, CH_2—O), 3.41 (s, 3H, CH_3—O); ^{13}C NMR δ 143.9 (C), 127.6 (CH), 125.3 (q, CH, J_{CF} = 3.82 Hz), 73.9 (CH_2—O), 58.4 (CH_3—O); GC/MS 190 ($M^{\cdot+}$, 34), 189 (33), 171 (19), 160 (32), 159 (77), 145 (17), 141 (28), 121 (100), 119 (14), 109 (38), 91 (30), 89 (16), 77 (19), 75 (15), 68 (16), 63 (19), 51 (18).

The toluenes (**10a-f**) were obtained from the Aldrich Chemical Co.

The coupling product **11c** (ethylbenzene) was obtained from the Aldrich Chemical Co. The coupling products (**11a,d,e**) were prepared by a Wolff–Kishner reduction of the corresponding acetophenone obtained from Aldrich Chemical Co. A mixture of 0.009 mol of the appropriate acetophenone, 1 mL of anhydrous hydrazine, and 40 mL of diethylene glycol was heated until the ketone had dissolved. Heating was continued for 5 min. To this solution was then added 6 g of KOH, and the solution was refluxed for 1 h. After the solution was cooled, water was added and the mixture was extracted with CH_2Cl_2. The CH_2Cl_2 layer was washed with 10% HCl, then with water several times, and dried over $MgSO_4$. The solvent was removed, and the compounds were purified by distillation or chromatography.

(4-Methoxyphenyl)ethane (11a): ^1H NMR δ 7.11 (d, 2H, J = 8.4 Hz), 6.83 (d, 2H, J = 8.6 Hz), 3.78 (s, 3H, CH_3—O), 2.59 (q, 2H, J = 7.6 Hz), 1.20 (t, 3H, J = 7.6 Hz); ^{13}C NMR δ 159.5 (C), 136.4 (C), 128.7 (CH), 113.7 (CH), 55.3 (CH_3—O), 28.0 (CH_2), 15.9 (CH_3); GC/MS 242 ($M^{\cdot+}$, 14), 122 (12), 121 (100), 91 (12), 78 (24), 77 (20).

(3-Methoxyphenyl)ethane (11d): ^1H NMR δ 7.19 (t, 1H, J = 7.8 Hz), 6.80-6.63 (m, 3H), 3.77 (s, 3H, CH_3—O), 2.61 (q, 2H, J = 7.6 Hz), 1.22 (t, 3H, J = 7.5 Hz); ^{13}C NMR δ 159.7 (C), 146.0 (C), 129.4 (CH), 120.5 (CH), 113.8 (CH), 111.0 (CH), 55.3 (CH_3—O), 29.0 (CH_2), 15.6 (CH_3).

(4-(Trifluoromethyl)phenyl)ethane (11e): ^1H NMR δ 7.53 (d, 2H, J = 8.1 Hz), 7.30 (d, 2H, J = 7.9 Hz), 2.71 (q, 2H, J = 7.5 Hz), 1.26 (t, 3H, J = 7.6 Hz); ^{13}C NMR δ 143.9 (C), 128.1 (CH), 125.2 (q, CH, J_{CF} = 3.82 Hz), 28.8 (CH_2), 15.3 (CH_3); GC/MS 174 ($M^{\cdot+}$, 39), 159 (100), 155 (12), 105 (67), 51 (10).

The coupling products (**11b,11f**) were not synthesized. For quantitative purposes in these cases, the response of the FID detector was assumed to be the same as for the unsubstituted compound (**11c**) with a correction factor of $^9/_8$ for the relative carbon content.

The coupling product (**12a**) was synthesized by a Friedel–Crafts acylation followed by a Clemmenson reduction. To a solution of 14 g (0.009 mol) of anhydrous aluminum chloride in 25 mL of CH_2Cl_2 was added 8.0 g (0.067 mol) of pivaloyl chloride in 15 mL of CH_2Cl_2. To this mixture was slowly added 8.1 g (0.075 mol) of anisole in 10 mL of CH_2Cl_2. The reaction was kept at room temperature for 30 min and then was poured into a mixture consisting of 50 g of ice in 25 mL of concentrated hydrochloric acid. The aqueous layer was extracted with CH_2Cl_2 (30 mL). The organic layer was washed with sodium bicarbonate (50 mL) and dried over $MgSO_4$. The CH_2Cl_2 was removed by rotary evaporation, and the remaining liquid was distilled under vacuum.

The ketone was reduced by a Clemmenson reduction. To 2.89 g (0.01 mol) of the ketone was added amalgamated zinc (4.19 g in 19 mL of concentrated HCl). The mixture was refluxed for 18 h and filtered, and the filtrate was extracted with ether. The ether layer was washed with water and saturated sodium bicarbonate and then dried over $MgSO_4$. Purification of the product was accomplished by chromatography. The product structure was confirmed by ^1H NMR: ^1H NMR δ 7.03 (d, 2H, J = 8.7 Hz), 6.80 (d, 2H, J = 8.9 Hz), 3.78 (s, 3H), 2.43 (s, 2H), 0.88 (s, 9H). This compound was previously synthesized and characterized by Jaxa-Chamiec *et al.*[45]

The coupling product (**12e**) was isolated from the photolysis mixture. The crude reaction mixture (0.6 g) was chromatographed on a column packed with 60 g of silica gel and eluted with 1:99 ethyl acetate:hexane. One 50-mL fraction followed by 20-mL fractions was collected. Fractions 4–6 were combined, and the solvent was removed to give **12e**: ^1H NMR δ 7.52 (d, 2H, J = 7.9 Hz), 7.22 (d, 2H, J = 7.9 Hz), 2.55 (s, 2H), 0.91 (s, 9H); GC/MS 216 ($M^{\cdot+}$, 2), 159 (25), 109 (11), 57 (100).

The remaining coupling products (**12b-d,f**) were quantified by GC/FID using **11c** as a standard and correcting for carbon content.

The dimer product, 1,2-diphenylethane (**13c**), was obtained from the Aldrich Chemical Co. Product **13e** was isolated from a photolysis mixture in the following manner: the crude reaction mixture (0.6 g) was chromatographed on a column packed with 60 g of silica gel and eluted with 1:99 ethyl acetate:hexane. One 50-mL fraction followed by 20-mL fractions was collected. Fractions 14–18 were combined, and the solvent was removed to give **13e**: ^1H NMR δ 7.53 (d, 2H, J = 7.9 Hz), 7.25 (d, 2H, J = 7.9 Hz), 2.98 (s, 2H); ^{13}C NMR δ 145.0 (C), 128.7 (CH), 127.0 (q, C, J_{CF} = 272 Hz), 125.4 (q, CH, J_{CF} = 3.82 Hz); GC/MS 318 ($M^{\cdot+}$, 42), 299 (19), 160 (9), 159 (100), 109 (18). The other dimers were quantified using the corresponding toluene as an equivalent on the basis of the expected identical UV detection response in HPLC detection.

Quantitative Photolyses. The procedure followed was the same as that described in the preparative photolysis section, except the solutions contained only 100–200 mg of the ester and analyses were done with less than 50% of the ester consumed. Standard solutions of each of the products were prepared to determine the yields of the products for the photolysis reaction. The photolysis 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, **13a-f**, were not volatile enough for GC analysis and thus were analyzed by HPLC. Quenched irradiations (Table 3) were done as described above except that 2,3-dimethyl-1,3-butadiene ((1–6) × 10^{-3} M) was added to the solution.

Analytical Determination of the Ether Yields (9a,e,f). As can be seen from Table 1, the yields of photoproducts **9a,e,f** are low. These yields are important because they are necessary to determine the rate constant for electron transfer. To insure that these numbers are accurate, the analyses were done more carefully. Two separate photolyses on each of the corresponding acetate esters and two separate standards were analyzed. Each photolysis and standard sample was injected twice on the GC/FID.

Acknowledgment. We thank NSERC of Canada for financial support. P.J.W. thanks Dalhousie University for a graduate fellowship and NSERC and the Killam Foundation for scholarships. J.W.H. thanks the Sumner Foundation for a scholarship. The authors also thank Dr. L. J. Johnston, at the Steacie Institute for Molecular Sciences (National Research Council, Ottawa), for the laser flash photolysis work.

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