

## Substituent Effects on the Photocleavage of Benzyl–Sulfur Bonds. Observation of the “Meta Effect”

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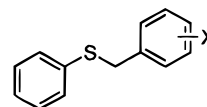
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Benzyl phenyl sulfide has been used to investigate the photocleavage mechanism for benzyl–sulfur bonds. Four experiments have shown that the reaction goes through a radical intermediate. First, the photoproducts observed can all be justified by radical mechanisms. Second, the radical intermediate was trapped with a five hexenyl tether. Third, UV analysis of analogs for the 4-NO<sub>2</sub> derivative indicate no exciplex or electron transfer pathway. Fourth, no strong correlation is observed between  $\sigma$  values and the quantum yields for loss of substituted benzyl phenyl sulfide. The effect of oxygen on quantum yields is best observed after samples are thoroughly outgassed with consecutive freeze–pump–thaw cycles. It is shown that oxygen diminishes the substituent effect. Upon photolysis of the outgassed samples, the *meta*-substituted derivatives showed more significant variances than the *para* derivatives. The *meta* derivatives are most efficiently cleaved in the following order: 3-CN > 3-NO<sub>2</sub> > 3-CF<sub>3</sub> > 3-CH<sub>3</sub> > 3-OCH<sub>3</sub>. These findings are justified by an increase in electron density of the radical *ipso* to the forming benzyl radical for the 3-OCH<sub>3</sub> derivative and a decrease in the electron density of the radical *ipso* to the forming benzyl radical for the 3-CN derivative.

### Background

**Excited State Benzyl Photocleavage.** We previously reported that the photocleavage of benzyl–sulfur bonds proceeds via a radical mechanism.<sup>1</sup> As part of that study we irradiated benzyl phenyl sulfide (BPS, **1a**) and several of its derivatives (see Figure 1). Over the last several years benzyl–heteroatom photocleavage has been a topic of increasing interest to organic photochemists. The most recent review related to this topic that we are aware of was published by Cristol in 1983.<sup>2</sup> In general, two types of photoproducts are formed in these reactions: photosolvolysis products (**2**) and radical products such as bibenzyl (**3**) (see Scheme 1). Typically radical products are favored, but in certain conditions photosolvolysis products are formed exclusively. It is not uncommon to have mixtures of radical and photosolvolysis products. Factors which affect the type of products formed are solvent,<sup>3</sup> photofugacity,<sup>4</sup> excited state multiplicity,<sup>5</sup> counterions (for salts),<sup>6</sup> and substituent effects. The different heteroatom leaving group moieties that have been studied include OAc,<sup>7</sup> O<sub>2</sub>CR,<sup>7j,8</sup> OH,<sup>7k,9</sup> O<sup>+</sup>H<sub>2</sub>,<sup>9b,10</sup> OR,<sup>7k,9c,11</sup> O<sub>2</sub>P(OR)<sub>2</sub>,<sup>7h,12</sup> OSO<sub>2</sub>R,<sup>13</sup> N<sup>+</sup>(R)<sub>3</sub>,<sup>7h,14</sup> S<sup>+</sup>(R)<sub>2</sub>,<sup>7h,15</sup>



1a X = H	1g X = 3-CF <sub>3</sub>
1b X = 4-OMe	1h X = 4-CN
1c X = 3-OMe	1i X = 3-CN
1d X = 4-Me	1j X = 4-NO <sub>2</sub>
1e X = 3-Me	1k X = 3-NO <sub>2</sub>
1f X = 4-CF <sub>3</sub>	

Figure 1.

S(O<sub>2</sub>)R,<sup>7h,16</sup> SOR,<sup>17</sup> SR,<sup>1,9c,18</sup> P<sup>+</sup>R<sub>3</sub>,<sup>14e,19</sup> AS<sup>+</sup>R<sub>3</sub>,<sup>14e</sup> SiR<sub>3</sub>,<sup>20</sup> F,<sup>7k</sup> Cl,<sup>7bch,9c,21</sup> Br,<sup>7bch,9c,21c,22</sup> I,<sup>7bc,21c,23</sup> H.<sup>9c</sup>

A summary of mechanisms which have been considered in benzyl–heteroatom photocleavages is shown in Scheme 2. For purpose of clarity, multiplicity and the extent of solvent separation of radical or ionic pairs (**6** and **7**) are

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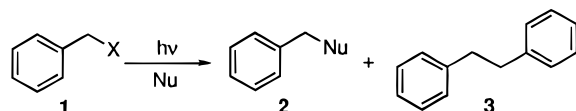
(3) In general as solvent nucleophilicity increases and radical abstractability decreases, photosolvolysis products are formed.

(4) Photofugacity refers to the rate of leaving group dissociation from the excited state. For a discussion, see ref 7h.

(5) Theoretically photosolvolysis should only occur from the singlet since heterolytic cleavage of the benzyl–heteroatom bond would involve concerted movement of unpaired electrons into the same bond. However, some evidence indicates that although spin forbidden this process may occur.<sup>7c,k,21b,c</sup> See: Cristol, S. J.; Schloemer, G. C. *J. Am. Chem. Soc.* **1972**, *94*, 5916.

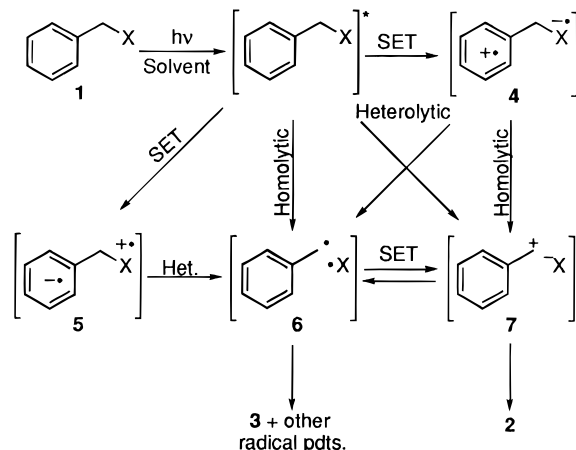
(6) Some counterions have been shown to reduce intermediate radical or ionic pairs. For an example, see ref 19b.

Scheme 1



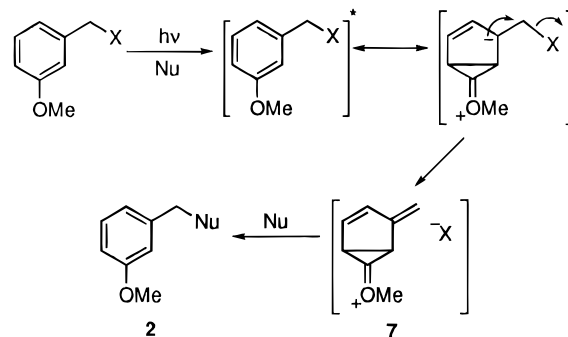
X = Heteroatom Leaving Group  
Nu = Nucleophilic Solvent

Scheme 2



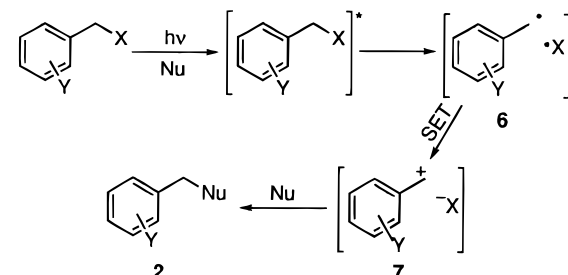
not indicated in the scheme. Intermediates **4** and **5**, involving intramolecular single electron transfer (SET), have received limited attention.<sup>24</sup>

Scheme 3



X = OAc  
Nu = H<sub>2</sub>O or EtOH

Scheme 4



X = acetate, pivalate  
Y = H, 3-OMe, 4-OMe, 3,5-OMe, 3-Me, 4-Me, 4-CF<sub>3</sub>, 4-CN

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Although other pathways are possible, the most logical explanation for radical pair (**6**) formation is homolytic cleavage directly from the excited state of **1**. Formation of the ionic pair (**7**) has been rationalized by two main theories. The original proposal, suggested by Zimmerman and Sandel,<sup>7a</sup> invoked formation of **7** via heterolytic cleavage from an excited state "resonance structure" of **1** (Scheme 3). This theory was based on substituent effect studies of benzyl acetate photolysis which showed increased formation of solvolysis products (**2**) upon photolysis of *m*-methoxy derivatives relative to the *p*-methoxy derivative. Electron density calculations indicate a higher electron density at the *meta* position than there is at the *para* position in the excited state for benzene substituted with electron-donating groups (EDG). More recent analysis further supports this excited state phenomenon.<sup>25</sup> The impact of substituents on excited state reactions has frequently been called the "meta effect" to explain particularly the formation of photosolvolysis products (**2**) arising from the heterolytic cleavage pathway.

The second theory for formation of the ionic pair (**7**) is that homolytic cleavage is the predominate pathway and the radical intermediate **6** can then form **3** and other radical products or undergo SET to form **7**. This theory was originally suggested by McKenna et al.<sup>7c</sup> and recently furthered by Pincock et al.<sup>7i,j</sup> The Pincock group uses Marcus electron transfer theory to explain increased photosolvolysis. They recently examined substituted benzyl acetates and pivalates (see Scheme 4) and found that when oxidation potentials of substituted benzyl radicals are plotted versus the rate of electron transfer, a classical Marcus curve with an inverted region is obtained. Their studies indicate that the 3-OMe benzyl

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radical is at the maximum of the curve. Hence, this substitution could lead to more efficient SET from the initial benzyl radical compared to other substituted derivatives. Unfortunately, the study was able to compare only a few substituents due to undesired side reactions of other substituted benzyl acetates.<sup>26</sup>

**General Substituent Effects.** In ground state ionic reactions, resonance effects on benzyl ions are greater in the *para* position than the *meta*, and in general, inductive effects are greater for *meta* than *para* substitution. In ground state radical studies, *para* substitution of any type tends to stabilize a benzyl radical and *meta* substituents have a minimal effect or destabilize the benzyl radical.<sup>27</sup> Ground state radical stabilization scales ( $\sigma$  scales) have been proposed for a variety of reaction types.<sup>28</sup>

In excited state chemistry, little work has been done on substituent effect scales. Yates and McEwen have shown that data from photohydration of styrene (presumed to involve an excited state benzyl cation intermediate) can be used to generate a  $\sigma$  scale for excited state ionic reactions ( $\sigma^{bv}$ ).<sup>29</sup> It is noteworthy that *meta* substituents demonstrated the greatest impact in the photohydration reaction. We are unaware of any attempt to develop a  $\sigma$  scale based on excited state radical reactions.

In this paper we report the substituent effects on an excited state radical reaction. This reaction is the photocleavage of benzyl sulfides. On the basis of our previous work,<sup>1</sup> and transient absorption studies,<sup>9c,18a</sup> it is apparent that benzyl sulfides undergo almost exclusive radical photocleavage. No products resulting from benzyl cations are detected.

## Results and Discussion

**Procedure.** We irradiated **1a–k** in cyclohexane with a low-pressure Hg arc lamp (254 nm) and measured the quantum yields ( $\Phi$ s) for loss of starting material at low conversions (typically 5–15%). We determined  $\Phi$  values after outgassing with N<sub>2</sub> for 1/2 h. Under these conditions we observed that benzaldehydes are formed as minor photoproducts at longer conversions (up to 95% conversion). Therefore, we reasoned that more accurate values would be obtained if oxygen were more thoroughly removed from the samples prior to photolysis. We subsequently irradiated **1a–k** after freeze–pump–thaw (F–P–T) degassing of the samples and redetermined the  $\Phi$ s on the basis of loss of starting benzyl sulfide. Both sets of  $\Phi$ s are shown in Table 1.

In general there are only two photoproducts detected at low conversions, substituted bibenzyls and diphenyl disulfide. Other products, including benzaldehydes if N<sub>2</sub>

**Table 1.**  $\Phi$  Values for **1a–k**

compd	N <sub>2</sub> $\Phi$	F–P–T $\Phi$
<b>1a</b>	0.12 ± 0.045	0.033 ± 0.015
<b>1b</b>	0.31 ± 0.021	0.071 ± 0.026
<b>1c</b>	0.054 ± 0.028	<0.020
<b>1d</b>	0.18 ± 0.073	0.18 ± 0.031
<b>1e</b>	0.11 ± 0.009	0.047 ± 0.003
<b>1f</b>	0.10 ± 0.059	0.078 ± 0.037
<b>1g</b>	0.096 ± 0.022	0.053 ± 0.002
<b>1h</b>	0.068 ± 0.015	0.044 ± 0.011
<b>1i</b>	0.139 ± 0.078	0.39 ± 0.01
<b>1j</b>	0.063	0.023
<b>1k</b>	0.081 ± 0.017	0.071 ± 0.016

outgassing was used for deoxygenation, were only detected when the sample was irradiated to higher conversions.

**F–P–T vs N<sub>2</sub> Outgassing.** F–P–T deoxygenation decreases the  $\Phi$  of nine of the compounds (BPS, 4-OMe, 3-OMe, 3-Me, 4-CF<sub>3</sub>, 3-CF<sub>3</sub>, 4-CN, 4-NO<sub>2</sub>, 3-NO<sub>2</sub>) with respect to those determined after N<sub>2</sub> outgassing. In one case (3-CN) the  $\Phi$  is significantly higher for F–P–T. The  $\Phi$  remains unchanged for the *p*-methyl studies.

From the data it is apparent that the degree of deoxygenation has a significant impact on the reaction efficiency for several of the BPS derivatives. Oxygen facilitates intersystem crossing (ISC) which is normally demonstrated by its triplet quenching ability; although it is highly unlikely, oxygen may also help the excited state singlet-to-triplet conversion (ISC), and perhaps it is the triplet state pathway that leads to cleavage so that the decrease in oxygen concentration (F–P–T) decreases the  $\Phi$ . Alternatively, a decrease in F–P–T  $\Phi$ s relative to N<sub>2</sub>  $\Phi$ s may be indicative of a long caged-radical lifetime, which in the absence of oxygen returns to starting material (i.e., recombination) since there is no oxygen for conversion to the corresponding benzaldehyde. Another explanation for diminished reactivity in the absence of oxygen is that there may be formation of an exciplex or a ground state complex between the sulfide and oxygen which enhances photocleavage of the benzyl bond.

We also reasoned that it might be possible to see photooxidation of the sulfur resulting in formation of sulfone or sulfoxide and then benzyl photocleavage as a secondary photochemical step. However, no oxidized sulfur products have been detected in this study or in that performed previously in our lab.<sup>1</sup> Furthermore, recent publications concerning the quantum yield for photocleavage of this type indicates that such reactions are relatively inefficient.<sup>30</sup>

It is clear from comparing  $\Phi$ s after N<sub>2</sub> bubbling and F–P–T cycles that it is important to remove oxygen in order to more accurately evaluate the substituent effects. This ought to be a priority in all attempts to compare the pathways for the general reaction of benzyl photocleavage. The remainder of our analysis for this discussion will consider the F–P–T quantum yields only.

**$\Phi$  Order.** The overall  $\Phi$  order for loss of starting material is 3-CN > 4-Me > 4-CF<sub>3</sub> > 4-OMe = 3-NO<sub>2</sub> > 3-CF<sub>3</sub> > 3-Me > 4-CN > H > 4-NO<sub>2</sub> > 3-OMe (see Table 1). Interestingly, when the *meta* substituents are separated from the *para* substituents a trend becomes evident. The differences from one *meta* to the other are all significant (greater than 1 standard deviation difference).

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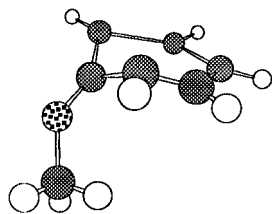


Figure 2.

Their relative quantum yields are  $3\text{-CN} \gg 3\text{-NO}_2 > 3\text{-CF}_3 > 3\text{-Me} > 3\text{-OMe}$ . The cyano and nitro compounds may involve the triplet excited state, while the others are presumably singlet pathways.<sup>31</sup> This order clearly obeys the following sequence: EWG with delocalizable electrons  $>$  EWG without delocalizable electrons  $>$  EDG without delocalizable electrons  $>$  EDG with delocalizable electrons.

Among the *para*-substituted compounds, with the exception of 4- $\text{CF}_3$ , the EWGs appear to result in a less efficient reaction while the EDGs appear to help reaction efficiency. If only the mean values (not standard deviations) are considered, then the order is  $4\text{-Me} \gg 4\text{-CF}_3 > 4\text{-OMe} > 4\text{-CN} > 4\text{-NO}_2$ . However, the difference from one *para* derivative to the next is only statistically significant for the 4-Me and 4- $\text{CF}_3$ . This is similar to a trend seen in ground state  $\sigma$  scales in which *para* EWGs stabilize and *meta* EWGs destabilize the radical to the greatest extent.<sup>27</sup>

Our  $\Phi$  order for the *meta*-substituted compounds can be explained by Zimmerman's *meta* effect. In addition to previous excited state calculations that describe the excited state for substituted aromatic rings, we have performed semiempirical calculations using MOPAC<sup>32</sup> which support the proposed deformation of the aromatic ring in the excited state. Our results indicate that there is an increase for C-2–C-6 bonding in anisole and significant positive charge buildup on the ipso carbon in addition to an increase in electron density at C-3 and C-5 (see Figure 2).<sup>33</sup> We interpret our results and these calculations as clear indication that there is a "*meta* effect". A substituent in the *meta* position will stabilize the excited state and/or provide a pathway of reactivity that is not available for the *para*-substituted analogue. Since an ipso carbon could be stabilized in the excited state by an electron-withdrawing as well as an electron-donating group, we propose that a reverse polarized excited state is possible.

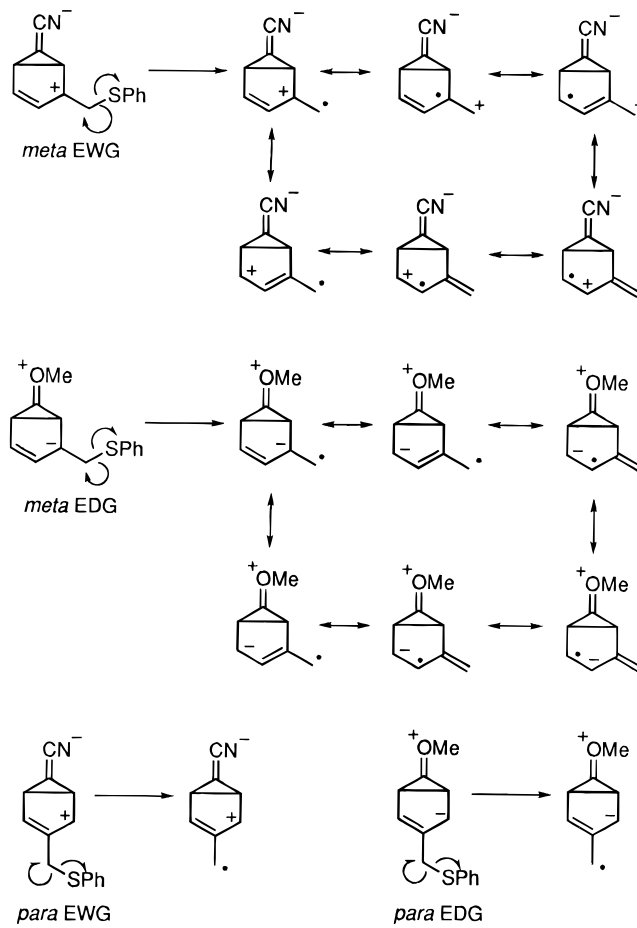
This analysis is consistent with significant differences observed in the  $\Phi$ s of the *meta*-substituted benzyl phenyl sulfides and relatively small differences between the *para*

(31) In order to determine the reaction multiplicity, we irradiated **1a** with acetone as the solvent. The result was that we saw no significant change in the quantum yield. However, similar attempts to determine reaction multiplicity<sup>21a,b</sup> have been justifiably criticized due to competitive absorption of the starting material and quencher.<sup>7th</sup> It has been suggested that a better method for determining reaction multiplicity in benzyl–heteroatom photocleavages is to use the naphthyl system instead of benzyl. Among the substituents we studied, it is likely that the nitro (**1j** and **1k**) and perhaps the cyano (**1h** and **1i**) involve a triplet excited state. See: Blakemore, D. C.; Gilbert, A. *J. Chem. Soc., Perkin Trans. 1* **1992**, *16*, 2265. For a recent example of excited state multiplicity playing a role in homolytic vs heterolytic cleavages, see: Jiménez, M. C.; Miranda, M. A.; Tormos, R. *Heterocycles* **1996**, *43*, 339.

(32) CACHEMOPAC version 94 with multiplicity = singlet, parameter = AM1, and CI level = 2; CACHE Scientific, Inc.

(33) For a similar proposed polarity in the excited state of aromatic compounds, see: Weber, G.; Runsink, J.; Mattay, J. *J. Chem. Soc., Perkin Trans. 1* **1987**, *11*, 2333.

Scheme 5



compounds. It should be emphasized that the *meta* effect does not predict formation of a full charge at the *meta* position; our calculations imply that the degree of charge is a function of the substituent on the ipso carbon. It is more accurate to view the anions and cations in the resonance structures as merely increased or decreased p-orbital electron density relative to one electron.

We have established that the benzyl cleavage process for the sulfides is a radical pathway. It is necessary, therefore, to compare the ease of radical formation next to a cationic center with radical formation next to an anionic center. Ground state  $\sigma$  values indicate that a radical which is able to delocalize with an electron deficient group is more stable than a radical which is able to delocalize with an electron rich group, as long as the substituent does not contain d orbitals adjacent to the radical.<sup>27a,d</sup> These established trends are consistent with our results. A *meta* EWG will favor radical cleavage of the sulfur bond compared to the *meta* EDG (see Scheme 5). One can rationalize this selectivity with orbital-following similar to the recent work by Wagner on photocleavage of aryl halide bonds.<sup>34</sup>

Recent work by Pincock also supports this explanation for the "*meta* effect". He reports, "substituents also exert a strong electronic effect on the rate of the homolytic cleavage step..."<sup>8c</sup>

**Proposal of a New  $\sigma$ - $h\nu$  Scale.** Since we believe that this reaction is an excited state radical reaction, we are in a position to propose, using these quantum yields as the basis, a new excited state radical scale. We can

(34) Wagner, P. J.; Sedon, J.; Waite, C.; Gudmundsdottir, A. *J. Am. Chem. Soc.* **1994**, *116*, 10284.

**Table 2. Proposed  $\sigma^{hv}$  Values for Excited State Radical Reactions**

substituent	$\sigma^{hv}$	substituent	$\sigma^{hv}$
H	0.00	4-CF <sub>3</sub>	0.37
4-OMe	0.33	3-CF <sub>3</sub>	0.21
3-OMe	<-0.22	4-CN	0.12
4-Me	0.74	3-CN	1.07
3-Me	0.15		

generate a new scale based on quantum yields by dividing the quantum yield of the substituent by the quantum yield of BPS and taking the log of the resulting fraction, in the same manner that the original  $\sigma$  values were obtained by Hammett using equilibrium constants.<sup>35</sup> The values generated by performing this transformation are shown in Table 2.

We do not claim that these  $\sigma$  values will have universal correlation with all excited state homolytic cleavage reactions. For example, it is clear that the benzyl cleavage reactions from the excited state vary with leaving group, solvent, and concentration of dissolved oxygen. Presumably this is due to the extent of polarization of the aromatic ring in the excited state. In order to test the validity of our scale, it would be desirable to compare these values against other reactions that are thought to go through excited state radical pathways. Unfortunately, most other benzyl-heteroatom photocleavages involve some type of partitioning between radical and ionic intermediates. Thus, the  $\sigma^{hv}$  values may suffer because they have been defined by too unique of a reaction path.

**Back Reaction.** One aspect of the benzyl-sulfur photocleavage reaction that is undetermined is the extent of back reaction or recombination of the radical pair. It might be possible to measure the rate of recombination using a chiral benzyl sulfide for each derivative and measuring the percent racemization. A few benzyl cleavages have been examined using chiral reagents; however, when chiral benzyl acetates with isotopically enriched carbonyl oxygens were photolyzed in a solvent cage, scrambling of the <sup>18</sup>O was observed *in the absence of racemization*.<sup>36</sup> This indicates that recombination within the solvent cage can be fast enough to retain benzyl stereochemistry. Such a chiral sulfide might then be useful only to estimate out-of-cage recombination. We are interested in continuing our study of these photocleavage pathways and expect that time-resolved studies will provide the best analysis of back reactions.

### Summary

Quantum yield determination has shown that the extent of deoxygenation plays a significant role in the efficiency of homolytic cleavage from the excited state.

(35) Hammett, L. P. *J. Am. Chem. Soc.* **1937**, *59*, 96.

(36) Givens, R. S.; Matuszewski, B.; Levi, N.; Leung, D. *J. Am. Chem. Soc.* **1977**, *99*, 1896.

In an effectively oxygen-free environment, *meta* substituents are shown to have a significant effect on overall cleavage efficiency. The *meta* EWGs appear to facilitate formation of **6** while *meta* EDGs appear to suppress it. This finding is different from ground state reactions and supports some type of excited state *meta* stabilization. In fact, it may be easily rationalized by the "meta effect" originally proposed by Zimmerman. Semiempirical calculations support the partial charge density at the ipso carbon and C-3/C-5.

### Experimental Section

**General Procedures.** Benzyl phenyl sulfide (**1a**) was purchased from Lancaster Synthesis and used as received. All other derivatives of **1a** (**1b-k**) were synthesized as previously reported.<sup>1</sup> Cyclohexane was washed with 1:1 concentrated nitric and sulfuric acid, washed with water, passed through a basic alumina column, dried with CaCl<sub>2</sub>, and distilled.

Gas chromatography (GC) was performed on a Hewlett Packard 5890 instrument equipped with a flame ionization detector (FID) and fused methyl silicone stationary columns (50 m and 18 m × 0.25 mm × 0.25 μm). Hydrogen was used as the carrier gas with compressed air mixing at the detector.

**Quantum Yields. (a) Quantum Yield for Valerophenone.** The quantum yield of disappearance of valerophenone at 313 nm is known (0.46).<sup>37</sup> Potassium ferrioxylate actinometry<sup>38</sup> was used on an optical bench equipped with an ISA Instruments monochromator, Oriel Model 66056 lamp, and Oriel photomultiplier tubes. Valerophenone (41.5 mg) was added to purified cyclohexane and outgassed with nitrogen for 1/2 h. The photolysis was allowed to run for 66 h, and GC analysis indicated that 5.6 mg of valerophenone reacted. A quantum yield of disappearance of 0.4 was calculated for valerophenone at 254 nm.

**(b) General Quantum Yield Procedure.** Samples were prepared by dissolving 1–30 mg of material in about 6 mL of purified cyclohexane. The samples were deoxygenated and irradiated for 5–10 min with valerophenone actinometry. Light was generated by a Rayonet RPR, 253.7 nm lamp, in a merry-go-round apparatus (Rayonet miniphotocatalytic reactor). The lamp was allowed to warm up for about 1/2 h prior to photolysis. The samples were cooled by a fan in the bottom of the merry-go-round.

**(c) Deoxygenation of Quantum Yield Samples.** The first method used was deoxygenation with purified nitrogen.<sup>39</sup> The second method involved freeze-pump-thaw degassing (1 × 10<sup>-5</sup> Torr for at least three consecutive cycles).

**Calibration Curves for Analytical Work.** To determine the amount of starting material lost for the quantum yield determinations, calibration curves were generated by preparing four–five samples of material. These samples contained between 0 and 30 mg of starting material spiked with a consistent amount of benzophenone internal standard. The correlation constants for the calibration curves of the derivatives ranged from 0.995 to 1.000.

JO9606923

(37) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 5898.

(38) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London A* **1956**, *235*, 518.

(39) Nitrogen was purified by being passed through an Ace-Burlitch inert atmosphere system containing a column packed with a BASF R3-11 catalyst followed by another column packed with Aquasorb drying agent.