The Photochemistry of Conformationally Rigid Benzylic Esters: 2,2-Dimethyl-1-indanyl Acetates and Pivalates

J. A. Pincock and P. J. Wedge

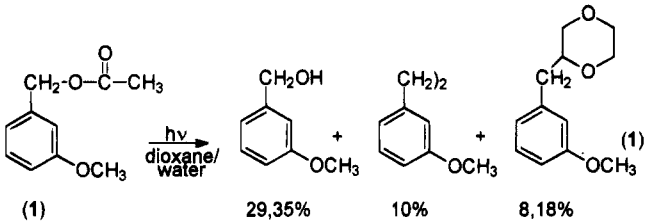
Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3

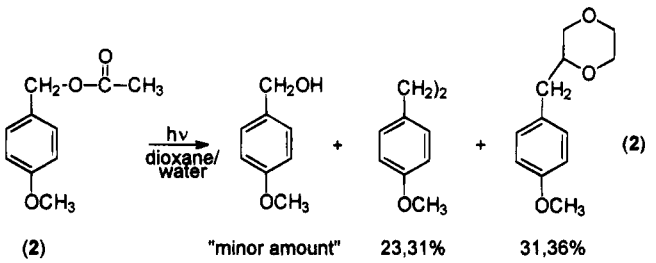
Received December 22, 1994[⊗]

The photochemistry, in methanol, of substituted 2,2-dimethyl-1-indanyl acetates **9a–c** and pivalates **10a–c** has been studied. In agreement with previous studies on benzylic esters, the results show that the substituents change the yield of products derived from the ion pair. The mechanistic conclusion reached is that the substituents change the oxidation potential of the indanyl radicals and thus the rate constant of electron transfer for converting the radical pair to the ion pair. The results also reveal two other substituent effects. First, substituents can increase the overall efficiency of the photoreaction by enhancing homolytic cleavage. The second effect is conformational. In compounds where the bond that is cleaving is conformationally mobile, such as the C–O bond in benzylic esters, substituents on the ring can change the population of the reactive conformer and thus the overall efficiency of the reaction. For the indanyl acetate esters, the difference in excited-state reaction rate between the *m*- and *p*-methoxy substituted ester is 15:1. For the *m*- and *p*-methoxy substituted benzyl acetates, this difference in reaction rate is 48:1. The larger difference in reaction rate for the conformationally mobile benzylic esters is attributed to a higher population of the unreactive conformer for the *p*-methoxy substituted ester.

Introduction

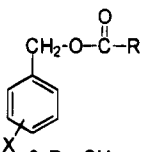
The photolysis of 3- and 4-methoxybenzyl acetate in aqueous dioxane, eqs 1 and 2, was studied by Zimmerman and Sandel.[1] As shown, the 3-methoxy isomer, **1**,





gave a higher yield of the alcohol that results from trapping of the cation by water than did the 4-methoxy isomer **2**.[2] As well, the quantum yield of reaction was higher for the 3-methoxy isomer. Zimmerman rationalized the higher yield of ionic product from the 3-methoxy isomer using the results from simple Hückel MO calculations. The calculations showed that, in the excited state, a methoxy group is a better electron-donor from the 3-position. The ability of a substituent to alter electron density in the 3- or *meta* position was termed the *meta* effect. On the basis of the above studies, the authors proposed a reaction mechanism for the photochemistry of benzylic esters in nucleophilic solvents. The excited state was assumed to undergo heterolytic cleavage to form an ion pair in competition with homolytic cleavage to form a radical pair. When the ester is 3-methoxy substituted, the changes in excited-state electron density facilitate heterolytic cleavage and both a higher yield of product from the ionic intermediate is observed and the quantum yield of reaction is increased.

Results, from Pincock and DeCosta,[3] on the photochemistry of 1-naphthylmethyl esters prompted us to do a more rigorous study on the solution photochemistry of benzylic esters. We have studied a large set of substituted benzyl acetates **3** and benzyl pivalates **4**.[4,5] After



3 R = CH_3
4 R = $C(CH_3)_3$

a careful study of product yields and photophysical properties as a function of R and X, a mechanism different from Zimmerman's was proposed (Scheme 1). The C–O bond cleaves homolytically (*i.e.* $k_R^S \gg k_I^S$) from the excited singlet state to give an in-cage radical pair. The radical pair then partitions between three pathways: electron transfer to form the ion pair (k_{ET}), diffusional separation (k_D) and decarboxylation (k_{CO_2}). The R group was shown to change the product ratios by changing the rate constants of decarboxylation of the acyloxy radicals. The rate constants of decarboxylation of the acyloxy radicals have been measured.[6] For R = CH_3, $k_{CO_2} = 1 \times 10^9\ s^{-1}$ and for R = $C(CH_3)_3$, $k_{CO_2} = 11$

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1995.

(1) Zimmerman, H. E.; Sandel, V. R *J. Am. Chem. Soc.* **1963**, *95*, 915.

(2) The yields in eqs 1 and 2 were determined by gravimetric analysis after chromatographic separation. Where there are two numbers, two separate determinations were made.

(3) DeCosta, D. P.; Pincock, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 2180.

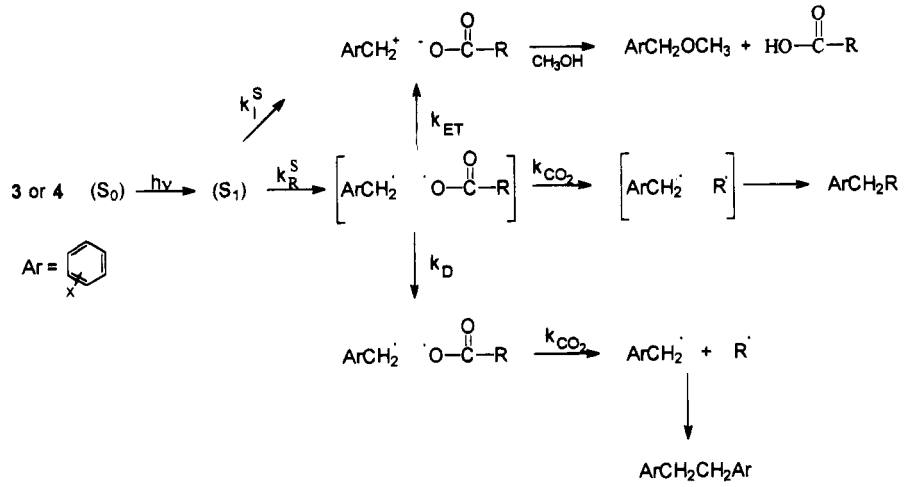
(4) Hilborn, J. W.; MacKnight, E.; Pincock, J. A.; Wedge, P. J. *J. Am. Chem. Soc.* **1994**, *116*, 3337.

(5) Pincock, J. A.; Wedge, P. J. *J. Org. Chem.* **1994**, *59*, 5587.

(6) Hilborn, J. W. and J. A. Pincock *J. Am. Chem.Soc.* **1991**, *113*, 2683.

0022-3263/95/1960-4067$09.00/0

Scheme 1



$\times 10^9\ s^{-1}$. The substituents on the aromatic ring were shown to influence product ratios by changing the oxidation potential of the benzylic radical and thus the rate constant of electron transfer. In agreement with Zimmerman's results,[1] the yield of the ether, derived from the ion pair, was greater for the 3-methoxy substituted ester, 32%, than for the 4-methoxy substituted ester, 2%. However, the enhanced yield of ion pair product is not due to enhanced heterolytic cleavage but is attributed to ground state reactions that occur after cleavage. More ether was formed from 3-methoxybenzyl acetate because the rate constant of electron transfer, for converting the radical pair to the ion pair, is greater for the 3-methoxy isomer than for the 4-methoxy isomer. However, the 3-methoxy ester was still found to be more reactive than the 4-methoxy ester.

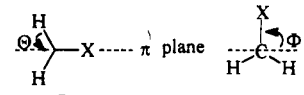
Zimmerman proposed that the enhanced reactivity of the *meta* substituted esters was due to an increased rate of heterolytic cleavage (*vide supra*). However, we have observed that the 3-methoxy substituted ester has enhanced reactivity even though heterolytic cleavage is not the important photochemical step. Others have previously observed enhanced rates of photochemical cation formation at benzylic carbons for substrates where the aromatic ring is *meta* substituted.[7,8] The fact that the *m*-methoxy group increases the efficiency of these reactions must result from either its ability to increase the rate of homolytic cleavage or from some, as yet, unknown effect. One possibility that has not been examined previously is the effect of substituents on conformational equilibria.

As is well known,[9] the importance of conformational populations in a reaction depends upon the rate of interconversion of the two conformers relative to their rates of reaction. A paradigm for this is shown below, eq 3, where A and B are two conformers of a compound

$$C \leftarrow A \rightleftharpoons B \rightarrow D \qquad (3)$$

and C and D are the products from each conformer. If the rate of interconversion of the two conformers is slow relative to their rate of reaction the Curtin–Hammett principle and the Winstein–Holness principle break down and product ratios are controlled, at least in part, by the rate of conformational interconversion. Examples of this are rare in ground state chemistry but not for photochemical reactions[10] because the rates of reaction can be fast enough to be competitive with conformational motion.

For benzylic compounds ($ArCH_2X$) there are two stable conformers of the C–X bond, one with the X group in the plane of the ring, **5**, and the other perpendicular, **6**. For photochemical benzylic cleavage reactions the reactive conformer will be the one with the C–X bond homoconjugated to the ring and therefore, perpendicular to the plane. This situation is a modification of the



5 **6**

systems mentioned above because only one of the conformers can react to give product. A simple kinetic scheme for this reaction is given below, eq 4.

$$\mathbf{5} \rightleftharpoons \mathbf{6} \rightarrow \text{cleaves} \qquad (4)$$

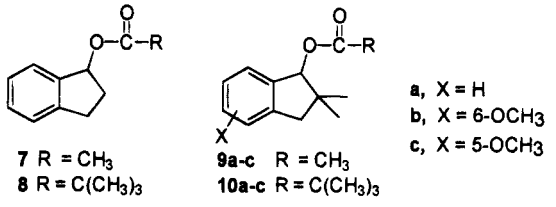
The barrier to rotation and the preferred conformation in benzylic compounds has been determined by the J-method,[11] a high resolution NMR technique. This method is applicable to benzene derivatives containing side chains and requires accurate measurement of the long-range coupling constant, ^6J, between a nucleus in the *para* ring position and a nucleus bonded to the carbon in the α position of the side chain.

To our knowledge conformational equilibria of benzylic esters have not been studied, but Schaefer et al.[12] have determined preferred conformations for the benzyl alkyl ethers, X = OR (R = CH_3, CH_2CH_3, $CH(CH_3)_2$, $C(CH_3)_3$). The difference in energy between the two conformers **5** and **6** is quite small, <2 kcal/mol. The lower energy conformer has the CH_2–O bond perpendicular to the plane of the aromatic ring. However, because the energy difference between the two conformers is quite small the stability of the two conformers can easily be reversed by changing the solvent or adding substituents to the

(7) McEwen, J.; Yates, K. *J. Phys. Org. Chem.* **1991**, *4*, 193.
(8) Wan, P.; Chak, B.; Krogh, E. *J. Photochem. Photobiol. A* **1989**, *46*, 49.
(9) Seeman, J. I. *Chem. Rev.* **1983**, *83*, 83.
(10) Wagner, P. J. *Acc. Chem. Res.* **1983**, *16*, 461.
(11) Parr, W. J.; Schaefer, T. *Acc. Chem. Res.* **1980**, *13*, 400.
(12) Schaefer, T.; Cox, K. J.; Morier, C. L.; Beaulieu, C.; Sebastian, R.; Penner, G. H. *Can. J. Chem.* **1990**, *68*, 1553.

aromatic ring. For instance, when chlorine substituents were added to the *meta* position the in-plane conformer became more stable. Substituent and solvent effects can only be important when the energy difference between the two conformers is small. For instance, Schaefer's results on benzyl chlorides using the J-method indicate that the energy difference between the two conformers is larger, >2 kcal/mol, and the stable conformer is always the out-of-plane one independent of solvent or substituent.

If the energy difference between the two conformers of benzylic esters is small and substituent dependent, as is the case with the benzylic ethers, then it is possible that the enhanced reactivity of the *meta* substrates is due to an increased population of the reactive conformer. To test this possibility, indanyl esters **7** and **8**, with a rigid homoconjugated C–X bond, were prepared and their photochemistry in methanol was studied. The photochemistry of esters **7** and **8** was more complicated than expected. Therefore, the photochemistry and photophysics of esters **9a–c** and **10a–c**, the dimethyl analogues of esters **7** and **8**, were also examined. The rigid indanyl esters allow the electronic effect of the substituents to be evaluated independent of conformational effects. Both the acetate esters (R = CH_3) and the pivalate esters (R = $C(CH_3)_3$) were chosen because decarboxylation of the acyloxy radical ($^{\bullet}O_2CR$) is an important probe for ground state reactions that occur after excited-state cleavage. The results from the 1-indanyl esters, **9a–c** and **10a–c**, are compared to the results from the conformationally unrestricted esters benzylic esters **3** and **4**.

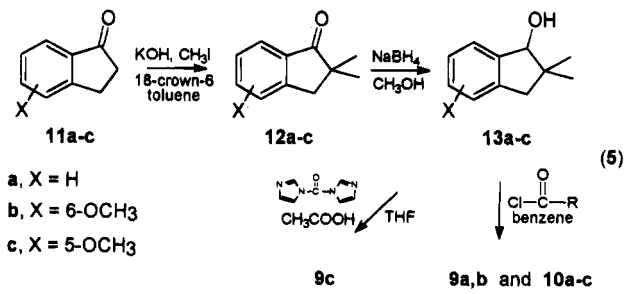


7 R = CH_3
8 R = $C(CH_3)_3$

9a-c R = CH_3
10a-c R = $C(CH_3)_3$

Results and Discussion

Preparation of Esters 7–10. Esters **7** and **8** were prepared by reaction of 1-indanol with acetyl and pivaloyl chloride, respectively. Esters **9a,b** and **10a–c** were prepared by the reactions shown in eq 5. The commercially available ketones **11a–c** were dimethylated and then reduced to give the alcohols **13a–c**. The alcohols were reacted with the appropriate acid chlorides to give the esters. Esterification with acid chloride was



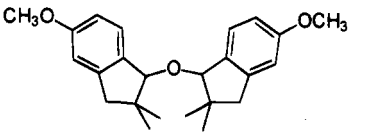
(5)

successful for all of the esters except for **9c**, the 5-methoxy substituted acetate ester. Several attempts to esterify 5-methoxy-2,2-dimethyl-1-indanol (**13c**) with acetyl chloride were unsuccessful. The reaction yielded only one product which was tentatively identified as the ether **14**,

Table 1. Product Yields for the Photolysis of Esters 7 and 8 in Methanol

ester	15	16	17	18	total
7, R = CH_3	23	1	9	39	72
8, R = $C(CH_3)_3$	5	14	34	31	84

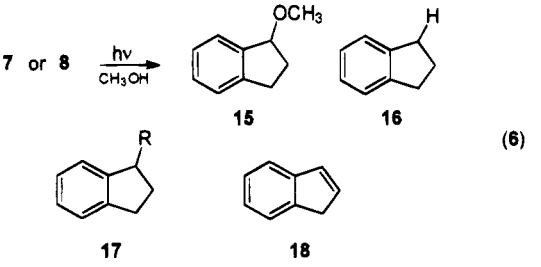
on the basis of ^1H and ^{13}C NMR data. It is not obvious



(14)

why the acetate ester could not be prepared by reaction of acetyl chloride with the alcohol since this procedure worked well for the pivalate ester. The ester **9c** was successfully synthesized from the alcohol using *N,N*-carbonyldiimidazole and acetic acid. Complete details for the above procedures are given in the Experimental Section.

Products and Yields on Irradiation of Esters 7 and 8. Esters **7** and **8** were photolyzed in methanol with a low-pressure mercury lamp. Four products were formed as shown in eq 6. In previous photochemical studies of esters, products could be isolated if a large amount (>500 mg) of ester was photolyzed to a high percent conversion. However, this was not possible for esters **7** and **8** because one of the products was indene. As the concentration of indene increased, significant product formation was observed from the photochemistry of indene. The primary products were identified by GC/MS. The identity of products **15**, **16**, and **18** was confirmed by comparing the retention times and mass spectra of authentic samples to the retention times and mass spectra of products in the photolysis mixture. No authentic sample of product **17** was available but on the basis of mass spectral fragmentation and retention time this is the most probable structure. Using the authentic samples, standards were prepared and the products were quantitified by GC/FID. The yield of product **17** was estimated using indan **16** and correcting for the difference in number of carbon atoms. The yields obtained in this way are given in Table 1.



(6)

The mechanism, shown in Scheme 1, that was used to rationalize product formation in the benzylic esters **3** and **4** can be used to explain product formation for esters **7** and **8**. The ether **15** is formed by trapping of the indanyl cation by methanol. Indan **16** and the coupling product **17** are formed from the indanyl radical. These products must be formed in-cage because no dimeric products were detected. Thus the radical pairs did not diffuse apart.

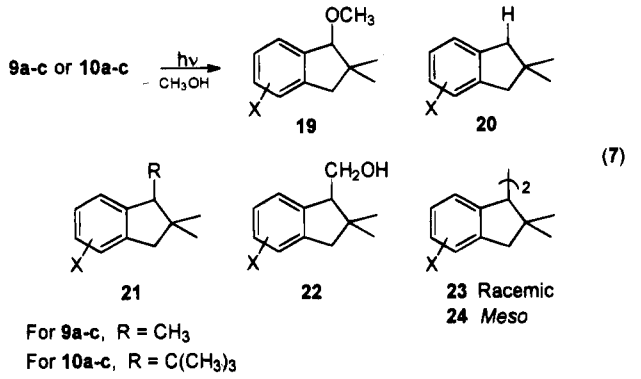
Table 2. Product Yields[a] for the Photolysis of Esters 9 and 10 in Methanol

ester	19	20	21	22	23	24	total
9a X = H	52 (26)	– (–)	12 (19)	11 (26)	5	9 (23)	89
10a	14 (5)	11 (14)	33 (45)	– (6)	8	16 (18)	82
9b X = 6-OCH_3	60 (32)	1 (–)	6 (14)	7 (12)	6	6 (38)	86
10b	13 (10)	14 (17)	19 (46)	–	9	9 (20)	64
9c X = 5-OCH_3	9 (2)	– (–)	18 (14)	41 (25)	12	18 (48)	98
10c	– (–)	11 (13)	34 (48)	– (4)	23	32 (24)	100

[a] Values in brackets are for the analogous benzylic esters, ref 4.

The origin of indene **18** is uncertain because it could be formed by loss of hydrogen from the indanyl radical, the indanyl cation or both. The determination of the mechanism for formation of indene was not possible and this made comparisons with previous results[4] for the kinetics of radical pairs and ion pairs impossible. In order to eliminate indene formation, esters **9** and **10**, with two methyl groups at carbon 2, were prepared.

Products and Yields on Irradiation of Esters 9a–c and 10a–c. When esters **9a–c** and **10a–c** were photolyzed in methanol the five major indanyl products shown in eq 7 were formed. The products were isolated by chromatography and identified by spectroscopic methods. Again product formation can be rationalized using Scheme 1. The methyl ether **19** was formed by trapping of the indanyl cation with methanol. The remaining products are radical derived. For these esters, out-of-cage radical products are also formed. The indanyl radical, in-cage or out-of-cage, can abstract a hydrogen atom to form indan. The indanyl radical can also couple with the R group to give the coupling product. Whether the coupling occurs in-cage or out-of-cage depends on the rate of decarboxylation relative to the rate of separation of the radical pairs. The alcohol product, **22**, results from



coupling of the out-of-cage indanyl radical with the solvent derived $^{\bullet}CH_2OH$ radical. Once the indanyl radical is out-of-cage it can also couple with itself to form dimers. Two diasteromeric dimers are possible because the compounds have two identical stereogenic centers. In fact, both dimers, racemic (*R,R*:*S,S*)-**23** and *meso* (*R,S*)-**24** were formed and isolated. These dimers have interesting temperature-dependent NMR spectra which are discussed in detail elsewhere.[13] The products were quantified by HPLC or GC/FID by comparison with standard samples and the yields are given in Table 2. The yields of the products are highly dependent on the substituent. The yield of ether varies from 60% for the 6-methoxy substituted acetate ester to 9% for the corresponding 5-methoxy substituted acetate. The product yields are also highly dependent on the R group. For instance, the yield of ether is 52% for the unsubstituted acetate but only 14% for the unsubstituted pivalate. Even though the C–O bond that is cleaving is homoconjugated to the aromatic ring, the R group still has a large effect on product ratios. The photophysical properties of the esters are independent of the R group (*vide infra*). This means that the pathways that control product distribution occur after the excited-state cleavage and rationalizing product ratios using Scheme 1 is valid. Speculation on the mechanism of indene formation in the photolysis of esters **7** and **8** is possible based on the results from esters **9a** and **10a**. For esters **9a**, the ion pair accounted for ~50% of the reactivity while it accounted for only ~14% of the reactivity for ester **10a**. The yield of ether for ester **7** was 23% and the yield of indene was 39%. For the pivalate ester **8**, the ether yield was 5% and the indene yield was 31%. These results indicate that the indene is most likely being formed from both the radical pair and the ion pair. The yields for the benzylic esters **3** and **4** have been analyzed quantitatively[4,5] and this will also be done for the indanyl esters **9a–c** and **10a–c**.

Quantitative Mechanistic Scheme for Esters 9a–c and 10a–c. Examination of Table 2 reveals that the products for the pivalates **10a–c** are predominantly radical-derived. Therefore, these substrates serve as good probes for reactivity of the radical pair. The two competing pathways of the radical pair are decarboxylation (k_{CO_2}) of the acyloxy radical and diffusional escape from the cage (k_D). The values for k_D can be determined using the rate constants of decarboxylation measured previously[6] and the product yields given in Table 2. Determination of k_D is not straightforward because the radical disproportionation product and the radical coupling product (*vide supra*) can be formed from either in-cage radical pairs or from a reencounter of out-of-cage radical pairs. In order to calculate k_D, an assumption is made that once the radical pair has separated by diffusion, reencounters leading to disproportionation and coupling should occur at the same rate as reencounters leading to the dimers. This is a reasonable assumption because the concentration of the two radicals Ar$^{\bullet}$ and $^{\bullet}C(CH_3)_3$ are equal. The relationship between product yields and rate constants is given in eq 8. This equation

$$\frac{\text{yield of } (\mathbf{20} + \mathbf{21})}{\text{yield of } (\mathbf{22} + \mathbf{23} + \mathbf{24})} = \frac{(k_{CO_2} + k_D/2)}{k_D/2} \qquad (8)$$

can be rearranged to give eq 9. The values for k_D

$$k_D = \frac{2k_{CO_2}}{\dfrac{\text{yield of } (\mathbf{20} + \mathbf{21})}{\text{yield of } (\mathbf{22} + \mathbf{23} + \mathbf{24})} - 1} \qquad (9)$$

calculated using eq 9 and $k_{CO_2} = 1.1 \times 10^{10}$ s^{-1} are given

(13) Pincock, J. A.; Wedge, P. J. Manuscript in preparation.

Table 3. Calculated Values of k_D and k_{ET} for esters 9 and 10

ester	k_D[a] $\times 10^{-10}$ s^{-1}	k_{ET}[b,c] $\times 10^{-9}$ s^{-1}
X = H	1.1	7.3 (1.8)
X = 6-OCH_3	1.1	10.6 (2.0)
X = 5-OCH_3	2.4	1.2 (0.1)

[a] Calculated from eq 9. [b] Calculated from eq 10. [c] Values in brackets are for the benzylic esters **3**, ref 4.

in Table 3. The values of k_D are comparable to the average value of 2×10^{10} s^{-1} that was obtained for the benzylic esters **3** and **4**.

The only rate constant that is still unknown in Scheme 1 is the rate constant of electron transfer, k_{ET}. As a starting point for this discussion, we will assume that the total yield of methyl ethers formed from photolysis of the pivalate esters results from direct heterolytic cleavage of the C–O bond in the excited state. This is a reasonable assumption because decarboxylation is very rapid for the $^{\bullet}O_2C(CH_3)_3$ radical and electron transfer would be less competitive. Heterolytic cleavage is maximized for the unsubstituted pivalate ester and the 6-methoxy pivalate ester with yields of 14 and 13%, respectively. No ether was detected for the 5-methoxy substituted ester. In order to calculate k_{ET}, the ether yields from the acetate esters will be used and several assumptions will be made. First, a correction will be made for heterolytic cleavage. It is assumed that the yield of ether coming from heterolytic cleavage for the acetate esters can be estimated using the ether yields from the pivalate esters. That is the yield of ether formed exclusively from the electron transfer pathway is equal to the yield of ether from the acetate ester minus the yield of ether from the pivalate ester. The second assumption is that the value of k_D is similar for both the acetate and pivalate esters. Using eq 10 the rate constant of electron

$$k_{ET} = \frac{(k_{CO_2} + k_D)}{1/(\mathbf{19}) - 1} \qquad (10)$$

transfer, corrected for heterolytic cleavage, can be obtained. The values of k_{ET} are listed in Table 3. The trends are similar to those observed for the benzylic esters. For the benzylic esters, the largest rate constant measured was for the 3-OCH_3 substituted ester (2.0×10^9 s^{-1}), followed by the unsubstituted ester (1.8×10^9 s^{-1}), and the 4-OCH_3 substituted ester had the smallest rate constant (0.12×10^9 s^{-1}). The obvious difference between the benzylic and indanyl esters is the relative magnitude of the rate constants. The rate constants of electron transfer for the indanyl esters are, on average, 6 times those for the benzylic esters. Electron transfer could be thermodynamically more favorable for the indanyl radicals. Without knowing the oxidation potentials of the indanyl radicals confirmation of this is not possible.

The products isolated from the indanyl esters have been shown to be analogous to those formed from the benzylic esters. As well, the same substituent effects on product ratios have been observed. This confirms that these esters will serve as good probes for the importance of conformational mobility in benzylic ester cleavage reactions. Singlet lifetimes, fluorescence and reaction quantum yields for these esters have been measured and the results will be discussed next.

Photophysical Data for Esters 9a–c and 10a–c. The singlet lifetimes, fluorescence and reaction quantum yields measured for the indanyl esters **9a–c** and **10a–c** are given in Table 4. An important point to note from this table is that these values are quite dependent on the substituents but independent of R, acetate versus pivalate. This reemphasizes our conclusion that changes in product yields for **9** versus **10** are not excited-state effects but are a result of changes in a ground state process, decarboxylation, after homolytic bond cleavage.

A comparison of the singlet lifetimes and fluorescence quantum yields for the esters **9** and **10** with the unreactive indanyl alcohols **13a–c** shows that the esters have different reactivities. The C–O bonds in the alcohols **13a–c** are not photolabile and the fluorescence quantum yields and lifetimes of the alcohols when compared to the fluorescence quantum yields and lifetimes for the esters provide a reasonable measurement of reactivity of the esters. These changes indicate that the unsubstituted esters **9a** and **10a** and the *m*-methoxy substituted esters **9b** and **10b** are quite reactive whereas the *para* substituted esters **9c** and **10c** are much less reactive. The quantum yields of fluorescence and the singlet lifetimes are diminished for the unsubstituted esters and *meta* substituted esters relative to the alcohol. However, the quantum yields of fluorescence and lifetimes of the *para* substituted esters do not differ from the alcohol. For comparison, the singlet lifetimes and quantum yields of fluorescence for the corresponding benzylic esters **3** and **4** are also given. The same trends were observed for the benzylic esters. The largest difference between the benzylic and indanyl esters is that the fluorescence quantum yields are slightly higher for the indanyl compounds. This is presumably due to loss of free rotor type decay[14] in the rigid indanyl compounds.

The differing reactivity of these esters was quantified by measuring the quantum yields of reaction using 3-methoxybenzyl acetate in aqueous dioxane as the actinometer. The esters were irradiated simultaneously with the actinometer and a plot was made of % conversion/time verus time. Typical plots are shown in Figure 1. These plots are curved because the products have the same chromophore as the starting material and as the % conversion increases more of the incident light is being absorbed by the products. This problem in quantum yield determinations has been discussed in detail.[15] These plots were extrapolated to zero time, and the intercepts were used to measure quantum yields based on the reported value of 0.13 for the 3-methoxybenzyl acetate in aqueous dioxane.[1] Further details are given in the Experimental Section. Using the quantum yields of reaction, the rate constants for bond cleavage, k_R, were calculated and are given in Table 4. These numbers allow the enhanced reactivity of the unsubstituted and *m*-methoxy substituted relative to the *p*-methoxy substituted esters to be expressed numerically. The *m*-methoxy esters have the largest rate constants of cleavage followed by the unsubstituted esters with the rate constants for cleavage being the smallest for the *p*-methoxy substituted esters. The relative ratio of the rate constants is ~15:1:2.5 for *meta*:*para*:unsubstituted.

The indanyl esters are restricted in a conformation that is ideal for cleavage yet the unsubstituted and *m*-methoxy substituted esters are still more reactive than the *para* substituted esters. At least one of the factors controlling

(14) Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: California, 1991; pp 170–72.
(15) Bunce, N. J. *J. Photochem.* **1987**, *38*, 99.

Table 4. Emission Properties of the Substituted Indanyl Alcohols 13a–c and Esters 9a–c and 10a–c in Methanol

alcohol or ester	X	τ_S (ns)	τ_S (ns)[a] benzyl	Φ_F[b]	Φ_F[c] benzyl	Φ_{RXN}	$k_R \times 10^{-8}$ s^{-1}
13a	H	21	21	0.41	0.07	–	–
9a		5	14	0.08	0.05	0.14 ± 0.02	0.28 ± 0.03
10a		5	12	0.09	0.03	0.16 ± 0.02	0.32 ± 0.04
13b	6-OCH_3	6	7	0.24	0.16	–	–
9b	(*meta*)	[e]	–	<0.005[d]	0.01	nd[f]	nd
10b		[e]	–	<0.007[d]	0.01	0.19 ± 0.02	>1.9 ± 0.2
13c	5-OCH_3	7	7	0.28	0.17	–	–
9c	(*para*)	7	6	0.29	0.17	0.08 ± 0.02	0.1 ± 0.03
10c		7	6	0.28	0.16	0.08 ± 0.02	0.1 ± 0.03

[a] Lifetimes for the substituted benzylic compounds **3** and **4**, ref 4. [b] Quantum yields of fluorescence were determined using a value of 0.13 for toluene in methanol.[19] [c] Fluorescence quantum yields for the substituted benzylic compounds **3** and **4**, ref 4. [d] These values are a maximum because the esters could be contaminated with a small amount of the alcohol which is highly fluorescent. [e] These lifetimes were too short (<1 ns) to be measured by our single photon counting equipment. [f] nd: not determined.

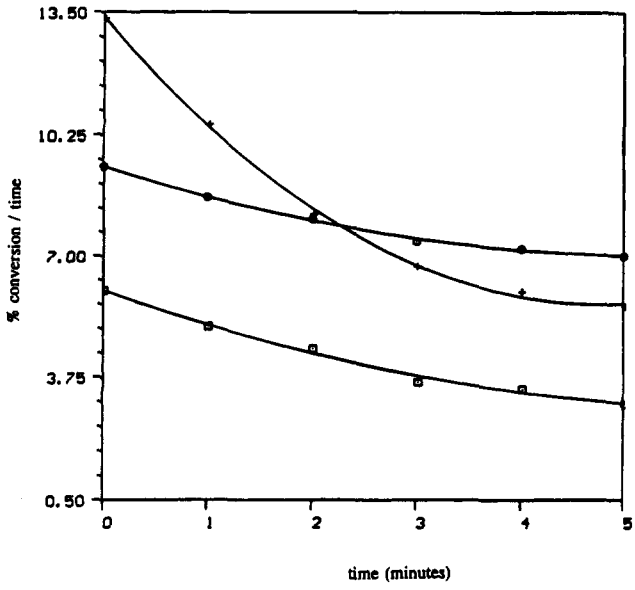


Figure 1. Plot of % conversion/time versus time for photolysis of esters **10b,c** and 3-methoxybenzyl acetate in aqueous dioxane. The circles are for 3-methoxybenzyl acetate in aqueous dioxane, the crosses are for 6-methoxy-2,2-dimethyl-1-indanyl pivalate (**10b**), and the squares are for 5-methoxy-2,2-dimethyl-1-indanyl pivalate (**10c**). The values at time zero are by extrapolation.

cleavage efficiencies must be independent of conformation. This factor could be the *meta* effect. However, instead of increasing the efficiency of heterolytic cleavage the step that must be enhanced is homolytic cleavage because we have shown that heterolytic cleavage is not an important pathway in these reactions. Substituent rate enhancements are generally small for reactions producing a benzylic radical intermediate. For example, in the free radical hydrogen abstraction reaction of toluene by bromine atoms, the reaction rates correlate with $\sigma+$ giving $\varrho+ = -1.4$.[16–18] This corresponds to relative rates of 10:0.9:1 for *para*:*meta*:unsubstituted.

Quantum yields of reaction for 3-methoxybenzyl acetate and 4-methoxybenzyl acetate in aqueous dioxane have been reported by Zimmerman *et al.*[1] The values are 0.13 and 0.016, respectively. Rate constants for reaction were calculated using these quantum yields and the measured singlet lifetimes. The ratio of rate constants for *meta* to *para* is 48:1. The authors did not study the unsubstituted ester. This ratio is much greater than the *meta*:*para* ratio of 15:1 calculated for the indanyl esters. The greater reactivity difference for the benzylic esters cannot be attributed to an enhanced reactivity of the *meta* isomer because the indanyl esters are locked into the reactive conformer. Therefore, the *para* isomer must be less reactive than expected in the benzylic system. This suggestion is confirmed by a calculation of $k_R = 0.027 \times 10^8$ s^{-1} for the 4-methoxy substituted benzylic ester from the quantum yield of reaction (0.016) and the singlet lifetime (6 ns). This value of k_R is lower by a factor of five than that obtained (0.13×10^8 s^{-1}) for the rigid indanyl ester. The obvious difference between the indanyl system and the benzyl system is loss of conformational motion. The likely reason for the lower reaction rate for the *p*-methoxy substituted ester is that the p-*methoxy* substituent is increasing the population of the unreactive conformer and thus causing the rate of cleavage to decrease.

To confirm that the differences between the indanyl system and the benzylic esters are not due to the different solvents used for the quantum yield determinations, quantum yields of reaction for 3-methoxybenzyl acetate and 4-methoxybenzyl acetate in methanol were also measured. The values determined were 0.18 and 0.02 which gives relative rate constants of cleavage for *meta* to *para* of 55:1. This ratio is comparable to Zimmerman's ratio of 48:1 measured in aqueous dioxane. Therefore, the differences in reactivity cannot be attributed to solvent differences and must be conformational.

The main goal of this work, to determine the importance conformational mobiltity on the photoreaction of benzylic esters, was achieved. However, the data presented in this paper also provides an opportunity to calculate rate constants for internal conversion, k_{IC}. The singlet excited states of esters **9** and **10** have four pathways of decay; fluorescence (k_F), reaction (k_R), intersystem crossing (k_{ISC}), and internal conversion (k_{IC}). Therefore, the total decay of the singlet excited state, k, is given by eq 11. The value of k is the reciprocal of the

$$k = k_F + k_R + k_{ISC} + k_{IC} = 1/\tau_S \qquad (11)$$

singlet lifetime, τ_S. Values for k_F and k_R have been calculated from the lifetimes and the quantum yields of fluorescence and reaction, respectively (Table 4). Values of k_{ISC} can be estimated by assuming that the values for toluene and anisole will be good models for the unsubstituted and methoxy substituted esters, respectively. The quantum yield of intersystem crossing, singlet lifetime, and the calculated k_{ISC} for toluene are 0.53,[19]

(16) Pearson, R. E.; Martin, J. C. *J. Am. Chem. Soc.* **1963**, *85*, 354, 3142.
(17) Walling, C.; Reiger, A. L.; Tanner, D. D. *J. Am. Chem. Soc.* **1963**, *85*, 3129.
(18) Walling, C.; Rieger, A. L. *J. Am. Chem. Soc.* **1963**, *85*, 3135.

35 ns,[19] and 1.4×10^7 s^{-1}, respectively. For anisole, the corresponding values are 0.64,[20] 7.5 ns,[20] and 8.9×10^7 s^{-1}, respectively.

Using the k_{ISC} values for toluene and anisole allows k_{IC} to be calculated from eq 11. This is only possible for the unsubstituted and the *p*-methoxy substituted indanyl esters for which reliable measurements of the lifetime and fluorescence quantum yield can be made. For these rigid indanyl esters the only reasonable pathway for internal conversion is homolytic cleavage of the C–O bond and reformation of that bond before conversion to product occurs. This internal return process will result in oxygen scrambling. The process of oxygen scrambling, by ^{18}O labeling experiments,[21,22] during the photolysis of esters has been observed previously and shown to vary between 50 and 75% of the rate of conversion to products. However, there is no information in the literature dealing with rates of internal conversion as a function of substituents on the aromatic ring.

Using eq 11, along with the values for the experimental (k, k_R, k_F) and estimated (k_{ISC}) rate constants, the value of k_{IC} for the unsubstituted indanyl ester is 13.6×10^7 s^{-1}. Therefore, this pathway is accounting for 68% of the reactivity of the singlet excited state. For the *p*-methoxy substituted ester, k_{IC} is 2.0×10^7 s^{-1}. The internal return/internal conversion pathway is now accounting for only 14% of the reactivity of the excited state. Recently,[23] efficiencies of internal return from ^{18}O scrambling experiments, as a function of substituent, have been determined in our laboratory for 1-naphthylethyl esters. The efficiency of internal return was also greatly diminished by the presence of a *p*-methoxy substituent on the aromatic ring.

Conclusions

This work has shown that the influence of substituents on photochemical benzylic reactivity is three-fold. First, the substituents control the oxidation potential of the benzylic radical and thus the rate of electron transfer. This is the major effect that controls the yield of the ion-pair. Second, substituents also exert a strong electronic effect on the rate of the homolytic cleavage step which is fastest for a *m*-methoxy substituted case. Finally, if the esters are conformationally unrestricted, the substituents also alter the populations of the two possible conformers. The results suggest that a methoxy group in the *para* position increases the population of the unreactive parallel conformer, **5**, and that this leads to a decrease in the rate of cleavage. Confirmation of this would require extensive NMR studies and *ab initio* MO calculations.

This work also provides rate constants for internal return as a function of substituents. The internal return pathway accounts for 68% of the excited singlet state reactivity for the unsubstituted ester and only 14% for the *p*-methoxy substituted ester.

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 5890 A 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 $M^{\bullet+}$. GC/FID analyses were performed using a Perkin Elmer autosystem GC. The column used was a 12 m × 0.22 mm 100% polymethylsilicone on fused silica with a film thickness of 0.23 μm. 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.

Dimethylation of Indanones 11a–c. The indanones were dimethylated using the procedure of Lissel *et al.*[24] Powdered KOH (0.34 mol, 19 g) was mixed with 100 mL of toluene and 0.1 mmol of 18-crown-6. The ketone (50 mmol) was added and the mixture was heated to 70 °C. To this heated mixture was added 0.32 mol of iodomethane. The solution was refluxed overnight. After cooling, water was added and the two layers were separated. The aqueous layer was washed with ether and the combined organic layers were washed with sodium bisulfite and dried with magnesium sulfate. The ketones were purified by column chromatography.

2,2-Dimethyl-1-indanone (12a). This compound has been previously prepared by Orliac-Le Moing *et al.*[25] The spectral data for this compound are provided below because the authors reported only a partial ^1H NMR spectrum: ^1H NMR δ 7.75 (d, 1H, J = 7.6 Hz), 7.59 (t, 1H, J = 7.5 Hz), 7.42 (d, 1H, J = 7.3 Hz), 7.36 (t, 1H, J = 7.5 Hz), 3.00 (s, 2H), 1.24 (s, 6H); ^{13}C NMR δ 211.4 (C=O), 152.2 (C), 135.3 (C), 134.8 (CH), 127.4 (CH), 126.7 (CH), 124.4 (CH), 45.5 (C), 42.9 (CH_2), 25.3 (CH_3); GC/MS 160 ($M^{\bullet+}$, 40), 146 (10), 145 (100), 142 (13), 117 (26), 116 (10), 115 (35), 91 (24), 90 (12), 89 (13), 77 (10), 65 (13), 63 (14), 51 (13).

6-Methoxy-2,2-dimethyl-1-indanone (12b): ^1H NMR δ 7.32 (d, 1H, J = 9.2 Hz), 7.21–7.18 (m, 2H), 3.84 (s, 3H), 2.93 (s, 2H), 1.24 (s, 6H); ^{13}C NMR δ 211.5 (C=O), 159.4 (C), 145.0 (C), 136.4 (C), 127.3 (CH), 124.3 (CH), 105.5 (CH), 55.6 (CH_3-O), 46.3 (C), 42.2 (CH_2), 25.3 (CH_3); GC/MS 190 ($M^{\bullet+}$, 51), 176 (13), 175 (100), 172 (21), 161 (13), 147 (21), 131 (12), 129 (10), 121 (13), 117 (10), 115 (22), 103 (19), 91 (43), 89 (12), 78 (19), 77 (40), 65 (12), 63 (25), 53 (10), 51 (38).

5-Methoxy-2,2-dimethyl-1-indanone (12c): ^1H NMR δ 7.69 (d, 1H, J = 8.4 Hz), 6.88 (m, 2H), 3.88 (s, 3H), 2.95 (s, 2H), 1.22 (s, 6H); ^{13}C NMR δ 209.6 (C=O), 165.5 (C), 155.13 (C), 128.5 (C), 126.1 (CH), 115.4 (CH), 109.7 (CH), 55.6 (CH_3-O), 45.6 (C), 42.9 (CH_2), 25.4 (CH_3); GC/MS 190 ($M^{\bullet+}$, 29), 176 (12), 175 (100), 115 (12), 91 (23), 77 (17), 63 (15), 51 (16).

Preparation of the Alcohols (13a–c). The alcohols were prepared by sodium borohydride reduction of the ketone in methanol, with the exception of 1-indanol which was purchased from the Aldrich Chemical Co.

2,2-Dimethyl-1-indanol (13a). This compound has been prepared previously by Orliac-Le Moing *et al.*[25] The spectral

(19) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1993; p 50.
(20) Reference 19, p 12.
(21) Givens, R. S.; Matuszewski, B.; Levi, N.; Leung, D. *J. Am. Chem. Soc.* **1977**, *99*, 1896.
(22) Jaeger, D. A. *J. Am. Chem. Soc.* **1975**, *97*, 902.
(23) Kim, J. M.; Pincock, J. A. *Can. J. Chem.*, in press.
(24) Lissel, M.; Neumann, B.; Schmidt, S. *Liebigs Ann. Chem.* **1987**, 263.
(25) Orliac-Le Moing. A.; Delaunay, J.; LeBouc, A.; Simonet, J. *Tetrahedron* **1985**, *20*, 4483.

data for this compound are provided below because the authors reported only a partial ^{1}H NMR spectrum. ^{1}H NMR δ 7.39–7.33 (m, 1H), 7.25–7.16 (m, 3H), 4.67 (d, 1H, J = 5.03 Hz), 2.78 (d, 1H, J = 15.5 Hz), 2.67 (d, 1H, J = 15.5 Hz), 1.97 (d, 1H, J = 5.8 Hz), 1.19 (s, 3H), 1.04 (s, 3H); ^{13}C NMR δ 144.5 (C), 141.9 (C), 128.0 (CH), 126.6 (CH), 125.0 (CH), 124.5 (CH), 83.5 (CH-O), 44.9 (CH_2), 44.6 (C), 26.8 (CH_3), 21.5 (CH_3); GC/MS 162 ($M^{\bullet+}$, 43), 161 (21), 147 (13), 144 (17), 143 (12), 130 (12), 129 (100), 128 (25), 127 (10), 120 (19), 119 (51), 115 (21), 91 (50), 89 (10), 77 (21), 65 (21), 63 (13), 51 (19).

6-Methoxy-2,2-dimethyl-1-indanol (13b): ^{1}H NMR δ 7.06 (d, 1H, J = 8.1 Hz), 6.91 (d, 1H, J = 2.0 Hz), 6.76 (dd, 1H, J_1 = 8.2 Hz, J_2 = 2.4 Hz), 4.63 (s, 1H), 3.78 (s, 3H), 2.68 (d, 1H, J = 15.1 Hz), 2.59 (d, 1H, J = 15.1 Hz), 1.85 (brs, 1H), 1.17 (s, 3H), 1.00 (s, 3H); ^{13}C NMR δ 158.9 (C), 145.9 (C), 133.6 (C), 125.7 (CH), 114.3 (CH), 109.4 (CH), 83.7 (CHO), 55.4 (CH_3O), 45.1 (C), 44.1 (CH_2), 26.8 (CH_3), 21.4 (CH_3); GC/MS 192 ($M^{\bullet+}$, 7), 177 (15), 174 (21), 159 (47), 150 (16), 149 (100), 131 (10), 121 (94), 116 (13), 115 (28), 105 (10), 103 (12), 91 (50), 89 (12), 79 (13), 78 (20), 77 (50), 65 (18), 63 (16), 55 (12), 53 (13), 52 (10), 51 (30).

5-Methoxy-2,2-dimethyl-1-indanol (13c): ^{1}H NMR δ 7.27 (d, 1H, J = 7.9 Hz), 6.78–6.74 (m, 2H), 4.59 (s, 1H), 3.79 (s, 3H), 2.76 (d, 1H, J = 15.7 Hz), 2.61 (d, 1H, J = 15.7 Hz), 1.59 (s, 1H), 1.14 (s, 3H), 1.06 (s, 3H); ^{13}C NMR δ 160.0 (C), 143.9 (C), 136.8 (C), 125.4 (CH), 112.4 (CH), 110.5 (CH), 83.1 (CHO), 55.4 (CH_3O), 45.0 (CH_2), 44.7 (C), 27.0 (CH_3), 21.7 (CH_3); GC/MS 192 ($M^{\bullet+}$, 66), 191 (100), 177 (32), 176 (11),175 (34), 174 (16), 173 (16), 162 (11), 161 (50), 159 (59), 158 (16), 150 (13), 149 (53), 145 (11), 144 (25), 135 (16), 131 (14), 129 (12), 128 (15), 121 (25), 116 (16), 115 (32), 105 (12), 103 (13), 91 (50), 89 (13), 79 (15), 78 (21), 77 (50), 65 (25), 63 (25), 55 (12), 53 (12), 51 (27).

Preparation of the Esters (7–10). 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 chromatography followed by recrystallization or bulb-to-bulb distillation. Attempts to prepare samples for elemental analyses for most of the esters that were oils were unsuccessful because of slight decomposition during distillation. Before distillation, no impurities in these samples were detected when analyzed by GC using two different columns (polymethylsilicone and phenyl methyl silicone). For these esters, high resolution mass spectra are given. For esters **8**, **9a**,**b**, **10a**, and **10c**, copies of the ^{1}H and/or ^{13}C NMR spectra are provided as supplementary material.

1-Indanyl Acetate (7). This compound has been prepared previously by Groenewold *et al.*[26] Because only a partial 70 eV mass spectrum was reported, spectral characterization of this ester is provided below: colorless oil; ^{1}H NMR δ 7.42–7.39 (d, 1H, J = 7.0 Hz), 7.29–7.20 (m, 3H), 6.19 (dd, 1H, J_1 = 6.9 Hz, J_2 = 3.7 Hz), 3.18–3.05 (m, 1H), 2.95–2.80 (m, 1H), 2.56–2.42 (m, 1H), 2.18–2.05 (m, 1H), 2.07 (s, 3H); ^{13}C NMR δ 171.1 (C=O), 144.4 (C), 141.0 (C), 128.9 (CH), 126.7 (CH), 125.4 (CH), 124.8 (CH), 78.3 (CHO), 32.3 (CH_2), 30.2 (CH_2), 21.3 (CH_3); GC/MS 176 ($M^{\bullet+}$, 0.1), 134 (12), 133 (24), 117 (73), 116 (100), 115 (96), 91 (23), 89 (12), 77 (21), 65 (11), 63 (18), 51 (20). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 75.19; H, 6.61.

2,2-Dimethyl-1-indanyl acetate (9a): colorless oil; λ_{max} (ϵ) 262 (818); ^{13}C NMR δ 171.1 (C=O), 143.6 (C), 141.1 (C), 128.8 (CH), 126.7 (CH), 126.1 (CH), 125.1 (CH), 84.1 (CH-O), 45.6 (CH_2), 43.3 (C), 27.3 (CH_3), 22.5 (CH_3), 21.2 (CH_3); GC/MS (No $M^{\bullet+}$ observed), 162 (20), 161 (13), 145 (25), 144 (97), 143 (28), 130 (19), 129 (100), 128 (48), 127 (13), 119 (17), 117 (12), 115 (38), 91 (38), 89 (11), 77 (19), 65 (17), 63 (12), 51 (14); calcd exact mass for $C_{13}H_{16}O_2$ 204.115; found 204.115.

6-Methoxy-2,2-dimethyl-1-indanyl acetate (9b): colorless oil; λ_{max} (ϵ) 279 (2800); ^{13}C NMR δ 171.1 (C=O), 158.8 (C), 142.3 (C), 135.5 (C), 125.7 (CH), 115.3 (CH), 110.8 (CH), 84.2 (CH-O), 55.5 (CH_3-O), 44.7 (CH_2), 43.8 (C), 27.4 (CH_3), 22.5 (CH_3), 21.2 (CH_3); GC/MS 234 ($M^{\bullet+}$, 10), 175 (21), 174 (100), 159 (36), 43 (15); calcd exact mass for $C_{14}H_{18}O_3$ 234.126, found 234.127.

1-Indanyl pivalate (8): colorless oil; ^{13}C NMR δ 178.6 (C=O), 144.1 (C), 141.4 (C), 128.7 (CH), 126.7 (CH), 125.2 (CH), 124.8 (CH), 78.0 (CHO), 38.7 (C), 32.3 (CH_2), 30.1 (CH_2), 27.1 (CH_3); GC/MS 218 ($M^{\bullet+}$, 0.1), 117 (100), 116 (49), 115 (30), 57 (18); calcd exact mass for $C_{14}H_{18}O_2$ 218.131, found 218.128.

2,2-Dimethyl-1-indanyl pivalate (10a): colorless oil; λ_{max} (ϵ) 262 (829); ^{13}C NMR δ 178.4 (C=O), 143.0 (C), 141.4 (C), 128.4 (CH), 126.6 (CH), 125.6 (CH), 124.9 (CH), 83.7 (CHO), 45.7 (CH_2), 43.7 (C), 39.0 (C), 27.3 (CH_3), 22.6 (CH_3); GC/MS 246 ($M^{\bullet+}$, 0.05), 146 (11), 145 (92), 144 (68), 143 (21), 130 (13), 129 (41), 128 (25), 117 (13), 115 (21), 91 (21), 57 (100); calcd exact mass for $C_{16}H_{22}O_2$ 246.162, found: 246.161.

6-Methoxy-2,2-dimethyl-1-indanyl pivalate (10b): recrystallized from hexanes mp 73–74 °C; λ_{max} (ϵ) 279 (3020); ^{1}H NMR δ 7.09 (d, 1H, J = 9.0 Hz), 6.82–6.79 (m, 2H), 5.78 (s, 1H), 3.77 (s, 3H), 2.80 (d, 1H, J = 15.2 Hz), 2.63 (d, 1H, J = 15.2 Hz), 1.22 (s, 9H), 1.16 (s, 3H), 1.08 (s, 3H); ^{13}C NMR δ 178.4 (C=O), 158.7 (C), 142.7 (C), 134.9 (C), 125.5 (CH), 114.7 (CH), 110.5 (CH), 83.7 (CHO), 55.4 (CH_3O), 44.8 (CH_2), 44.2 (C), 39.1 (C), 27.3 (CH_3), 22.6 (CH_3); GC/MS 276 ($M^{\bullet+}$, 0.2), 175 (37), 174 (100), 160 (16), 159 (37), 115 (15), 91 (11), 57 (61). Anal. Calcd for $C_{17}H_{24}O_3$: C, 73.87; H, 8.76. Found: C, 73.87; H, 8.22.

5-Methoxy-2,2-dimethyl-1-indanyl pivalate (10c): colorless oil; λ_{max} (ϵ) 273 (2200); ^{13}C NMR δ 178.5 (C=O), 160.3 (C), 145.2 (C), 133.6 (C), 126.8 (CH), 112.4 (CH), 110.1 (CH), 83.5 (CHO), 55.3 (CH_3O), 45.8 (CH_2), 43.8 (C), 31.6 (C), 27.2 (CH_3), 22.7 (CH_3); GC/MS 276 ($M^{\bullet+}$, 1), 176 (13), 175 (100), 174 (27), 160 (10), 159 (10), 115 (11), 91 (10), 57 (43); calcd exact mass for $C_{17}H_{24}O_3$ 276.173, found 276.174.

Preparation of 5-Methoxy-2,2-dimethyl-1-indanyl Acetate (9c). Several attempts to prepare this ester using the above method were unsuccessful. The procedure used was a combination from papers by Staab and Rohr[27] and Carpenter and Moore.[28] Acetic acid (24 mmol, 1.5 g) in 60 mL of THF was added to a stirring solution of *N*,*N*-carbonyldiimidazole (21 mmol, 3.32 g) in 60 mL of THF. After the solution was stirred for 1 h at room temperature, 5-methoxy-2,2-dimethyl-1-indanol (5.2 mmol, 1.0 g) in 40 mL of THF and a small piece of sodium metal was added. The reaction was monitored by HPLC. After 44 h of refluxing, most of the alcohol was converted to ester. The reaction was stopped and the solvent was removed. Water was added (50 mL), and the product was extracted into ether (3 × 25 mL). The combined organic layers were washed with 1 M Na_2CO_3, water, and then dried over magnesium sulfate. The ester was separated from the alcohol by chromatography on silica gel: yield 0.62 g, 50%; colorless oil; λ_{max} (ϵ) 273 (1790); ^{1}H NMR δ 7.27 (d, 1H, J = 9.3 Hz), 6.75–6.72 (m, 2H), 5.71 (s, 1H), 3.79 (s, 3H), 2.92 (d, 1H, J = 15.7 Hz), 2.60 (d, 1H, J = 15.7 Hz), 2.06 (s, 3H), 1.14 (s, 3H), 1.10 (s, 3H); ^{13}C NMR δ 171.1 (C=O), 160.5 (C), 145.8 (C), 133.3 (C), 127.2 (CH), 112.5 (CH), 110.2 (CH), 83.8 (CHO), 55.3 (CH_3O), 47.5 (CH_2), 43.5 (C), 27.5 (CH_3C=O), 22.6 (CH_3), 21.3 (CH_3); GC/MS 234 ($M^{\bullet+}$, 7), 191 (13), 176 (11), 175 (66), 174 (100), 173 (13), 161 (16), 160 (16), 159 (53), 158 (13), 121 (12), 115 (25), 91 (25), 77 (16). Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.76; H, 7.75. Found: C, 71.71; H, 7.39.

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 sepa-

(26) Groenewold, G. S.; Gross, M. L.; Zey, R. *Org. Mass. Spect.* **1982**, *17*, 416.

(27) Staab, H. A.; Rohr, W. Syntheses Using Heterocyclic Amides (Azolides). In *Newer Methods of Preparative Organic Chemistry*; Academic Press: Germany, 1968.

(28) Carpenter, J. G. D.; Moore, J. W. *J. Chem. Soc. C* **1969**, 1610.

rated by column chromatography and identified by spectroscopic methods.

Characterization of the Ethers. The ethers were isolated from the photolysis mixture. Also, authentic samples were prepared by reacting the alcohol with sodium hydride in DMSO followed by addition of iodomethane.

1-Indanyl methyl ether (15): ^{1}H NMR δ 7.41–7.38 (m, 1H), 7.26–7.19 (m, 3H), 4.84–4.79 (m, 1H), 3.40 (s, 3H), 3.14–3.02 (m, 1H), 2.87–2.75 (m, 1H), 2.37–2.26 (m, 1H), 2.14–2.02 (m, 1H); ^{13}C NMR δ 144.0 (C), 142.5 (C), 128.4 (CH), 126.2 (CH), 125.1 (CH), 125.0 (CH), 84.5 (CHO), 56.1 (CH_3O), 31.9 (CH_2), 30.2 (CH_2); GC/MS 148 ($M^{\bullet+}$, 32), 147 (46), 118 (18), 117 (100), 116 (42), 115 (88), 105 (12), 103 (12), 91 (28), 89 (19), 79 (12), 77 (24), 65 (12), 63 (24), 51 (24).

2,2-Dimethyl-1-indanyl methyl ether (19a): ^{1}H NMR δ 7.36–7.24 (m, 1H), 7.23–7.20 (m, 3H), 4.20 (s, 1H), 3.52 (s, 3H), 2.86 (d, 1H, J = 15.5 Hz), 2.62 (d, 1H, J = 15.5 Hz), 1.17 (s, 3H), 1.16 (s, 3H); ^{13}C NMR δ 142.9 (C), 128.1 (CH), 126.0 (CH), 125.4 (CH), 125.2 (CH), 92.1 (CHO), 58.1 (CH_3O), 45.6 (CH_2), 44.6 (C), 27.9 (CH_3), 22.0 (CH_3); GC/MS 176 ($M^{\bullet+}$, 19), 145 (25), 144 (23), 143 (13), 131 (11), 130 (13), 129 (100), 128 (30), 127 (10), 117 (12), 115 (24), 91 (25), 77 (11), 65 (12), 63 (11), 51 (13).

6-Methoxy-2,2-dimethyl-1-indanyl methyl ether (19b): ^{1}H NMR δ 7.07 (d, 1H, J = 8.1 Hz), 6.89 (d, 1H, J = 2.30 Hz), 6.77 (dd, 1H, J_1 = 8.3 Hz, J_2 = 2.4 Hz), 4.16 (s, 1H), 3.80 (s, 3H), 3.51 (s, 3H), 2.72 (d, 1H, J = 15.1 Hz), 2.53 (d, 1H, J = 15.1 Hz), 1.16 (s, 3H), 1.09 (s, 3H); ^{13}C NMR δ 158.5 (C), 144.3 (C), 134.4 (C), 125.7 (CH), 114.0 (CH), 110.5 (CH), 92.2 (CHO), 58.4 (CH_3O), 55.4 (CH_3O), 45.1 (C), 44.8 (CH_2), 28.0 (CH_3), 21.9 (CH_3); GC/MS 206 ($M^{\bullet+}$, 206), 191 (11), 175 (29), 174 (49), 173 (14), 161 (16), 160 (16), 159 (100), 158 (16), 145 (12), 144 (16), 131 (13), 128 (13), 121 (16), 116 (13), 115 (32), 91 (32), 78 (12), 77 (25), 65 (11), 63 (13), 51 (16).

5-Methoxy-2,2-dimethyl-1-indanyl methyl ether (19c): ^{1}H NMR δ 7.26 (d, 1H, J = 7.92 Hz), 6.74 (m, 2H), 4.10 (s, 1H), 3.79 (s, 3H), 3.45 (s, 3H), 2.85 (d, 1H, J = 15.55 Hz), 2.55 (d, 1H, J = 15.55 Hz), 1.16 (s, 3H), 1.11 (s, 3H); ^{13}C NMR δ 160.0 (C), 145.0 (C), 135.0 (C), 126.4 (CH), 111.7 (CH), 110.6 (CH), 91.4 (CH), 57.4 (CH_3O), 55.3 (CH_3O), 45.8 (CH_2), 44.7 (C), 28.0 (CH_3), 22.2 (CH_3); GC/MS 206 ($M^{\bullet+}$, 18), 176 (15), 175 (100), 160 (13), 159 (25), 115 (21), 91 (19), 77 (15).

Characterization of the Radical Coupling Products. All of the radical coupling products were isolated from preparative photolysis mixtures by silica gel chromatography.

2,2-Dimethylindan (20a): ^{1}H NMR δ 7.21–7.12 (m, 4H), 2.75 (s, 4H), 1.18 (s, 6H); ^{13}C NMR δ 143.6 (C), 126.0 (CH), 124.8 (CH), 47.8 (CH_2), 43.12 (C), 28.9 (CH_3); GC/MS 146 ($M^{\bullet+}$, 39), 132 (12), 131 (100), 129 (13), 128 (11), 116 (13), 115 (25), 91 (39), 77 (12), 64 (11), 63 (13), 51 (13).

6-Methoxy-2,2-dimethylindan (20b): ^{1}H NMR δ 7.04 (d, 1H, J = 8.1 Hz), 6.72 (s, 1H), 6.67 (d, 1H, J = 8.1 Hz), 3.77 (s, 3H), 2.69 (s, 2H), 2.65 (s, 2H), 1.14 (s, 6H); ^{13}C NMR δ 158.5 (C), 145.0 (C), 135.6 (C), 125.1 (CH), 111.7 (CH), 110.4 (CH), 55.4 (CH_3O), 48.0 (CH_2), 46.9 (CH_2), 40.6 (C), 28.9 (CH_3); GC/MS 176 ($M^{\bullet+}$, 76), 162 (11), 161 (100), 146 (19), 145 (29), 135 (13), 131 (15), 129 (11), 128 (11), 121 (11), 117 (17), 115 (33), 105 (18), 103 (17), 91 (43), 77 (21), 65 (17), 63 (11), 51 (19).

5-Methoxy-2,2-dimethylindan (20c): ^{1}H NMR δ 7.04 (d, 1H, J = 8.1 Hz), 6.72 (s, 1H), 6.67 (d, 1H, J = 8.2 Hz), 3.77 (s, 3H), 2.69 (s, 2H), 2.65 (s, 2H), 1.14 (s, 6H); ^{13}C NMR δ 158.5 (C), 138.2 (C), 134.9 (C), 125.1 (CH), 111.7 (CH), 110.4 (CH), 55.4 (CH_3O), 48.0 (CH_2), 46.9 (CH_2), 40.5 (C), 28.9 (CH_3); GC/MS 176 ($M^{\bullet+}$, 77), 175 (12), 162 (12), 161 (100), 146 (19), 145 (25), 135 (12), 131 (12), 129 (11), 128 (10), 121 (11), 117 (12), 115 (25), 105 (19), 103 (12), 91 (39), 77 (20), 65 (13), 63 (12), 51 (19).

1,2,2-Trimethylindan (21a, R = CH_3): ^{1}H NMR δ 7.16–7.10 (m, 4H), 2.81 (q, 1H, J = 7.2 Hz), 2.72 (d, 1H, J = 15.5 Hz), 2.64 (d, 1H, J = 15.5 Hz), 1.17 (s, 3H), 1.15 (d, 3H, J = 7.2 Hz), 0.84 (s, 3H); ^{13}C NMR δ 148.2 (C), 142.6 (C), 126.0 (CH), 124.4 (CH), 123.3 (CH), 48.9 (CH), 47.2 (CH_2), 44.0 (C), 27.6 (CH_3), 22.4 (CH_3), 13.0 (CH_3); GC/MS 160 ($M^{\bullet+}$, 27), 146 (12), 145 (100), 131 (13), 130 (10), 129 (13), 128 (15), 117 (29), 115 (24), 91 (20).

1-*tert*-Butyl-2,2-dimethylindan (21a, R = $C(CH_3)_3$): ^{1}H NMR δ 7.28–7.26 (m, 1H), 7.15–7.05 (m, 3H), 2.93 (d, 1H, J = 15.4 Hz), 2.49 (s, 1H), 2.41 (d, 1H, J = 15.4 Hz), 1.33 (s, 3H), 1.04 (s, 9H), 1.02 (s, 3H); ^{13}C NMR δ 147.5 (C), 143.9 (C), 127.9 (CH), 125.9 (CH), 124.7 (CH), 124.5 (CH), 64.8 (CH), 48.1 (CH_2), 44.8 (C), 35.3 (C), 33.0 (CH_3), 29.4 (CH_3), 25.9 (CH_3); GC/MS 202 ($M^{\bullet+}$, 0.8), 146 (27), 145 (100), 131 (11), 130 (11), 129 (13), 128 (15), 117 (20), 115 (20), 91 (12), 57 (13).

6-Methoxy-1-*tert*-butyl-2,2-dimethylindan (21b, R = $C(CH_3)_3$): ^{1}H NMR δ 7.04 (d, 1H, J = 8.1 Hz), 6.84 (d, 1H, J = 2.3 Hz), 6.69 (dd, 1H, J_1 = 8.1 Hz, J_2 = 2.4 Hz), 3.79 (s, 3H), 2.86 (d, 1H, J = 15.0 Hz), 2.44 (s, 1H), 2.33 (d, 1H, J = 15.0 Hz), 1.32 (s, 3H), 1.04 (s, 9H), 1.00 (s, 3H); ^{13}C NMR δ 157.3 (C), 147.8 (C), 136.1 (C), 124.7 (CH), 114.4 (CH), 111.0 (CH), 65.0 (CH), 55.4 (CH_3-O), 47.2 (CH_2), 45.3 (C), 35.3 (C), 33.0 (CH_3), 29.4 (CH_3), 25.9 (CH_3); GC/MS 232 ($M^{\bullet+}$, 6), 176 (20), 175 (100), 160 (13), 115 (13), 57 (13).

5-Methoxy-1-*tert*-butyl-2,2-dimethylindan (21c, R = $C(CH_3)_3$)): ^{1}H NMR δ 7.14 (d, 1H, J = 8.2 Hz), 6.71 (s, 1H), 6.64 (d, 1H, J = 8.4 Hz), 3.78 (s, 3H), 2.89 (d, 1H, J = 15.4 Hz), 2.41 (s, 1H), 2.36 (d, 1H, J = 15.4 Hz), 1.31 (s, 3H), 1.00 (s, 12H); ^{13}C NMR δ 158.3 (C), 145.4 (C), 138.3 (C), 128.4 (CH), 110.4 (CH), 109.9 (CH), 64.1 (CH), 55.2 (CH_3O), 48.3 (CH_2), 45.1 (C), 35.3 (C), 33.0 (CH_3), 29.3 (CH_3), 25.9 (CH_3); GC/MS 232 ($M^{\bullet+}$, 2), 176 (13), 175 (100).

6-Methoxy-1,2,2-trimethylindan (21b, R = CH_3). This compound was not isolated from the preparative photolysis mixture. It was quantified using product **20b**, correcting for the difference in carbon atoms.

5-Methoxy-1,2,2-trimethylindan (21c, R = CH_3). A preparative photolysis was not done for ester **9c** because of difficulties encountered in making a sufficient quantity of the ester. This product was quantified using product **20c**, correcting for the difference in carbon atoms.

5-*tert*-Butyl-6-methoxyindan. This compound was isolated from a preparative photolysis of ester **10b**. It results from coupling of an out-of-cage *tert*-butyl radical with the aromatic ring of the indanyl radical. It was formed in less than 1% yield and was not quantified: ^{1}H NMR δ 7.05 (s, 1H), 6.71 (s, 1H), 3.80 (s, 3H), 2.68 (s, 2H), 2.65 (s, 2H), 1.35 (s, 9H), 1.14 (s, 6H); ^{13}C NMR δ 157.5 (C), 141.8 (C), 136.1 (C), 134.6 (C), 122.6 (CH), 108.4 (CH), 55.2 (CH_3O), 48.0 (CH_2), 47.5 (CH_2), 40.3 (C), 34.7 (C), 30.0 (CH_3), 29.2 (CH_3); GC/MS 232 ($M^{\bullet+}$, 16), 218 (16), 217 (100).

2,2-Dimethyl-1-indanylmethanol (22a): ^{1}H NMR δ 7.32–7.28 (m, 1H), 7.19–7.15 (m, 3H), 3.90 (q, 1H, J_1 = 10.8 Hz, J_2 = 5.6 Hz), 3.81 (q, 1H, J_1 = 10.8 Hz, J_2 = 6.6 Hz), 2.86 (t, 1H, J_1 = 6.6 Hz, J_2 = 5.6 Hz), 2.79 (d, 1H, J = 15.4 Hz), 2.68 (d, 1H, J = 15.4 Hz), 1.52 (brs, 1H), 1.17 (s, 3H), 1.10 (s, 3H); ^{13}C NMR δ 144.2 (C), 143.4 (C), 126.8 (CH), 126.2 (CH), 124.9 (CH), 124.8 (CH), 63.6 (CH_2O), 56.7 (CH), 47.4 (CH_2), 42.3 (C), 29.7 (CH_3), 23.3 (CH_3); GC/MS 176 ($M^{\bullet+}$, 14), 146 (13), 145 (100), 143 (10), 130 (13), 129 (19), 128 (21), 117 (24), 115 (21), 105 (10), 91 (19).

6-Methoxy-2,2-dimethyl-1-indanylmethanol (22b): ^{1}H NMR δ 7.08 (d, 1H, J = 8.1 Hz), 6.87 (brs, 1H), 6.72 (dd, 1H, J_1 = 8.2 Hz, J_2 = 2.4 Hz), 3.92–3.67 (m, 2H), 3.79 (s, 3H), 2.81 (t, 1H, J = 6.0 Hz), 2.70 (d, 1H, J = 15.1 Hz), 2.60 (d, 1H, J = 15.1 Hz), 1.15 (s, 3H), 1.08 (s, 3H); ^{13}C NMR δ 158.6 (C), 145.8 (C), 135.3 (C), 125.4 (CH), 112.3 (CH), 110.6 (CH), 63.5 (CH_2O), 57.0 (CH), 55.4 (CH_3O), 46.5 (CH_2), 42.7 (C), 29.7 (CH_3), 23.3 (CH_3); GC/MS 206 ($M^{\bullet+}$, 21), 176 (13), 175 (100), 160 (13), 145 (11), 128 (10), 115 (14), 91 (13).

5-Methoxy-2,2-dimethyl-1-indanylmethanol (22c). A preparative photolysis was not done for ester **9c** because of difficulties encountered in a making sufficient quantity of the ester. This product was quantified using the isomer **22b**.

Racemic 1,1′-Bi(2,2,2′,2′-tetramethylindan) (23a): recrystallized from hexanes; mp 187–188 °C; ^{1}H NMR δ 7.23 (d, 1H, J = 7.5 Hz), 7.10 (t, 1H, J = 7.5 Hz), 6.91 (t, 1H, J = 7.5 Hz), 6.52 (d, 1H, J = 7.5 Hz), 3.07 (s, 1H), 2.84 (d, 1H, J = 15.0 Hz), 2.77 (d, 1H, J = 15.0 Hz), 1.30 (s, 3H), 1.00 (s, 3H); ^{13}C NMR δ 143.3 (C), 143.2 (C), 127.5 (CH), 125.6 (CH), 124.9 (CH), 124.4 (CH), 52.8 (CH), 47.4 (CH_2), 45.4 (C), 27.5 (CH_3), 24.0 (CH_3); GC/MS 290 ($M^{\bullet+}$, 0.2), 146 (18), 145 (100), 130 (11), 129 (14), 128 (12), 117 (20), 115 (18), 91 (18).

Meso **1,1′-Bi(2,2,2′,2′-tetramethylindan) (24a).** This compound gave broad signals indicating exchange at room temperature. This exchange is the subject of another paper.[13] ^{1}H NMR (233 K) δ 7.40 (d, 1H, J = 7.30 Hz), 7.32–7.24 (m, 2H), 7.19 (d, 1H, J = 7.0 Hz), 7.13–7.11 (m, 2H), 6.87 (td, 1H, J_1 = 6.65 Hz, J_2 = 2.1 Hz), 6.07 (d, 1H, J = 7.56 Hz), 3.18 (s, 1H), 3.07 (d, 1H, J = 16.05 Hz), 2.65 (d, 1H, 16.05 Hz), 2.32 (s, 2H), 1.35 (s, 3H), 1.09 (s, 3H), 1.00 (s, 3H), 0.82 (s, 3H). ^{13}C NMR (233 K) δ 149.5, 144.9, 143.5, 143.1, 128.6, 126.5, 125.9, 125.4, 125.3, 124.6, 62.3 (CH), 56.5 (CH), 48.4 (CH_2), 47.4 (CH_2), 41.2 (C), 41.0 (C), 34.2 (CH_3), 33.0 (CH_3), 25.8 (CH_3), 23.9 (CH_3); GC/MS 290 ($M^{\bullet+}$, 0.1), 146 (20), 145 (100), 130 (14), 129 (21), 128 (19), 117 (23), 115 (24), 91 (21).

Racemic 1,1′-Bi(6,6′-dimethoxy-2,2,2′,2′-tetramethylindan) (23b): recrystallized from ethanol; mp 139–142 °C; ^{1}H NMR δ 7.08 (d, 1H, J = 8.2 Hz), 6.63 (dd, 1H, J_1 = 8.1 Hz, J_2 = 2.3 Hz), 6.12 (brs, 1H), 3.49 (s, 3H), 3.00 (s, 1H), 2.72 (d, 1H, J = 14.7 Hz), 2.65 (d, 1H, J = 14.7 Hz), 1.24 (s, 3H), 0.98 (s, 3H); ^{13}C NMR δ 158.4 (C), 145.0 (C), 135.3 (C), 124.6 (CH), 113.8 (CH), 111.4 (CH), 55.3 (CH_3O), 52.9 (CH), 46.5 (CH_2), 45.7 (C), 27.6 (CH_3), 24.1 (CH_3).

Meso **1,1′-Bi(6,6′-dimethoxy-2,2,2′,2′-tetramethylindan) (24b):** This compound was isolated as a mixture and was not separated. For the quantitative photolysis the diastereomer **23b** was used to quantify the yield of **24b**.

Racemic 1,1′-Bi(5,5′-dimethoxy-2,2,2′,2′-tetramethylindan) (23c): recrystallized from hexanes: mp 187–188 °C; ^{1}H NMR δ 6.78 (s, 1H), 6.49–6.39 (m, 2H), 3.75 (s, 3H), 2.95 (s, 1H), 2.78 (d, 1H, J = 15.2 Hz), 2.69 (d, 1H, J = 15.2 Hz), 1.26 (s, 3H), 0.97 (s, 3H); ^{13}C NMR δ 158.1 (C), 144.9 (C), 135.3 (C), 128.0 (CH), 110.3 (CH), 110.2 (CH), 55.3 (CH_3O), 52.1 (CH), 47.6 (CH_2), 45.6 (C), 27.4 (CH_3), 24.0 (CH_3); GC/MS 350 ($M^{\bullet+}$, 0.4), 176 (14), 175 (100).

Meso **1,1′-Bi(5,5′-dimethoxy-2,2,2′,2′-tetramethylindan) (24c):** ^{1}H NMR (250 MHz, 233 K) δ 7.28 (d, 1H, J = 7.9 Hz), 6.85 (d, 1H, J = 7.9 Hz), 6.74 (s, 1H), 6.67 (s, 1H), 6.44 (d, 1H, J = 8.6 Hz), 6.00 (d, 1H, J = 8.0 Hz), 3.92 (s, 3H), 3.77 (s, 3H), 3.08–3.00 (m, 3H), ~2.60 (d, 1H, J = 15.8 Hz, the other half of the AB quartet is obscured under the multiplet at 3.08–3.00 ppm), 2.62 (s, 2H), 1.33 (s, 3H), 1.09 (s, 3H), 0.99 (s, 3H), 0.82 (s, 3H); ^{13}C NMR δ 158.3 (C), 158.2 (C), 144.9, 144.5, 141.4, 136.8, 112.1, 111.6, 109.3, 109.2, 125.88, 125.85, 61.8 (CH_3O), 55.5 (CH), 55.3 (CH), 48.5 (C), 47.5 (C), 41.5 (CH_2), 41.3 (CH_2), 34.3 (CH_3), 33.0 (CH_3), 25.8 (CH_3), 24.0 (CH_3). GC/MS 350 ($M^{\bullet+}$, 0.3), 176 (13), 175 (100).

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.

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.[19] Singlet lifetimes were measured using a PRA single photon counting apparatus with a hydrogen flash lamp of pulse width about 1 ns.

Quantum Yield Measurements. The quantum yield of reaction for the esters **6–10** in methanol were determined using 3-methoxybenzyl acetate in aqueous dioxane as the standard. The quantum yield of reaction for 3-methoxybenzyl acetate, measured previously by Zimmerman,[1] is 0.13. The esters, as well as the standard, were irradiated in a merry-go-round apparatus using a Hanovia reactor with five 75 W 253.7 nm lamps. Samples were taken every 1 min for 5 min. Each sample was run in duplicate. A plot of percent conversion of the ester divided by time versus time was extrapolated to zero time. The ratio of the zero time values for the ester and the standard multiplied by 0.13 provided the quantum yield of reaction.

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.

Supplementary Material Available: Copies of ^{1}H and/or ^{13}C NMR spectra of **8**, **9a**, **9b**, **10a**, and **10c** (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO942166M