

# 1,3-Dimethoxy-5-methylene-1,3-cyclohexadiene Compounds with Leaving Groups at C6: Generation, Solvolytic Reactivity, and Their Importance in the Photochemistry of 3,5-Dimethoxybenzyl Derivatives

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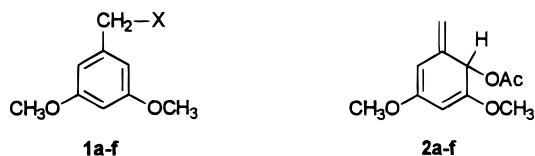
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The photochemistry of 3,5-dimethoxybenzyl compounds with the leaving groups acetate (**1a**), chloride (**1b**), bromide (**1c**), iodide (**1d**), diethyl phosphate (**1e**), and trimethylamine (**1f**), as the chloride, was examined by both product studies and flash photolysis. The isomeric triene, 5-methylene-1,3-cyclohexadiene derivative was observed for the acetate (**2a**), diethyl phosphate (**2e**) and trimethylammonium chloride (**2f**). The solvolysis of these derivatives, **2**, was examined in alcohol solvents and the rate correlation with  $Y_{\text{OTS}}$  values gave  $m = 0.47$  (**2a**) and  $0.63$  (**2e**), suggesting  $S_{\text{N}}1$  reactivity but with an early transition state. Quantum yields for formation of **2a** and **2e** indicated that these trienes play only a minor role (~16%) in the overall photochemistry of the corresponding arylmethyl substrates.

## Introduction

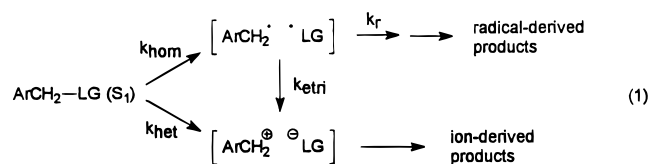
Recently we reported that the photolysis of 3,5-dimethoxybenzyl acetate, **1a**, in either methanol or hexanes, resulted in the formation of the isomeric triene **2a**, Scheme 1.<sup>1</sup> In hexanes, secondary photochemistry converted **2a** to another isomer, the bicyclic ester **3**, which was purified by silica gel chromatography and characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The bicyclic



**a** (X = OAc), **b** (X = Cl), **c** (X = Br), **d** (X = I),  
**e** (X = O(PO)(OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), **f** (X = N(CH<sub>3</sub>)<sub>3</sub> Cl).

isomer **3** could then be converted by thermolysis in hexane at 50 °C back to **2a** which was also characterized spectroscopically. In methanol, **2a** was found to react by ground-state solvolysis with a half-life of 2.7 min to give the ether **4** (60%) and the original ester **1a** (40%). Finally, nanosecond laser flash photolysis (LFP) with a Nd:YAG laser at 266 nm gave a transient with the same absorption spectrum as **2a** and with a lifetime (>10ms) longer than the instrument's response time. However, multiple flashes over about a minute duration allowed sufficient quantity of this transient to be generated that its decay could be monitored by conventional UV absorbance spectra. That this transient was indeed **2a** was confirmed by measuring an identical solvolysis rate in methanol as that obtained by generating **2a** from **3**, as described above.

This observation that the ether **4**, formed on photolysis of **1a** in methanol comes, at least in part, from ground state solvolysis of a photochemically generated intermediate **2a**, is relevant to the general question of considerable recent interest as to the pathway(s) for formation of ion-derived products in benzylic photosolvolysis reactions.<sup>2</sup> As outlined in eq 1, two different proposals have been made: (1) competition between heterolytic ( $k_{\text{het}}$ ) and homolytic ( $k_{\text{hom}}$ ) cleavage occurs in the originally formed excited singlet state and this competition is the major factor controlling the yields of ion- and radical-derived products; (2) the main excited-state process is homolytic cleavage ( $k_{\text{hom}}$ ) and the competition is then between electron transfer ( $k_{\text{etri}}$ ) converting the radical pair to the ion pair and other chemistry of the radical pair ( $k_r$ ). These concepts have been recently reviewed.<sup>2</sup>



In the case of arylmethyl esters,  $k_r$  is mainly the decarboxylation ( $k_{\text{CO}_2}$ ) of the acyloxy radical ( $\text{R}-\text{CO}_2\cdot$ ). On the basis of the second mechanism, we have used product yields and the radical clock method to obtain a large number of values for both  $k_{\text{etri}}$  and  $k_{\text{CO}_2}$  as a function of systematic variation in ester structure that seem to make chemical sense;<sup>3</sup> the  $k_{\text{etri}}$  values can be fitted to Marcus

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## Scheme 1. Photochemical Formation and Reactivity of 2a in Methanol

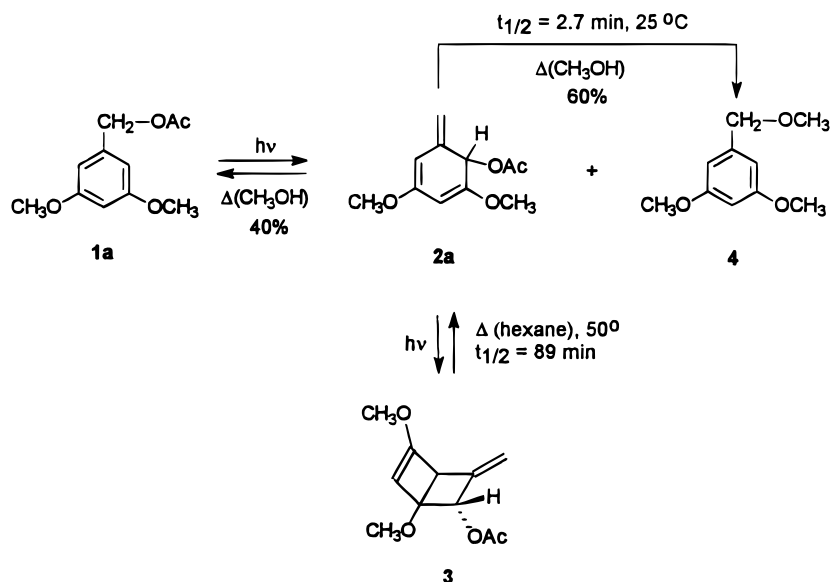


Table 1. Product Yields for the Photolysis of 3,5-Dimethoxybenzyl Acetate in Alcohol Solvents

solvent	ArCH <sub>3</sub>	ArCH <sub>2</sub> CH <sub>3</sub>	ArCH <sub>2</sub> -2 <sup>a</sup>	isomer 9	ArCH <sub>2</sub> OS	M.B. <sup>b</sup>	% C <sup>c</sup>	R/I <sup>d</sup>	Y <sub>OTS</sub>
<i>t</i> -BuOH	1.7	57.3	16.6	1.3	23.0	97	37	77/23	-3.74
<i>i</i> -PrOH	4.7	47.1	ND	6.0	42.4	86	34	58/42	-2.83
CH <sub>3</sub> CH <sub>2</sub> OH	1.2	39.1	ND	ND	40.1	88 <sup>e</sup>	33	59/41	-1.96
MeOH	3.0	20.8	11.7	4.7	59.8	96	64	40/60	-0.92
TFE	3.8	27.3	ND	ND	68.8	98	21	31/69	+1.77

<sup>a</sup> Twice the molar yield. <sup>b</sup> Mass balance based on amount of 1a reacted. <sup>c</sup> Percent conversion. <sup>d</sup> Ratio of radical- to ion-derived product normalized to 100%. <sup>e</sup> 9% of an unknown compound was also observed.

theory in both the normal and inverted region and the  $k_{CO_2}$  values increase, as expected, with the stability of the alkyl radical formed.<sup>4</sup> Moreover, recent direct measurement of rates of decarboxylation of acyloxy radicals by LFP are in agreement with our indirectly determined ones.<sup>5</sup>

However, mechanism (1) above, direct heterolytic cleavage from  $S_1$ , is certainly occurring for some substrates. For instance, contact ion pairs have been observed by LFP within the 20 ps instrument response time for a set of substituted diphenylmethyl chlorides followed by further growth of the ion pair by electron-transfer conversion of the radical pair.<sup>6</sup> Moreover, 3,5-dimethoxybenzyl substrates have been advocated as useful chromophores for the development of photolabile protecting groups on the basis of their ability to give high yields of ion derived products with good efficiency.<sup>7</sup> These studies were founded on the pioneering study by Zimmerman and Sandel<sup>8</sup> that demonstrated enhanced yields of solvolysis products on irradiation of both 3-methoxy and 3,5-dimethoxybenzyl acetate in aqueous dioxane. These observations have been rationalized on the basis of MO calculations, originally at the Hückel level<sup>8</sup> but more recently at much higher levels,<sup>9,10</sup> that demonstrate that resonance electron donating groups such as methoxy are better donors, in the excited singlet state, from the meta (and ortho) positions than from the para position. This observation, which contrasts with ground state observations of ortho/para activation has been termed the photochemical "meta effect".<sup>8-10</sup>

Explanation of product yields for ion- and radical-derived products will be made more difficult to interpret for both of these mechanistic proposals if the isomeric triene 2a, is a major product resulting from primary

photochemistry of 1a. For instance, if 2a is formed from an in-cage singlet radical pair, as in the accepted mechanism for the photo-Fries reaction,<sup>11</sup> and then it reacts by rapid ground-state solvolysis, then the ion-derived product 4 results from the initial photochemical generation of radicals, i.e., the homolytic pathway,  $k_{hom}$ . To assess the importance and reactivity of the 5-methylene-1,3-cyclohexadiene isomers 2a-f as a function of leaving group in 3,5-dimethoxybenzyl chromophore chemistry, we have now examined the derivatives 1a-f.

## Results and Discussion

**Solvent Effects on the Photochemistry of 1a (X = OAc).** We first examined the effect of solvent on the product distribution for 1a. These results are shown in

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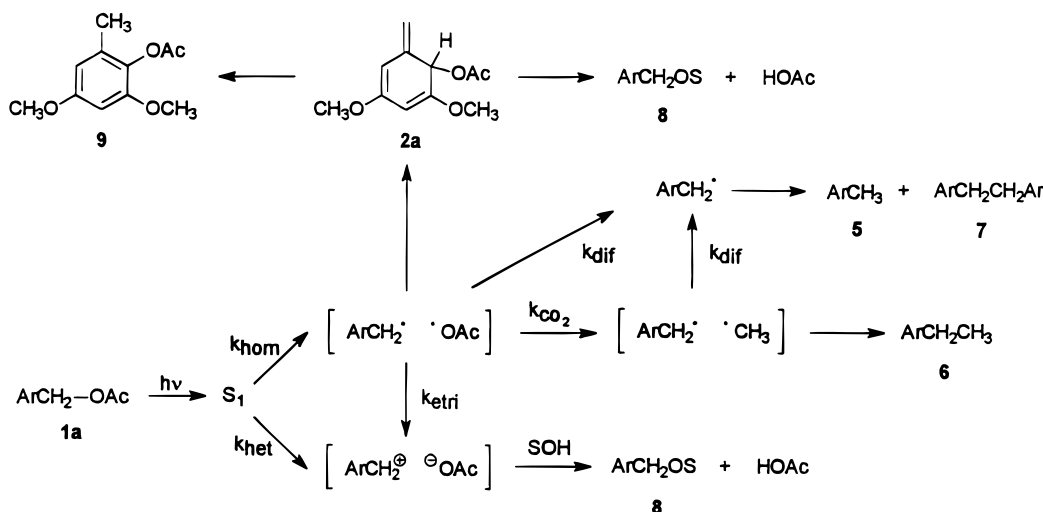
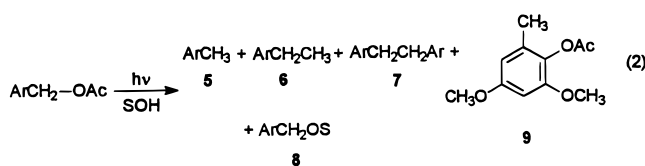
Scheme 2. Mechanism for the Photolysis of **1a** in Alcohol Solvents

Table 1 and eq 2 (Ar = 3,5-dimethoxybenzyl). All reac-



tions were done at 25 °C with nitrogen purging using all 16 lamps (254 nm) in a Rayonet Reactor. The percent conversion and mass balance are given for samples taken after 5 min of irradiation of 100 mg of substrate in 100 mL of solvent. The high percentage conversion after such short times attests to the very high reactivity of this particular substrate. In fact the excited-state lifetime of **1a** is likely very short (<1 ns) but cannot be determined because **1a** does not fluoresce. In our previous publication on the photochemistry of **1a** in methanol,<sup>1</sup> we had not reported the yield of the isomer **9**, because the yield is low and we were not specifically looking for it. Its retention time (GC) is nearly identical to that of the starting material but our current high resolution column gives baseline separation. It has been characterized previously<sup>12</sup> from irradiation of **1a** in hexane and is derived by tautomerization of the initially formed isomeric triene **2a**, Scheme 2. It can, therefore, most likely be regarded as a radical pair derived product as can 3,5-dimethoxytoluene, **5**, 3,5-dimethoxyethylbenzene, **6**, and the dimer **7**. These products are rationalized by the general mechanism shown in Scheme 2. The ratio of radical-derived to ion-derived products, R/I = yield[(**5** + **6** + **7** + **9**)/(**8**)], changes systematically in favor of the ion-derived ether **8**, as the ionizing power of the solvent increases as measured by the  $Y_{OTS}$  values.<sup>13</sup> There is also a systematic increase in the yield of the ethylbenzene as the viscosity increases and the ionizing power of the solvent decreases over the series methanol, ethanol, 2-propanol, *tert*-butyl alcohol. This result is likely a consequence of the increased lifetime of the radical pair allowing decarboxylation of the acyloxy radical followed by in-cage coupling. The rate constant for this decarboxylation is  $\sim 1 \times 10^9 \text{ s}^{-1}$ ,<sup>4</sup> slower than the rate of diffusion ( $k_{dif} = 5 \times 10^9 \text{ s}^{-1}$ ) in methanol ( $\eta = 0.59 \times 10^{-3}$

Pa·s)<sup>14</sup> estimated from the diffusional escape equation ( $k = (RT/2\pi Nr^3\eta)$ )<sup>15</sup> assuming 6 Å spheres but faster than in *tert*-butyl alcohol ( $k_{dif} = 5 \times 10^8 \text{ s}^{-1}$ ,  $\eta = 5.9 \times 10^{-3}$  Pa·s).<sup>14</sup>

**Flash Photolysis of 1a.** As reported in our preliminary communication,<sup>1</sup> nanosecond laser flash photolysis at 266 nm of **1a** in methanol, either with or without nitrogen purging, gave a weak transient ( $\lambda_{max}$  at 320 nm) which did not decay at the long time limit of the instrument response (10 ms). This transient was assigned to the triene **2a**. Higher concentrations of the transient were generated by multiple pulses (~50 at a repetition rate of 1 Hz) and the decay of the transient monitored by conventional UV spectra, Figure 1. The same transient was also generated by classical microsecond flash lamp photolysis<sup>16</sup> and, again, its decay monitored by UV. This transient was observed in all the solvents in Table 1, except TFE. First-order rate constants for its decay are given in Table 2.

The values in methanol with added salt (entries 2–4) indicate a very modest salt effect, as expected for an  $S_N1$  ionization in a solvent as polar as methanol.<sup>17</sup> There is no indication of increased rate in the presence of the added nucleophile (chloride ion), no internal return (acetate ion) and no special salt effect (perchlorate ion). A plot of  $\log(k/T)$  versus  $1/T$  according to the Eyring equation (entries 1, 5, and 6) gives  $\Delta H^\ddagger = 16.3 \text{ kcal/mol}$  and  $\Delta S^\ddagger = -14 \text{ eu}$ . The  $\Delta S^\ddagger$  value is comparable to those observed in the solvolysis of benzyl tosylates in 80% aqueous acetone ( $Y_{OTS} = -0.94$ )<sup>18</sup> and in 30% ethanol: 70% water ( $Y_{OTS} = 3.32$ ).<sup>19</sup>

An estimate of the enhanced reactivity of **2a** relative to 3,5-dimethoxybenzyl acetate **1a** can be made as

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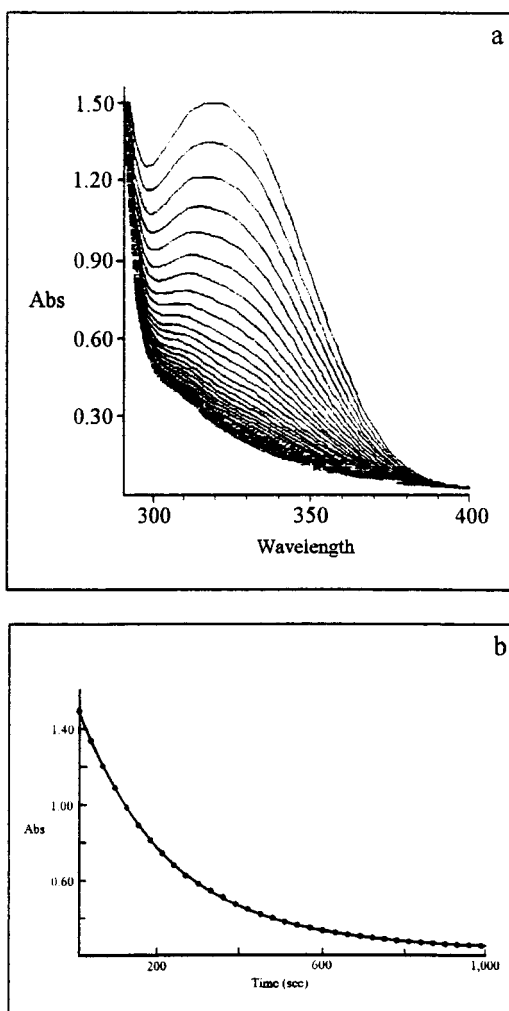
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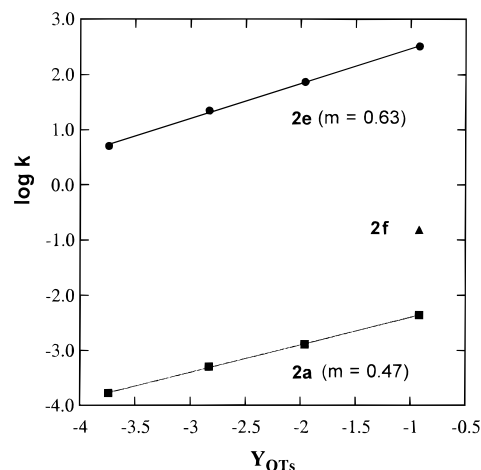
**Figure 1.** (a) UV spectra of the decay of the intermediate **2a** in methanol at 25 °C. (b) First-order fit to the decay.

**Table 2. Rate Constants for the Disappearance of 6-Acetoxy-3,5-dimethoxy-5-methylene-1,3-cyclohexadiene, **2a****

entry	$k$ (s <sup>-1</sup> )/10 <sup>-3</sup> <sup>a</sup>	$t$ (°C)	solvent	added
1	3.80 ± 0.06	25.0	MeOH	
2	4.27 ± 0.03	25.0	MeOH	0.1 M NaCl
3	4.15 ± 0.02	25.0	MeOH	0.1 M NaOAc
4	4.22 ± 0.10	25.0	MeOH	0.1 M NaClO <sub>4</sub>
5	6.85 ± 0.09	30.5	MeOH	
6	2.25 ± 0.08	18.9	MeOH	
7	1.26 ± 0.05	25.0	EtOH	
8	0.500 ± 0.009	25.0	<i>i</i> -PrOH	
9	0.164 ± 0.008	25.0	<i>t</i> -BuOH	

<sup>a</sup> Errors quoted are the average deviations for at least three determinations of the rate constant.

follows. The rate constant for solvolysis of 3-methoxybenzyl tosylate in 80% acetone:20% water ( $Y_{\text{OTS}} = -0.94$ ) at 25 °C is  $1.08 \times 10^{-5} \text{ s}^{-1}$ .<sup>18</sup> The additional methoxy group in **1a** and the change in solvent to methanol ( $Y_{\text{OTS}} = -0.92$ ) should have only a minor effect on the rate. However, the change in leaving group from tosylate to acetate gives an estimated change in rate by a factor  $3.8 \times 10^{-11}$ , on the basis of leaving group abilities obtained from the solvolysis of 1-phenylethyl derivatives.<sup>20</sup> Therefore, the estimated rate constant for solvolysis of 3,5-dimethoxybenzyl acetate, **1a**, in methanol at 25 °C is  $4.2 \times 10^{-16} \text{ s}^{-1}$ , approximately  $10^{13}$  slower in rate than its



**Figure 2.** Grunwald–Winstein plots for the first-order decay of **2a** ( $X = \text{OAc}$ ), **2e** ( $X = \text{O}(\text{PO})(\text{OCH}_2\text{CH}_3)_2$ ), and **2f** ( $X = \text{N}(\text{CH}_3)_3\text{Cl}$ ).

nonaromatic isomer **2a**. Because the entropies of activation are similar for solvolysis of both substrates, this very large change in rate can be attributed almost entirely to a lower enthalpy of activation as a consequence of the decreased stability of the nonaromatic isomer **2a**.

Finally, the data in Table 2 (entries 1, 7–9) allow the construction of a Grunwald–Winstein<sup>13</sup> plot. Because acetate is a poor leaving group, only very limited data is available for its  $\text{S}_{\text{N}}1$  reactivity. However, a kinetic study of solvent effects for ferrocenylmethyl acetate has provided a  $Y_{\text{OAc}}$  scale<sup>21</sup> but it only includes one of the solvents (ethanol) used in the results in Table 2. We have therefore used the  $Y_{\text{OTS}}$  scale which gives a fair correlation ( $r = 0.830$ ) with the  $Y_{\text{OAc}}$  scale.<sup>21</sup> The  $mY_{\text{OTS}}$  plot gives  $m = 0.47$ , Figure 2. There is some uncertainty in this value because of the limited number of solvents examined but it is certainly low for an  $\text{S}_{\text{N}}1$  solvolysis. For instance, for benzyl tosylate solvolysis, using the modified Grunwald–Winstein equation that includes a term for solvent nucleophilicity,  $m = 0.83$  at 50 °C<sup>22</sup> and  $m = 0.80$  (without including the term for solvent nucleophilicity) for the solvolysis of 4-methoxybenzyl chloride at 25 °C.<sup>23</sup> A reasonable explanation for the reduced value for **2a** is that the lower  $\Delta H^\ddagger$  will make the transition state for ion-pair formation earlier so that the charge development will be less and the response to ionizing power of the solvent lower.

The products obtained in the solvolysis of **2a** were examined only in methanol. This was done by converting **3** (isolated by column chromatography) back to **2a** by thermolysis in hexane at 50 °C. This reaction could be monitored by the appearance of **2a** by UV spectra, Figure 3. The first-order rate constant is  $1.3 \times 10^{-4} \text{ s}^{-1}$ . Evaporation of the hexane and addition of methanol resulted in the formation of 3,5-dimethoxybenzyl acetate, **1a** ( $X = \text{OAc}$ ), (40%) and 3,5-dimethoxybenzyl methyl ether **4**, (60%) as determined by <sup>1</sup>H NMR integration.

**Quantum Yield for Formation of **2a** ( $X = \text{OAc}$ ) from **1a** ( $X = \text{OAc}$ ).** The quantum yield of formation ( $\Phi$

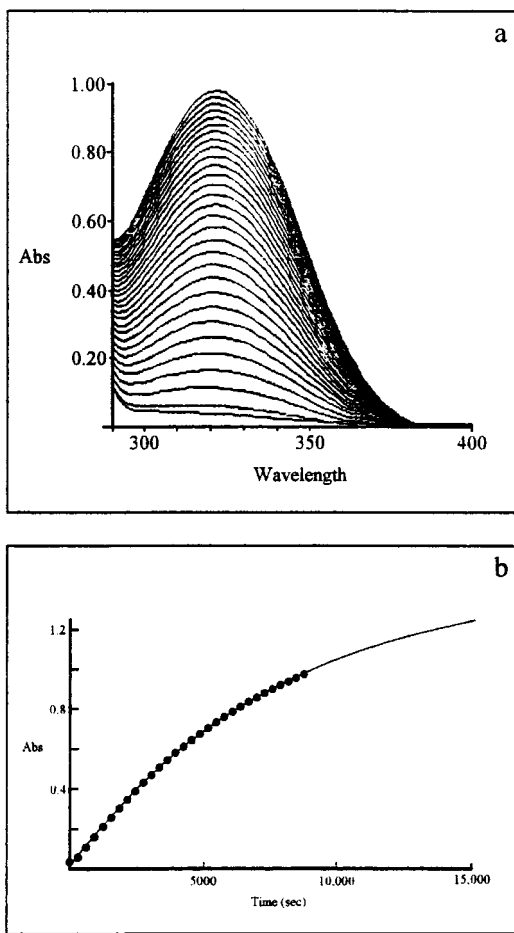
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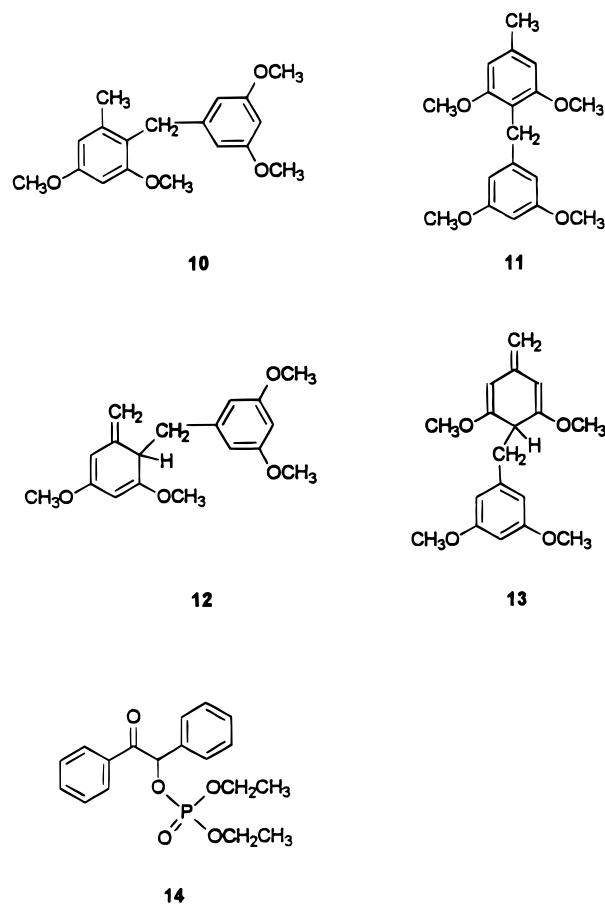
**Figure 3.** (a) UV spectra for the formation of **2a** (X = OAc) from **3** in hexane at 50 °C. (b) First-order fit to the growth.

= 0.061) of the triene **2a** was determined by measuring its absorbance ( $\epsilon = 5.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  at 320)<sup>1</sup> after generation by nanosecond LFP. The power of the laser pulse was determined using the absorbance of the solvated electron created from aqueous solutions of iodide ion ( $\epsilon = 1.33 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  at 600 nm,  $\Phi = 0.29$ ).<sup>24</sup> Because only 60% of **2a** proceeds to the methyl ether **4**, the quantum yield of formation of the ether by this pathway is 0.036. To assess the importance of this pathway in the overall photochemistry of **1a**, we have also measured the quantum yield ( $\Phi = 0.37$ ) for its disappearance in methanol. From the data in Table 1, the yield of the methyl ether **5**, is 60% and, therefore, the quantum yield for ether appearance is 0.22. We conclude that the yield for ether formation by the pathway of excited-state conversion of **1a** to **2a** followed by ground-state solvolysis of **2a** accounts for only  $(0.036/0.22) \times 100 = 16\%$  of the total. Therefore, this pathway does not significantly perturb the more normal excited-state conversion of **1a** to radical pairs and ion pairs.

**Photolysis of 3,5-Dimethoxybenzyl Derivatives (1b–f) in Methanol.** Results for the photolysis, again at 254 nm in methanol at 25 °C, are given in Table 3, along with literature values where available.<sup>25,26</sup>

**(a) 3,5-Dimethoxybenzyl Chloride, 1b (X = Cl).** As shown in Table 3, the chloride is unusual for the high yield of the dimer **7**, of the arylmethyl radical. This presumably reflects the formation of triplet radical pairs, which will be longer lived and allow cage escape. A closer examination, by GC/MS, indicated that there were actu-

ally three dimers. They were shown to be the bibenzyl derivative **7**, eq 2, (65% of the total), and the two possible aromatic coupled products **10** (25%) and **11** (10%). The latter two products are formed by ortho and para coupling of one arylmethyl radical to the other as has been observed previously for unsubstituted benzyl radicals.<sup>27,28</sup> The ratio of ortho to para coupling is almost statistical (2:1) and quite different from that for benzyl radicals where the ortho to para ratio in benzene at 28 °C is 1.04, i.e., para is formed in a yield that is higher than statistically predicted.<sup>28</sup> The first of these dimers was available from previous work in our laboratory<sup>29</sup> and **10** and **11** were synthesized by Friedel–Crafts coupling of 3,5-dimethoxybenzyl chloride with 3,5-dimethoxytoluene. These two dimers were not separated (despite attempts on both normal and reverse phase silica gel) but could be easily distinguished by <sup>1</sup>H NMR at 400 MHz, **10** having three different methoxy groups with an intensity ratio of 2:1:1 whereas **11** has only two different methoxy groups in the ratio of 2:2.



Nanosecond LFP of **1b** in methanol gave the expected transient at 320 nm that again did not decay on the millisecond time scale. Because chloride is a considerably better leaving group than acetate,<sup>20</sup> we expected that the

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**Table 3. Product Yields for the Photolysis of 3,5-Dimethoxybenzyl Derivatives 1b–f in Methanol**

X	ArCH <sub>3</sub>	ArCH <sub>2</sub> CH <sub>2</sub> OH	ArCH <sub>2</sub> ) <sub>2</sub>	ArCH <sub>2</sub> OCH <sub>3</sub>	R/I <sup>a</sup>
<b>1b</b> , X = Cl	3	14	48	34	66/34
<b>1c</b> , X = Br	1 (trace) <sup>b</sup>	6	5	74 (95) <sup>b</sup>	14/86
<b>1d</b> , X = I	6			90	6/94
<b>1e</b> , X = O(PO)(OEt) <sub>2</sub>	3		2	82	6/94
<b>1f</b> , X = N(CH <sub>3</sub> ) <sub>3</sub> Cl	55 (46) <sup>c</sup>	7	7 (low) <sup>c</sup>	21 (12) <sup>c</sup>	77/23

<sup>a</sup> Ratio of radical- to ion-derived product normalized to 100%. <sup>b</sup> Value in brackets from ref 25. <sup>c</sup> Values in brackets from ref 26.

intermediate **2b** (X = Cl) would decay considerably faster than the corresponding acetate **2a**. To our surprise the lifetime of the transient species was considerably longer, with a half-life around 15 min, but the decay was unusual in that there was considerable variation from experiment to experiment. Our conclusion is that the main species that we observed at 320 nm is the precursor to the dimer **10**, i.e., **12**, which has the same chromophore as **2b**. We also observed a band with  $\lambda_{\max}$  at 270 nm, consistent with the expected precursor of the dimer **11**, i.e., **13**. For the unsubstituted compound, 1-methylene-2,5-cyclohexadiene,  $\lambda_{\max} = 242$  nm,<sup>30</sup> and the added methoxy groups will shift the band to longer wavelength by about 16 nm.<sup>31</sup> This band also decays with a half-life of around 15 min. The erratic decay of these transients is likely a result of the formation of HCl as a byproduct in the photolysis of **1b** (X = Cl) because the conversion of **12** to **10** and **13** to **11**, a tautomerization by hydrogen atom migration, will be acid catalyzed. If any of the isomer **2c** is formed in the photolysis of **1c**, its absorbance is probably hidden under the large absorption band of **12**.

**(b) 3,5-Dimethoxybenzyl Bromide, 1c (X = Br) and 3,5-Dimethoxybenzyl iodide, 1d (X = I).** The higher yields of the ion-derived product, the methyl ether **4**, seems surprising for these two compounds because the heavy atoms, bromine and iodine, should induce intersystem crossing to the triplet followed by homolytic dissociation to triplet radical pairs. A similar high yield of ether has been observed for 1-naphthylmethyl bromide (88%,<sup>32</sup> 74%<sup>33</sup>) and iodide (>90%)<sup>32</sup> for irradiation in methanol. High yields of carbocation intermediates have also been observed by LFP of diphenylmethyl bromide ( $\Phi = 0.12$ ) and chloride ( $\Phi = 0.13$ )<sup>34</sup> in acetonitrile. Moreover, sensitization experiments with acetophenone<sup>34</sup> have shown that these cations are formed, along with radicals, from the triplet state of a number of substituted diphenylmethyl chlorides. This observation has been explained by the suggestion that bond scission and ion solvation are concerted in polar solvents so that triplet state to ion pair conversion occurs by a solvent induced intersystem crossing. Relevant to this question, very recently the important observation has been made (LFP) that the triplet state of benzoin diethyl phosphate **14**,<sup>35</sup> first forms the triplet state of the cation resulting from heterolytic cleavage of the carbon–oxygen bond. As expected these cations have very different reactivity from

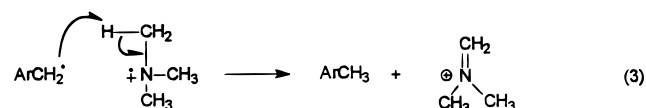
their singlet state counterparts. This surprising process may be specific to  $\alpha$ -keto carbocations.

Nanosecond LFP experiments for **1c** and **1d** in methanol gave no observable transient with  $\lambda_{\max}$  at 320 nm as expected for the triene isomers **2c** and **2d**. For both substrates, a broad transient from 330 to 450 nm with  $\lambda_{\max} = 380$  nm was observed in both nitrogen and air saturated samples. For the bromide **1c**, the absorbance was quite low. Similar transients have been observed in the LFP study of 1-naphthylmethyl bromide and iodide<sup>32</sup> and were assigned to the dihalide radical ion,  $X_2^{\cdot-}$ , resulting from combination of halide anion with halogen atoms.

**(c) Diethyl (3,5-dimethoxybenzyl) Phosphate, 1e (X = O(PO)(OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>).** Again, nanosecond LFP in methanol gave a transient at 320 nm which did not decay on the long time scale of the instrument. The quantum yield for its formation was 0.064. Because we were not able to isolate this very reactive compound, we do not know the yield of product(s) formed from its solvolysis in methanol. As in the case of the acetate **2a**, some probably goes back to starting material **1e**. The quantum yield for disappearance of **1e** in methanol was determined to be 0.45 and because the phosphate gives a 94% yield of the methyl ether, the quantum yield for ether formation is 0.42. Therefore, as in the case of the acetate derivative **1a**, the isomeric triene **2e**, accounts for a maximum of only about 16% of the excited-state chemistry. The very high yield of ion-derived products in benzylic phosphate photochemistry is well documented.<sup>36</sup>

The transient **2e** could also be generated by conventional flash lamp photolysis in methanol at 25 °C and its decay monitored in the usual alcohol solvents (k, s<sup>-1</sup>): methanol (32.4 ± 10); ethanol (74.6 ± 2.8); 2-propanol (22.7 ± 1.1); *tert*-butyl alcohol (5.11 ± 0.20). In methanol, the rate enhancement for the better leaving group, phosphate, relative to acetate, is ~10<sup>5</sup>. The  $mY_{OTs}$  plot, Figure 2, gives  $m = 0.63$ , somewhat higher than for the acetate **2a**.

**(d) (3,5-Dimethoxybenzyl)trimethylammonium Chloride, 1f (X = N(CH<sub>3</sub>)<sub>3</sub>Cl).** As the results in Table 3 indicate, photolysis of the ammonium salt in methanol is unusual in that a high yield of 3,5-dimethoxytoluene is obtained. This is a consequence of the rapid disproportionation possible in the (radical/radical ion) pair generated from homolytic cleavage from  $S_1$ , eq 3. This observation has been made before for arylmethylammonium salt photochemistry.<sup>26,37</sup>



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Nanosecond LFP in methanol again generated a transient at 320 nm assigned to the triene, **2f**. Its decay could be monitored by conventional flash photolysis ( $k = 0.15 \pm 0.02 \text{ s}^{-1}$ ), a value a factor of 39 faster than the acetate **2a**, Figure 2. This rate ratio, determined for methanol, will be very solvent dependent because the rate of solvolysis for a substrate with a neutral leaving group (triethylamine) will be only slightly affected by solvent changes in contrast to the large effect for an anionic leaving group (acetate). For reasons that we do not understand, this transient was not observed in other alcohol solvents.

### Conclusions

The most important conclusion reached from this study is that the reactive trienes produced in the photochemistry of 3,5-dimethoxybenzyl derivatives are formed in only low yield (~16% for the acetate **2a**, and the phosphate **2e**) if at all (chloride, bromide and iodide). Therefore, they do not play a significant role in the photochemistry of these substrates and their formation does not complicate previous mechanistic arguments. However, the solvolytic reactivity of these trienes is of interest. They react by an  $S_N1$  mechanism via a transition state that has less charge development than their benzylic counterparts. Moreover, as expected, they have very large rate enhancements: **2a** ( $X = \text{OAc}$ ) reacts about  $10^{13}$  times faster than the benzylic acetate **1a**. Finally, we obtained an order of leaving group ability in methanol of acetate < trimethylamine  $\ll$  phosphate (1:39:10<sup>5</sup>). We have been unable to find a literature value for trimethylamine as a leaving group in  $S_N1$  reactions of benzylic compounds but one is available for the reactions of *tert*-butyl substrates. In that case, trimethylamine is more reactive than acetate by a factor of about 65,<sup>38</sup> again in methanol. The rate ratio for phosphate to acetate in benzylic solvolysis has been estimated<sup>20</sup> at almost  $10^9$ . Therefore, the order we have obtained agrees with previous leaving group studies, although the magnitude of the change in leaving group ability is compressed, presumably because of the very high reactivity of the compounds, **2**.

### Experimental Section

Methanol (Caledon HPLC grade) was used without further purification. Ethanol was dried by distillation from magnesium ethoxide and 2-propanol and *tert*-butyl alcohol by distillation from sodium.

**Synthesis of Substrates.** The ester, 3,5-dimethoxybenzyl acetate **1a**, was prepared previously in our laboratory from the alcohol.<sup>29</sup> 3,5-Dimethoxybenzyl chloride, **1b**, was obtained from Aldrich. Spectral data (<sup>1</sup>H and <sup>13</sup>C NMR, GC/MS) are given in Table S1 (Supporting Information) for the other substrate, **1c–f**.

3,5-Dimethoxybenzyl bromide, **1c**, and 3,5-dimethoxybenzyl iodide, **1d**, were prepared in the same way using either NaBr or NaI.<sup>39</sup> A mixture of 3,5-dimethoxybenzyl alcohol (1.68 g, 10 mmol) and NaBr or NaI (15 mmol) and 15 mmol of freshly distilled boron trifluoride etherate in 25 mL of acetonitrile was stirred for 2 h at room temperature. Then, 10 mL of saturated NaHCO<sub>3</sub> was added and the mixture was extracted with dichloromethane. The organic layer was washed (10% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and sat. NaCl), dried and concentrated to give the crude

halides as solids. Both were chromatographed on silica gel with 5% ethyl acetate/hexanes and then recrystallized from hexanes to give the pure compounds. The bromide, **1c** (22%)<sup>25</sup> and iodide, **1d** (30%)<sup>40</sup> have been reported previously but without spectral data (Table S1, Supporting Information).

Diethyl (3,5-dimethoxybenzyl) phosphate, **1e**. To 2.52 g (15 mmol) of 3,5-dimethoxybenzyl alcohol and 2.01 g of pyridine at 0 °C was added 2.59 g (16.5 mmol) of diethylchlorophosphate (Aldrich) and the mixture was stirred for 6 h at 0 °C. Water (25 mL) was then added and the mixture was extracted with ether. The ether was washed with 0.1 M H<sub>2</sub>SO<sub>4</sub>, 5% NaHCO<sub>3</sub>, and water, dried, and concentrated. The crude phosphate was chromatographed on silica gel with 10% ethyl acetate/hexanes to give the pure phosphate as a clear liquid (21% yield). <sup>1</sup>H (Figure S1) and <sup>13</sup>C NMR (Figure S2) spectra are included in the Supporting Information.

**(3,5-Dimethoxybenzyl)trimethylammonium Chloride, 1f.** To 4.00 g (22.0 mmol) of 3,5-dimethoxybenzyl chloride, **1b**, in 100 mL of anhydrous ether was added, by slow bubbling, gaseous trimethylamine (Matheson). The solution was then left to stand for 16 h and the solid collected by vacuum filtration to give 5.2 g (20.7 mmol) of crude salt. The salt was washed with anhydrous ether and then dried under vacuum at 100 °C and stored in a desiccator: mp 196–198 °C. This compound has been prepared previously (mp 190–192 °C)<sup>41</sup> but without <sup>13</sup>C NMR spectral data (Table S1).

**Synthesis of 2- (10) and 4-(3,5-Dimethoxybenzyl)-3,5-dimethoxytoluene (11).** Following the procedure of Miquel et al.,<sup>42</sup> 1.21 g (7.2 mmol) of 3,5-dimethoxybenzyl chloride (Aldrich), 2.00 g (13.1 mmol) of 3,5-dimethoxytoluene (Aldrich) and 0.35 g of anhydrous ZnCl<sub>2</sub> were stirred in 8.0 mL of chloroform for 24 h. After adding 15 mL more chloroform, the organic layer was washed with water, dried and concentrated to give 2.5 g of crude material. GC/MS analysis indicated two compounds of the appropriate *m/z* equal to 302. This material was chromatographed on reversed-phase silica gel (EM Li-Chroprep RP-18) using 80% methanol/20% water as eluent. The dimers were removed from the eluate by adding 3× the volume of water and extracting with 2× the volume of hexanes. The hexanes were then dried (MgSO<sub>4</sub>) and concentrated to give a mixture of **10:11** in a ratio of 65:35. The structures were assigned by <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) on the basis of the higher symmetry for **11** (Supporting Information).

**Photolysis.** In a typical reaction, 58 mg of 3,5-dimethoxybenzyl bromide, **1c**, in 100 mL of HPLC grade methanol was irradiated in a quartz tube in a Rayonet reactor with 254 nm low-pressure mercury lamps while being purged with nitrogen. The reaction was thermostated at 25 °C with an immersion circulating water tube. The reactions were monitored by GC on a 30 m by 0.25 mm J & W DB 200 column using helium as carrier gas (split) and temperature programming (60 °C for 1 min, 15 °C/min to 180 °C, 180 °C for 7 min). Standard samples of the products, except the dimers **10** and **11**, (see above), were available from previous work in our laboratory.<sup>29</sup> Dark samples were checked for ground-state reactions but none were observed over the short times required for photolysis and analysis.

**Laser Flash Photolysis.** The nanosecond laser flash photolysis system at Dalhousie is of standard design using, as excitation source, the fourth harmonic from a Continuum Nd:Yag NY-61 laser (266 nm;  $\leq 8 \text{ ns/pulse}$ ;  $\leq 15 \text{ mJ/pulse}$ ). For compounds **1a** and **1b** where the transient triene **2a** and **2b** decays in the minutes time domain, samples of  $A \approx 0.5$ , in a standard 1 cm cuvette, were subjected to repeated pulses at a 1 Hz repetition rate for about a minute and then transferred to a thermostated HP-diode array spectrometer to measure the decay kinetics. Light intensity for quantum yield measurements was determined by KI actinometry as described previously.<sup>24</sup>

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**Conventional Flash Photolysis.** These experiments were done in the laboratory of Professor A. J. Kresge in the Department of Chemistry at the University of Toronto on an apparatus previously described.<sup>16</sup> Samples in 10 cm cylindrical cuvettes were flashed perpendicularly to the long axis of the cell by two Xenon Corp. FPA-5-100 C xenon flash lamps and the absorbance monitored parallel to the same axis using an Osram Model XBO 150-W xenon lamp. The transients generated from **1e** and **1f** were monitored on this instrument.

**Quantum Yield Measurements.** Samples of **1a** or **1e** in methanol were irradiated in a carousel apparatus at 25 °C along with 4-methylbenzotrile in acetonitrile. The quantum yield for conversion of 4-methylbenzotrile ( $\Phi = 0.025$ ) to 3-methylbenzotrile, used as an actinometer, can be measured accurately at low conversions.<sup>43</sup>

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**Supporting Information Available:** Spectral data for compounds **1c-f** (Table S1), **10**, and **11** and 250 MHz <sup>1</sup>H and <sup>13</sup>C NMR spectra for **1e**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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