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Photochemistry of Aryl *tert*-Butyl Ethers in Methanol: The Effect of Substituents on an Excited State Cleavage Reaction

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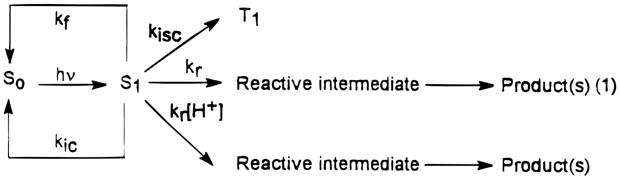
The photolysis of a set of 10 substituted aryl *tert*-butyl ethers, **8a**−**j**, in methanol gave, as the major product, the corresponding phenol along with *tert*-butyl-substituted phenols resulting from photo-Fries reaction. The corresponding 4-cyanophenyl 1-adamantyl ether, **9**, also gave 1-methoxyadamantane **16** (16%), indicating that, at least for this ether, some of the products were ion-derived. Quenching studies with 2,3-dimethylbutadiene for the *tert*-butyl ethers indicated that these reactions were occurring from the singlet excited state. Rate constants for the reaction, obtained from quantum yields and singlet lifetimes, were found to correlate reasonably well with $\sigma^{h\nu}$ values, $\rho = -0.77$ ($r = 0.975$), a result that is unexpected for a reaction where the polarity of the bond breaking in the transition state is expected to be $-\mathrm{O}(\delta-)\cdots\mathrm{C}(\delta+)$.

Introduction

The effect that substituents have on the excited state reactivity of functional groups adjacent to benzene rings continues to attract experimental and theoretical interest. Recent examples, where quite a wide range of electron-donating and -withdrawing substituents have been examined include (1) the photolysis of benzylic compounds with leaving groups ($\mathrm{ArCH_2}$-LG) where the LG's studied were trimethylamine ($\mathrm{NR_3}$),[1] water ($\mathrm{OH_2}$),[2] carboxylates ($^{\ominus}\mathrm{O{-}CO{-}R}$),[3] phosphates ($^{\ominus}\mathrm{PO_3R_2}$),[4] sulfides ($^{\ominus}\mathrm{SR}$),[5] triphenylphosphine ($\mathrm{PR_3}$),[6] and halides ($^{\ominus}\mathrm{Cl}$);[7] (2) the acid-catalyzed photohydration of styrenes[8] and phenylacetylenes;[9] and (3) the excited state pK_a of phenols.[10,11] The interesting trend that has been observed in most (not $\mathrm{NR_3}$ or $^{\ominus}\mathrm{PO_3R_2}$) of these studies is that, contrary to expectations based on ground state observations, *meta* substitutents result in enhanced reactivity. This effect, the photochemical *meta* effect, has been rationalized by MO[12−14] calculations which indicate that, for instance, a methoxy group is a better electron donor in the excited state from the *meta* (and the *ortho*) position than it is from the *para* position. Electron-withdrawing groups are also predicted to be more effective electron-withdrawing groups from the *meta* (and the *ortho*) position.[12]

To reliably correlate substitutent effects with excited state rate constants, the ideal case would have an unambiguous first (k_r) or second ($k_r[\mathrm{H}^{\oplus}]$) order rate constant from a single excited state, S_1, eq 1. The rate



constant can then be determined by the measurement of the quantum efficiency of the reaction (Φ_r) and the singlet lifetime, τ_s, eqs 2 and 3. However, few photoreactions satisfy these simple requirements. For instance, in the examples (1) above, the photolysis of benzylic compounds with leaving groups, both the excited singlet, S_1, and triplet, T_1, states may react. Moreover, the excited singlet may react by either homolytic (k_{hom}) or heterolytic (k_{het}) cleavage of the σ bond; both radical- and ion-derived products are observed in most cases, eq 4. Because the initially formed radical pair may be converted to the more stable (in polar solvents) ion pair by electron transfer, k_{etri} in eq 4, the measured product ratio may not be a reliable measure of k_{hom} vs k_{het}. These concepts have been recently reviewed.[15]

$$\Phi_r = \frac{k_r}{k_r + k_f + k_{ic} + k_{isc}} = k_r\tau_s \tag{2}$$

$$\Phi_r = \frac{k_r[\mathrm{H^+}]}{k_r[\mathrm{H^+}] + k_f + k_{ic} + k_{isc}} = k_r[\mathrm{H^+}]\tau_s \tag{3}$$

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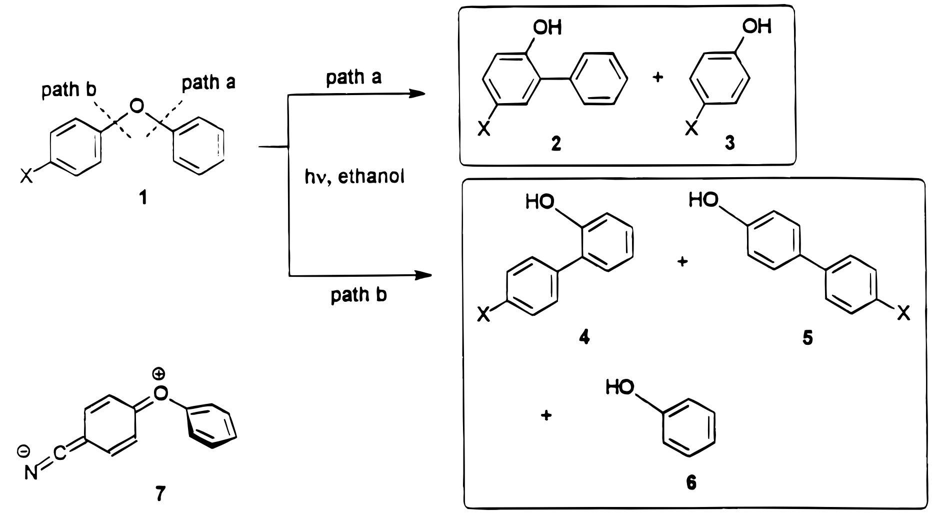
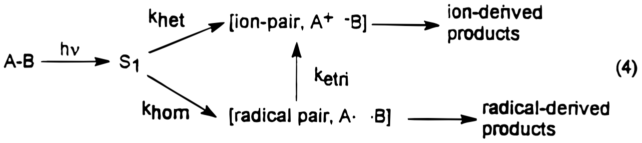
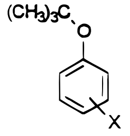
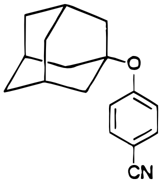
Scheme 1. Products Obtained from the Photolysis of the Diaryl Ethers, 1, in Ethanol







8a (X = H),
8b (X = 4-OCH$_3$), **8c** (X = 3-OCH$_3$),
8d (X = 4-CH$_3$), **8e** (X = 3-CH$_3$),
8f (X = 4-F), **8g** (X = 3-F),
8h (X = 4-CF$_3$), **8i** (X = 3-CF$_3$),
8j (X = 4-CN)



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We were intrigued by a recent observation of the unusual substitution effects reported for the photochemical reactivity of diaryl ethers, **1** (Scheme 1), in ethanol.[16] The major products, **2**, **4** and **5**, result from photo-Fries type rearrangement with **2** derived from path a cleavage and **4** and **5** from path b. Phenols **3** (path a) and **6** (path b) were also formed. The ratio of (**2** + **3**):(**4** + **5** + **6**) = path a:path *b* = 42:0 (X = CH$_3$O), 69:0 (X = OH), 64:0 (X = NH$_2$), 62:7 (X = CH$_3$), 25:3 (X = F), 0:85 (X = CO$_2$CH$_3$), 0:86 (X = CN), varies considerably with substituents, electron-donating by their resonance effects (CH$_3$O, OH, NH$_2$) having a marked preference for path a and, in contrast, electron-withdrawing ones (CO$_2$CH$_3$, CN) selecting path b. No explanation for this observation was given. Moreover, a recent study,[17] by MO calculations and UV spectra, of the conformational surface for substituted diaryl ethers gave results that supported the opposite of this observation. For resonance electron-withdrawing groups, such as CN, diaryl ethers adopt a conformation, **7** (Scheme 1), allowing intramolecular charge transfer that shortens and presumably strengthens the C$-$O bond for path b cleavage. In fact, path b cleavage is preferred for electron-withdrawing groups.

We reasoned that substituent effects in aryl ether photochemistry could be better studied using the set of compounds, **8a**$-$**j**, as well as the adamantyl derivative, **9**, to compare with **8j**. In contrast to the diaryl ethers **1**, these compounds have only one chromophore so there is no question as to where the excited state energy will be localized. As well, the bond cleavage should be highly regioselective in the direction of the weaker tertiary carbon$-$oxygen bond as opposed to the aryl carbon$-$oxygen bond. Therefore, substituent effects on the efficiency and rate of the photochemical cleavage of a simple single bond could be determined. Finally, the bond cleavage would be either homolytic with a polarity such that the substituents would interact with the oxygen having a partial negative charge, $-$O($\delta-$), or heterolytic, in which case the charge would be more fully developed. Because this polarity is in the opposite direction to that which has been studied in the past where the substituent interaction was with a benzylic carbon and a developing positive charge, $-$C($\delta+$), the manner in which the substitutents would influence the bond cleavage is obviously of interest.

The photochemistry of arylalkyl ethers has been studied to some extent previously but usually with compounds where the alkyl group was substituted in such a way as to stabilize radical intermediates by delocalization. Alkyl groups examined include triarylmethyl,[13,18] diarylmethyl,[18] benzyl,[19,20-22] and allyl.[19,20,23,24] Again photo-Fries compounds (photo-Claisen for the allyl compounds) and phenols are the major products. In none of these cases have substituent effects on the product distribution or photochemical efficiency been examined.

Results and Discussion

Synthesis of Ethers. The ethers **8a**$-$**i** were synthesized by the reaction of the Grignard reagent of the

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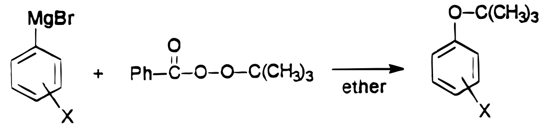
Table 1. Photophysical Properties of the Ethers 8a−j

compd	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	$\lambda_{0,0}$, [a] nm	E_s, [b] kcal/mol	$\tau_s/10^{-9}$ [c] ns	Φ_f [d]
8a, X = H	271	1840	220 (sh)	7650	281	102	4.7	0.21
8b, X = 4-OCH_3	280	1730	225	8890	300	95	2.4	0.17
8c, X = 3-OCH_3	272	1760	220	7670	284	101	2.2	0.16
8d, X = 4-CH_3	278	1910	223	8660	290	99	5.1	0.17
8e, X = 3-CH_3	272	1640	217	6810	284	101	5.7	0.19
8f, X = 4-F	269	1200	206 (sh)	6930	281	102	3.4	0.28
8g, X = 3-F	263	947	211	7330	289	99	3.0	0.035
8h, X = 4-CF_3	260	551	224	8190	281	102	2.3	0.19
8i, X = 3-CF_3	273	1163	211	6894	289	99	2.7	0.50
8j, X = 4-CN	274 (sh)	1460	245	14400	284	101	2.8	0.11
9, X = Ad 4-CN	274 (sh)	1220	244	14400	284	101	2.6	0.11

[a] Wavelength of the crossing point between the absorbance and emission spectra. [b] Singlet excited state energy calculated from $\lambda_{0,0}$. [c] Singlet lifetime by time-resolved fluorescence decay. [d] Quantum yield of fluorescence.

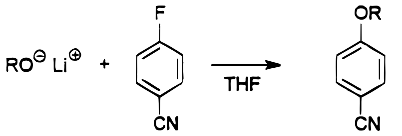
corresponding bromobenzene with *tert*-butyl peroxybenzoate according to the method described previously, eq 5.[25] Because we were also interested in studying cyano-



(5)

8a-i

substituted substrates, which are incompatible with Grignard reagents, the 4-cyano compounds **8j** and **9** were prepared by a different method. Reaction of the lithium salt of the corresponding alcohol with 4-fluorobenzonitrile, eq 6, according to the method of Woiwode et al.,[26] was successful. This nucleophilic aromatic substitution only works if the fluorine is activated by the electron-withdrawing group in the *para* position. No ether was obtained when 3-fluorobenzonitrile was used, and therefore *meta*-cyano derivatives could not be prepared.



(6)

8j (R = t-butyl)
9 (R = 1-adamantyl)

Photophysical Properties of Ethers. UV absorption spectra, quantum yields of fluorescence, singlet energies (from the wavelength of the (0,0) band of the overlap between the absorbance and fluorescence spectra), and singlet state lifetimes (from time correlated single photon counting) in methanol are given in Table 1. As expected, there are two absorbance bands on the UV, the long wavelength/low molar absorptivity, L_b, transition and the shorter wavelength/higher molar absorptivity, ${}^1L_a$, band. For the 4-cyano compounds **8j** and **9**, the conjugation between the electron-donating oxygen of the ether and electron-withdrawing cyano group shifts this ${}^1L_a$ band some 20 nm to longer wavelength so that the ${}^1L_b$ band appears only as a weak shoulder. The singlet energies are all very similar (around 100 kcal/mol) with the exception of the 4-methoxy compound **8b**, which has a somewhat lower energy at 95 kcal/mol. These values are well above the carbon−oxygen bond dissociation energy which should be somewhat lower than 64 kcal/mol, the value for anisole.[27] Therefore, homolytic cleavage from S_1 would be clearly exergonic for all substrates.

Although we have not obtained phosphorescence spectra, triplet energies are available for some analogous compounds: anisole (85 kcal/mol), 4-methoxyanisole (75 kcal/mol), and 4-methylanisole (78 kcal/mol).[28] Therefore, homolytic cleavage from T_1 would also be exergonic.

Finally, on the basis of the reduction potential of the phenoxy radical, 0.43 V vs NHE in DMSO,[29] and the oxidation potential of the *tert*-butyl radical, 0.33 V vs NHE in CH_3CN,[30] conversion of the radical pair to the ion pair by electron transfer, eq 7, should be only slightly

$$\left[ArO\cdot \;+\; \cdot C(CH_3)_3 \right] \xrightarrow{k_{etri}} \left[ArO^{\ominus} \;+\; {}^{\oplus}C(CH_3)_3 \right] \quad (7)$$

exergonic (2.3 kcal/mol). This estimate omits the Coulombic attraction term which would contribute another 1.7 kcal/mol to stabilize the ion pair at a distance of 7 Å. Moreover, for electron-donating groups (4-OCH_3), the reduction potential (0.134 V)[29] of the phenoxy radical becomes less favorable and the electron transfer becomes endergonic by 0.2 V (4.6 kcal/mol). In contrast, for the highly stabilized 4-cyano anion, the reduction potential (0.90 V)[29] makes the electron transfer favorable by 0.57 V (13 kcal/mol).

Photochemistry of the *tert*-Butyl Ethers 8a−j. The ethers were irradiated in methanol at 25 °C using 254 nm lamps in a Rayonet reactor. The reactions were purged with N_2 [31] before and during photolysis. For all the ethers, except **8j**, this wavelength results in excitation into an upper vibrational level of S_1, the long wavelength absorption band. For **8j**, the excitation will be principally into S_2. For the *tert*-butyl ethers, **8a−j**, the products, eq 8, obtained were simple, as the yield of the corresponding phenol **10a−j**, was always greater than 80% (GC). Minor amounts of the photo-Fries products **11** were obtained in all cases (GC/MS). These latter products were not

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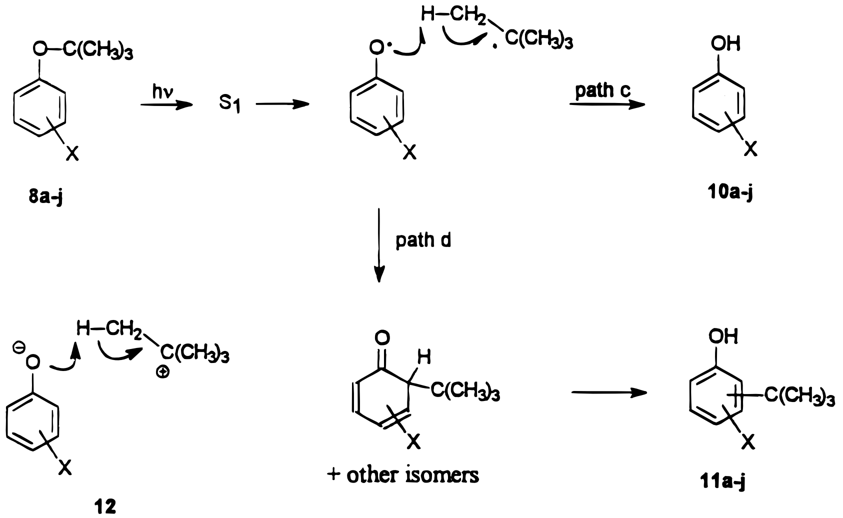
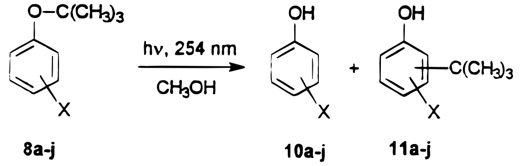
(31) The more efficient removal of oxygen by freeze−pump−thaw (FPT) cycles has been shown to be important in the photochemistry of thioethers (ref 5), residual oxygen having an effect on quantum yields. For the ethers studied here, the fact that the singlet lifetimes are short (under 6 ns for all cases, Table 1) and also that the products are all formed from an in-cage process, means that traces of oxygen will have little effect. We have confirmed this in a few FPT experiments.

Scheme 2. Mechanism for the Photolysis of the Ethers, 8a–j from S_1 in Methanol





(8)

characterized, except for **11a** (using authentic samples of 2- and 4-*tert*-butylphenol available from Aldrich), but the GC peaks were counted. For instance, for **8a** (X = H), there were two such products (13%, ratio 1:1.4 of 2-*tert*-butylphenol:4-*tert*-butylphenol); for **8b** (X = 4-OCH_3) only one (4%) was observed and for **8c** (X = 3-OCH_3) three (18%, ratio 1:2:5) were observed. This is the number expected for coupling *ortho* and *para* to the phenolic oxygen as has been observed previously for benzyl phenyl ethers.[22] For the 4-methoxy compound **8b**, we also observed the formation of **8a** (13%) as a result of demethoxylation. These observations are consistent with a mechanism of formation of radical pairs from the excited state followed by disproportionation (path c) and coupling (path d), Scheme 2. The intermediate 2,4-cyclohexadienones shown in path d have recently been observed by CIDNP,[21] isolated[32] in other photo-Fries type reactions and also detected as transients in laser flash photolysis experiments.[33]

Because both products in Scheme 1 could be derived from in-cage radical pairs, the singlet excited state, S_1, would seem to be the likely precursor. However, triplet yields for aromatic ethers are quite high (Φ_{isc} for anisole = 0.64),[28] and, moreover, recent CIDNP experiments with naphthyl ethers[23,24] demonstrated that products are derived from both singlet and triplet radical pairs. Earlier CIDNP results for phenyl ethers[21] indicated that only singlet radical pairs were involved. Additional evidence that S_1 was the reactive excited state for the ethers studied here was provided by the following quenching studies.

Stern–Volmer fluorescence quenching plots for **8a** (X = H), **8c** (X = 3-OCH_3), and **8i** (X = 3-CF_3) with 2,3-dimethylbutadiene in methanol were linear and gave $k_Q\tau_s$ values equal to 33, 31, and 32 M^{-1}, respectively. Combined with the τ_s values in Table 1, the k_q values for quenching the excited singlet state of these ethers by the diene are 7.0, 14, and 14 $\times 10^9$ M^{-1} s^{-1}, respectively, close or equal to the diffusional value, 14 $\times 10^9$ M^{-1} s^{-1}, for methanol.[28] At 5 $\times 10^{-3}$ M diene, the ratio of quenching of S_1 ($k_Q[M] = 7 \times 10^9\ M^{-1}\ s^{-1} \times 5 \times 10^{-3}\ M = 3.5 \times 10^7\ s^{-1}$) to decay of S_1 ($1/\tau_s = 21 \times 10^7\ s^{-1}$) is 0.16. Therefore, significant quenching of S_1 occurs. In agreement with this value, when the ether **8a** (X = H) was irradiated in the presence of 5 $\times 10^{-3}$ M 2,3-dimethylbutadiene, products (GC/MS) were observed that were photoadducts of the two. The corresponding reaction of anisole with this diene to give cycloadducts has been documented.[34]

In contrast, irradiation at diene concentrations that were a factor of 10 lower (5 $\times 10^{-4}$ M) gave only very low yields (<1%) of cycloadducts. Therefore, as expected, S_1 is essentially unquenched ($k_Q[M]/\tau_s = 0.016$). Moreover, simultaneous irradiation of **1a**, in a carousel apparatus, with (5 $\times 10^{-4}$ M) and without the quencher present, resulted in an identical rate of disappearance of the starting material. If triplet states were involved, they would be expected to be longer lived and therefore still quenched. Because the triplet lifetimes are not known or easily determined because they are not detected by triplet–triplet absorption in laser flash experiments, this evidence for singlet reactivity is strong but not conclusive. Irradiation of each of the ethers **8a–j** in the presence and absence of 2,3-dimethylbutadiene at 5 $\times 10^{-5}$ M gave identical rates of disappearance in all cases. We conclude that the reactions of these ethers occur from S_1, the excited singlet state.

The mechanism in Scheme 2 indicates radical pair intermediates as in the accepted mechanism for photo-Fries reactions. However, ion pairs cannot be easily excluded because an intermediate ion-pair, **12** (Scheme 2), could give the same products. If the *tert*-butyl cation were formed in methanol, it should perhaps give methyl *tert*-butyl ether as a product, at least some of the time. Because the yield of this volatile ether cannot be easily determined by GC, we examined the adamantyl derivative **9**, where the alkyl fragment is considerably larger.

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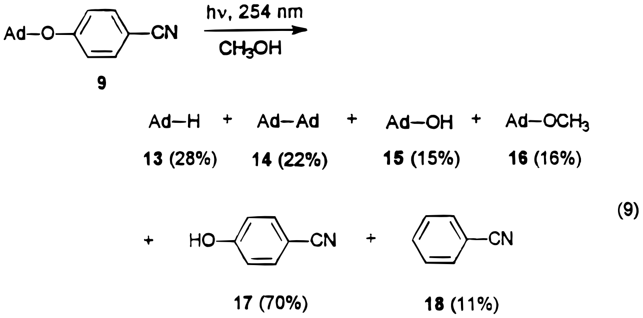
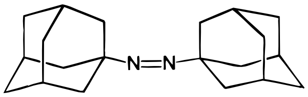
Photochemistry of the Adamantyl Ether 9. The adamantyl ether **9** provides a good comparison with *tert*-butyl ether **8j** for two main reasons: (1) the chemistry of the alkyl fragment of the ether can be studied and (2) the adamantyl radical, in contrast to the *tert*-butyl radical, is known to be very unreactive toward disproportionation[35] by H atom donation as a consequence of the low stability of 1-adamantene. Kropp and co-workers[36] have shown that the adamantyl group can be used to study the partitioning between radical and ionic behavior in the photochemistry of phenyl thio and seleno ethers.

Photolysis of **9** in methanol as described previously gave the products shown in eq 9. The yields given are based on reacted starting material (69% conversion), with that for the dimer given as twice the molar yield. We see no peaks (GC/MS) for photo-Fries products. The products **13**, **14**, and **17** are those expected from the radical pair in methanol. The adamantyl radical has been shown to be a very reactive H atom abstractor from studies on the photochemistry of azoadamantane, **19**.[35] In fact, evidence was presented that the dimer **14**, formed from **19**, was only formed from in-cage recombination. Adamantyl radicals that escaped the cage seemed to result only in adamantane or aromatic addition products in solvents such as benzene, toluene, cyclohexane, pentane, and *tert*-butyl alcohol. For our results in methanol, the diadamantane must be formed from cage-escaped radicals so there is competition between dimerization and H atom abstraction. The same observation was made by Kropp and co-workers[36] for photolysis of adamantyl thio and seleno ethers in methanol, although reliable yields were not obtained because of the low solubility of the dimer in methanol. We also noticed poor reproducibility for the yield of the dimer but feel that the value given in eq 9 is reliable because the substrate concentration was low enough that solubility of the products should not be a problem. The source of the H atom for formation of Ad-H was probed by photolysis in methanol-d_4. Authentic Ad-D has an (M/M + 1) ratio in the mass spectrum of 0.281;[35] the adamantane formed by photolysis of **9** in methanol-d_4 had an (M/M + 1) ratio equal to 0.85, indicating that it was less than 100% monodeuterated. However, the adamantyl radical has a large isotope effect for H atom abstraction with k_H/k_D values of 11 (toluene) and 26 (cyclohexane) at 65° C.[35] Therefore, the adamantyl radical must be abstracting hydrogen atoms from methanol-d_4 in competition with some other nondeuterated source, probably the adamantane group of the starting ether, **9**.



(9)



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The products **15** and **18** are best explained by photochemical cleavage of the aromatic ether bond rather than the adamantyl one. If, as seems likely, aryl–oxygen bond cleavage is the pathway leading to these products, this would be surprising because this bond will be considerably stronger. Moreover, these products were not observed for the *tert*-butyl ethers.

Finally, the methyl ether **16** is clearly derived from the adamantyl cation and indicates that, at least to a small extent, ionic intermediates are involved. In principle, the ion pair could undergo an E_1 like elimination as in **12** (Scheme 2) to form 1-adamantene which is known to react very rapidly with methanol to give **16**.[37] This was shown not to be the case, again by irradiation in methanol-d_4. The molecular ion of **16** had an $m/z = 169$, three more than the undeuterated material at $m/z = 166$. If **16** was formed from 1-adamantene, it would have $m/z = 170$, i.e., all four of the hydrogens from methanol-d_4 would be in the product.

These results clearly indicate that the 1-adamantyl cation is an intermediate in the photochemistry of **9**. We have no evidence to indicate whether it is derived from direct heterolytic cleavage of S_1 or by electron transfer in the initially formed radical pair. Also, we do not know if the *tert*-butyl cation is an intermediate in the photochemistry of the ethers **8**, although it seems likely for **8j**, the analogous 4-cyano compound to **9**. In fact, as discussed above, the ion pair for **8j** and **9** will be more stable than that for any of the other cases, but whether this factor will make its yield higher or lower is difficult to predict. Results for more adamantyl ethers would clearly be of interest and we are in the process of trying to synthesize some substituted derivatives.

Rate Constants for the Photochemical Cleavage of the Ethers 8a–j. Quantum yields (Table 2) for the disappearance of the ethers in methanol at 25 °C were measured in a carousel apparatus again using the 254 nm Rayonet reactor. These values, along with the singlet lifetimes (Table 1), give the rate constants for photochemical cleavage, k_r, according to eq 2. Notice that for the *meta*/*para* pairs the *meta* isomer is more reactive than the *para* for all cases except for the strong, inductively electron-withdrawing group, CF_3. The photochemical *meta* effect seems to be operating but in a way which suggests that electron donation from the *meta* position is rate enhancing. This seems surprising for a reaction that has an expected polarity with oxygen $\delta-$ and carbon $\delta+$. In fact, in a recent study of substituted benzyl phenyl thioethers,[5] the quantum yields reported for bond cleavage are in the ratio > 3.6 (4-OCH_3:3-OCH_3), 3.8 (4-CH_3:3-CH_3), 0.11 (4-CN:3-CN), and 0.32 (4-NO_2:3-NO_2). Therefore, electron-donating groups inhibit the reaction from the *meta* position and electron-withdrawing groups enhance it from the *meta* position, again surprising for

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Table 2. Quantum Yields of Reaction and Derived Rate Constants for the Reactions of Ethers 8a–j

compd	Φ_r [a]	$k_r/10^7\ s^{-1}$ [b]	σ_{ex} [c]	$\sigma^{h\nu}$ [d]	$k_f/10^7\ s^{-1}$ [e]	$k_d/10^7\ s^{-1}$ [f]	$k_{dt}/10^7\ s^{-1}$ [g]
8a, X = H	0.020	0.43	0	0	4.4	16	21
8b, X = 4-OCH_3	0.064	2.7	−0.39	−1.17	7.0	32	42
8c, X = 3-OCH_3	0.14	6.3	−0.10	−1.47	7.3	31	45
8d, X = 4-CH_3	0.032	0.63	−0.13	−0.53	3.3	16	20
8e, X = 3-CH_3	0.071	1.2	−0.10	−0.79	3.3	14	18
8f, X = 4-F	0.009	0.26	0	0.18	8.2	11	20
8g, X = 3-F	0.028	0.93	−0.05	−0.37	2.7	29	33
8h, X = 4-CF_3	0.15	6.5	0.58		8.2	28	43
8i, X = 3-CF_3	0.021	0.66	0.74		19	17	37
8j, X = 4-CN	0.044	1.7	1.6		3.9	30	36

[a] Quantum yield for disappearance of ether **8**. [b] Rate constant for disappearance of ether **8** from eq 2. The estimated error in these values is ±15% on the basis of estimated error (±10%) in the Φ values and ±5% in the τ_s values. [c] From refs 10 and 11. [d] From ref 9. [e] Rate constant for fluorescence from $k_f = \Phi_f\tau_s$. [f] Rate constant for the decay of the excited singlet state by modes other than fluorescence and reaction from $k_d = k_{dt} - k_f - k_r$. [g] $k_{dt} = 1/\tau_s$.

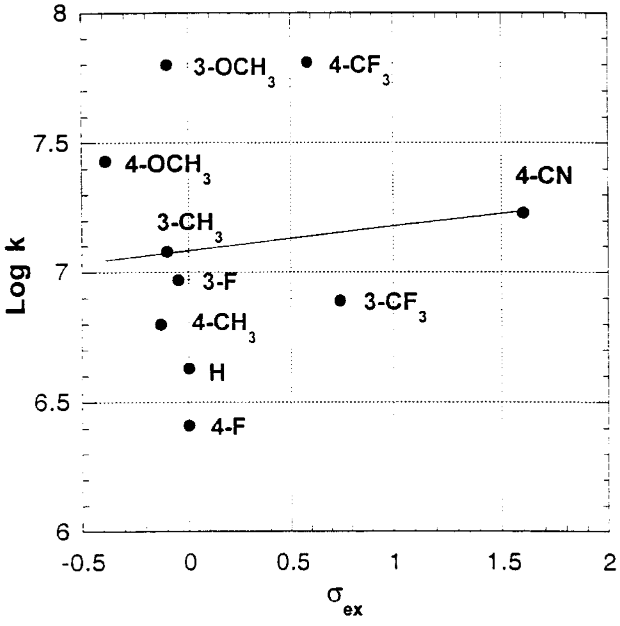


Figure 1. Plot of log k versus σ_{ex} for the rates of reaction of the aryl ethers, **8a–j**.

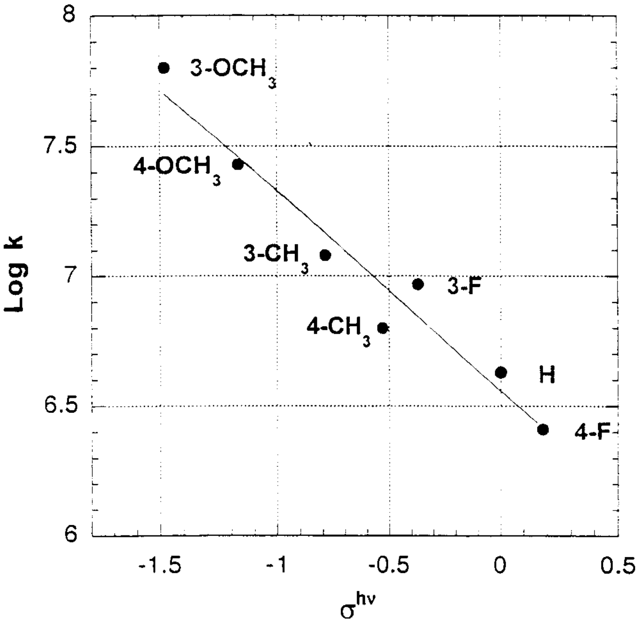


Figure 2. Plot of log k versus $\sigma^{h\nu}$ for the rates of reaction of the aryl ethers, **8a–e** ($\rho = -0.77$).

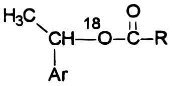
a reaction with the polarity of substituted benzylic carbon $\delta+$ and sulfur $\delta-$.

We also wanted to correlate our rate constant data with known scales of substituent effects for photochemical reactions (Hammett plots). We thought that the data would probably correlate with σ_{ex} (Table 2) obtained from the excited singlet state pK_a values of substituted phenols[10,11] because the two reactions seemed likely to be similar in electron demand, ARO−H (S_1) → ArO($\delta-$)$\cdots$H($\delta+$) and ArO−C$(CH_3)_3$ (S_1) → ArO($\delta-$)$\cdots$C(CH_3)($\delta+$). In fact, the correlation was very poor (Figure 1) with $\rho = 0.096$ ($r = 0.12$). A correlation with σ^-, obtained from the ground state pK_a values for substituted phenols, was also poor, $\rho = 0.27$ ($r = 0.34$). The data did however correlate quite well with $\sigma^{h\nu}$ values (Figure 2), $\rho = -0.77$ ($r = 0.975$). These values are based on the excited state protonation of arylalkenes and alkynes, a reaction that generates $\delta+$ on the benzylic carbon.[9] Unfortunately that photoprotonation reaction is too slow to be studied for electron-withdrawing groups so that $\sigma^{h\nu}$ values are unavailable for CF_3 and CN substituents. Finally, Fleming and Jensen have recently proposed some $\sigma^{\cdot h\nu}$ values on the basis of quantum yield ratios for the fragmentation of substituted benzyl phenyl thioethers with the suggestion that these values could be used to correlate data for the rates of photochemical homolytic cleavage reactions.[5] These values also give a very poor correlation with our data, $\rho = -0.39$ ($r = 0.24$).

The negative ρ value obtained in the $\sigma^{h\nu}$ plot confirms that these reactions proceed in such a way that electron-donating substituents enhance the reactions and *meta* electron donation is preferred to *para*. In fact, the ρ value of −0.77 is not much smaller than the value of −1.0 for the defining reaction, the photoprotonation of S_1 of alkenes and alkynes, indicating that the response of the reaction to substituents is comparable. Also noteworthy is the fact that the compounds with strongly electron-withdrawing groups in the *para* position are also quite reactive, particularly **8h** (X = 4-CF3). In contrast, **8i** (X = 3-CF_3) is a factor of 10 less reactive than its *para* analogue. We can assign $\sigma^{h\nu}$ values to these substituents by placing them on the correlation line in Figure 2, $\sigma^{h\nu} = -1.62$ (4-CF_3), −0.42 (3-CF_3), −0.87 (4-CN); but only future studies with other substrates will confirm whether they are reliable and useful values.

A possible reason for the unexpected correlation in Figure 2 is that for these substrates the reactive center is the aryl ether oxygen which will have its own effect on electron distribution in the excited state, i.e., it is electon donating itself. This situation is very different from the previous cases studied, where the substituent was interacting with a benzylic carbon. How this oxygen will interact with other substituents in the excited state could be complicated and probably not obvious from valence bond pictures. Perhaps high quality MO calculations will be of some help. The results may also be affected by the intervention of reactive triplet states. The rate constants for reaction (k_r) and fluorescence ($k_f = \Phi_f/\tau_s$) account only for a relatively small fraction of the total rate of decay ($k_{dt} = 1/\tau_s$) of S_1. These values are given in Table 2. Quite likely, the major remaining path for decay (k_d) is intersystem crossing to T_1. Our quenching studies discussed above are not conclusive because we do not know the triplet lifetimes. If both singlet and triplet states are reacting to give products, then the correlation with $\sigma^{h\nu}$ values, defined from singlet state reactions, will not likely be meaningful.

A referee has pointed out that determination of k_r, as in eq 2, may be an oversimplification because of internal return of the radical pair by in-cage radical coupling to the starting ether. This is a valid concern common to all radical and ion pair chemistry. In fact, for photochemical benzylic cleavage reactions, internal return has been observed by ^{18}O exchange in carboxylates, **20**,[38−40] and phosphates, **21**,[41] and the magnitude is somewhat substituent dependent. In effect, $k_r(\text{determined}) = k_r(\text{correct}) \times k_p/(k_p + k_i)$, where $k_p/(k_p + k_i)$ gives the fraction of the radical pair that proceeds to product (k_p) relative to return to starting ether (k_i), i.e., k_r(determined) is less than k_r(correct) by this factor. If this term is constant for all substituents, then the rate constants would be wrong by a constant factor but the correlation in Figure 2 (which is logarithmic) would have the same slope. If the effect is strongly substituent dependent, then the correlation might be completely misleading. Experimentally, for the radical pairs in the work reported here, there is no convenient way to monitor internal return. Fortunately, in the cases where internal return has been measured, k_i is always less than k_r so that the error created by internal return is always less than a factor of 2. Moreover, *tert*-butyl radicals do not couple very efficiently with other radicals, disproportionation normally being preferred; for the ethers studied here, disproportionation (greater than 80%) of the radical pair to phenol **10** in eq 1 dominates coupling to photo-Fries products **11**. Errors in k_r of a factor of less than 2 will not significantly effect the fundamental trend in Figure 2.



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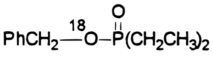

$PhCH_2{-}^{18}O{-}\overset{O}{\overset{\|}{P}}(CH_2CH_3)_2$

21

Finally, there is the possibility that both homolytic and heterolytic cleavage are occurring from S_1, particularly in view of the formation of the methyl ether **16** from the adamantyl substrate **9**, eq 9. If k_r is composed of two rate constants (k_{het} and k_{hom}, eq 4), and in a way which varies from substitutent to substitutent, again the correlation in Figure 2 would be fortuitous. Results from other substituted adamantyl ethers would help to clarify this question.

Experimental Section

Preparation of the Ethers. The ethers **8a−i** were prepared by the reaction of *tert*-butyl peroxybenzoate (Aldrich) with the Grignard reagent from the corresponding bromobenzene (Aldrich) using the procedure described by Frisell and Lawesson.[25] They were purified by vacuum distillation. All have been reported previously but spectral data were not given (Supporting Information). Photophysical data (UV absorbance spectra, fluorescence quantum yields, excited singlet state energies and excited singlet state lifetimes) are reported in Table 1.

The ethers **8j** and **9** were prepared by the reaction of the lithium salt of the alcohols, *tert*-butyl alcohol and 1-adamantanol (Aldrich), respectively, with 4-fluorobenzonitrile (Aldrich) according to the method of Woiwode et al.[26] Spectral data are in the Supporting Information.

Irradiation of Ethers. The ethers were irradiated as follows. A solution of 0.5−0.7 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 GC, and the reaction was stopped when the ether was >90% consumed. The methanol was removed by rotary evaporation and the mixture taken up in methylene chloride which was washed with water and extracted into 5% NaOH. The basic layer was then acidified and extracted with methylene chloride and analyzed by GC/MS and NMR. The photoproduct phenols **10a−j** and **11a** (*ortho* and *para*) were characterized by comparison with with authentic samples (Aldrich).

Quantitative photolyses were done in the same way as described above except at lower concentrations, typically 50−100 mg of the ether in 100 mL of methanol. Standard solutions of the products **10a−j** were prepared to determine their yields in the photolysis reactions by comparing integrated areas by GC/FID.

Fluorescence Measurements. Fluorescence measurements were carried out using a Shimadzu fluorescence spectrometer at 25 °C. Corrected spectra were obtained. Fluorescence quantum yields were determine by comparison with the known fluorescence quantum yield of 0.13 for toluene[42] in methanol. Singlet lifetimes were measured using a PRA time correlated 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 ethers in methanol were determined using 3-methoxybenzyl acetate ($\Phi = 0.13$) in aqueous dioxane as the standard.[12] The ethers, as well as the standard, were irradiated in a thermostatted (25 °C), carousel apparatus using a Rayonet reactor with four 75 W 254 nm lamps. Samples were taken every 2 min for 14 min. Each sample was analyzed by GC/FID in triplicate. A plot of percent conversion of the ether or the ester divided by time versus time was extrapolated to zero time. The ratio of the zero time values for the ether and the standard multiplied by 0.13 provided the quantum yield of reaction.

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Supporting Information Available: Spectral data for compounds **8a−j** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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