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Substituent Effects on the Rate Constants for the Photo-Claisen Rearrangement of Allyl Aryl Ethers

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Abstract: The photochemistry of 11 substituted allyl 4-X- and 3-X-aryl ethers **3** ($ArOCH_2{-}CH{=}CH_2$) has been examined in both methanol and cyclohexane as solvents. The ethers react by the photo-Claisen rearrangement to give allyl substituted phenols as the major primary photoproducts, as expected from the well-established radical pair mechanism. The excited singlet state properties (absorption spectra, fluorescence spectra, fluorescence quantum yields, and singlet lifetimes) were compared with a parallel set of unreactive 4-X- and 3-X-anisoles **4**. The excited-state properties of three substituted 4-X-aryl 4-(1-butenyl) ethers **14** ($ArOCH_2CH_2{-}CH{=}CH_2$) were also examined. The model compounds **4** and the reactive allyl ethers **3** have essentially identical rate constants for the excited-state processes with the exception of k^{s}_{hom}, the rate constant for homolytic cleavage from S_1 of the allyl ethers to give the radical pair. The difference between the fluorescence quantum yields and/or singlet lifetimes for **3** and **4** were used to obtain values of k^{s}_{hom} for all of the allyl ethers. These values exhibit a large substituent effect, spanning almost 2 orders of magnitude with electron-donating groups (CH_3O, CH_3) accelerating the reaction and electron-withdrawing ones (CN, CF_3) slowing it down. The parallel range of rate constants observed in both methanol and cyclohexane indicates that ion pairs are not important intermediates in these rearrangements. Quantum yields of reaction (Φ_r) for several of the more reactive ethers demonstrate that neither these values nor rate constants of reaction (k^{r}_{hom}) derived from them are reliable measures of the actual excited-state process. In fact, the k^{r}_{hom} values are significantly lower than the k^{s}_{hom} ones, indicating that the radical pairs undergo recombination to generate starting material. Finally, the k^{s}_{hom} rate constants were found to parallel a trend for the change in bond dissociation energy (ΔBDE) for the O−C (allyl) bond of the allyl ethers, indicating that other possible substituent effects are of minor importance.

Introduction

The effect that substituents (X) on aromatic rings have on the rates of organic reactions of the type $XC_6H_4Y{-}Z$, i.e., Hammett $\rho\sigma_x$ correlations, continues to be a fundamental tool for understanding reaction mechanisms in the ground electronic state. Numerous σ_x scales have been developed as probes for the changes in electron density that occur as the reactant proceeds along the reaction coordinate to the rate-determining transition state. The same statements cannot be made about σ scales for photochemical reactions that proceed through electronically excited states. Therefore, there is a continuing interest in measuring the effect that substituents have on the rates of photochemical reactions. The four most extensive excited-state σ scales are σ_{ex} (on the basis of the excited singlet state pK_a values for substituted phenols with ρ_{ex} defined as -3.1),[1,2] σ^* (also on the basis of excited singlet state pK_a values for phenols but rescaled to give $\rho^* = 1$ for the ionization of benzoic acids in the excited state),[3] $\sigma^{h\nu}$ (on the basis of the rate constants for protonation of the excited state of substituted styrenes and phenylacetylenes),[4] and $\sigma^{\bullet h\nu}$ (on the basis of photochemical quantum yields of homolytic σ bond cleavage for benzyl sulfides).[5]

We have been particularly interested in σ bond cleavage reactions[6,7] and have recently reported[8] on the photochemical reactivity of the substituted aryl *tert*-butyl ethers **1a−k** in methanol. The rate constants of product formation from the excited singlet state, obtained from quantum yields of product formation and singlet-state lifetimes, were correlated reasonably well with $\sigma^{h\nu}$; $\rho = -0.77$ ($r = 0.975$). Unfortunately, strong electron-withdrawing groups (CN, CF_3) could not be included in the correlation because $\sigma^{h\nu}$ values are not known for these substituents; the substituted styrenes are too unreactive in the photoprotonation reaction used to establish the scale. Moreover,

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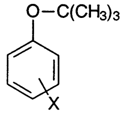
we obtained evidence for the 4-cyano analogue **2** that some of the products were ion pair rather than radical pair derived.



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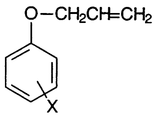

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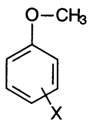

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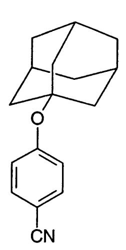
a: X = H
b: X = 4-OCH$_3$
c: X = 3-OCH$_3$
d: X = 4-CH$_3$
e: X = 3-CH$_3$
f: X = 4-F
g: X = 3-F
h: X = 4-CF$_3$
i: X = 3-CF$_3$
j: X = 4-CN
k: X = 3-CN



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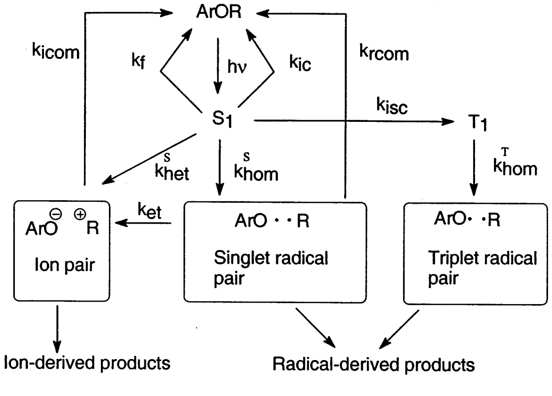
A generalized mechanism for the photocleavage of an aryl ether (ArOR) is given in Scheme 1. Obtaining the rate constant of interest, k^{s}_{hom}, for the reaction of the excited singlet state is not simple because of three complications.[9] First, intersystem crossing (k_{isc}) from S_1 gives T_1 which may also be reactive (k^{T}_{hom}) and therefore radical-derived products will be obtained from two pathways. Second, the excited singlet state may react by heterolytic cleavage (k^{s}_{het}) to give ion pairs so that ion-derived products are obtained. Also, because ion-derived products can be obtained from initially formed singlet radical pairs that undergo redox electron transfer (k_{et}), the measured yields of ion- and radical-derived products will not be a reliable measure of the values for either k^{s}_{het} or k^{s}_{hom}. Finally, both radical pairs (k_{rcom}) and ion pairs (k_{icom}) may undergo in-cage recombination to form the starting substrate. Internal return has been observed in every case where it has been tested for in photochemical benzylic ($ArCH_2{-}X$) cleavage reactions;[7] examples are for X = O−CO−R, $^{+}NH_3$, and O−PO−(OR)$_2$. As is well-known, if any of these complications occur, measured quantum yields of product formation will not reflect the initial reactivity of the excited state.

Scheme 1. Mechanistic Scheme for the Photochemical σ Bond Cleavage of a Generalized Aryl Ether



A solution to overcome these complications is possible if a suitable unreactive model for the substrates of interest can be found. The idea is that the model mimics the excited-state properties of S_1 in all ways except that it is unreactive. In this case, either static or dynamic fluorescence spectroscopy can be used to obtain k^{s}_{hom} values directly.[10] In the static case, the quantum yields of fluorescence for the substrate (Φ_f), eq 1,[11] and the model (Φ^{M}_{f}), eq 2, give eq 3; in the dynamic case, the measured singlet lifetime of the substrate (τ^{s}) and the model excited (τ^{s}_{M}) give eq 4. In both cases the assumption is made that all rate constants (k_f, k_{ic}, k_{isc}) for the singlet state except k^{s}_{hom} are the same for the substrate and the model. This method has been used very successfully and extensively in studies of intramolecular electron transfer in bichromophoric molecules where the model chromophore is identical except for the absence of the remote second chromophore.[12]

$$\Phi_f = \frac{k_f}{k_f + k_{ic} + k_{isc} + k^{s}_{hom}} = \frac{k_f}{k_{dt}} = k_f\tau^{s} \tag{1}$$

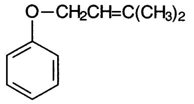
$$\Phi^{M}_{f} = \frac{k_f}{k_f + k_{ic} + k_{isc}} = k_f\tau^{s}_{M} \tag{2}$$

$$k^{s}_{hom} = \left(\frac{\Phi^{M}_{f}}{\Phi_f} - 1\right)/\tau^{s}_{M} \tag{3}$$

$$k^{s}_{hom} = \left(\frac{1}{\tau^{s}} - \frac{1}{\tau^{s}_{M}}\right) \tag{4}$$

We now report on the application of this idea for determining the rate constants for cleavage from the excited singlet state of a set of substituted allyl aryl ethers **3a**−**k** in both methanol and cyclohexane. In both solvents, these substrates undergo an efficient photo-Claisen reaction by the well-established radical pair mechanism.[13]

This kind of comparison has been used previously in studies of the photo-Claisen reaction, first in an early study by Carroll and Hammond of the ether **5**.[14] A more recent study by Pohlers et al.[15,16] of the fluorescence of the allyl naphthyl ethers **6** and **7**, compared to their unreactive methyl naphthyl ether analogues, was used to verify photo CIDNP results that indicated that both singlet and triplet states of **6** and **7** were reactive at 298 K but by 373 K only the singlet state reacted. The effects that substituents on the aromatic ring have on the efficiency or rate constant of reaction were not reported in either of the above examples.



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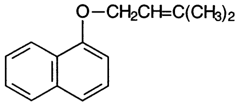

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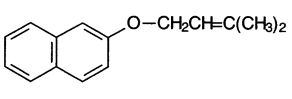

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Results and Discussion

Photochemical Product Studies. The allyl aryl ethers **3c**−**k** were synthesized from the corresponding phenols by reaction

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(9) These problems have been discussed in detail for excited-state σ bond cleavage reactions in ref 7.

(10) As will be discussed below, k^{s}_{hom} values will not be the same as k^{r}_{hom} values obtained from quantum yields of reaction.

(11) Equation 2 assumes that S_1 reacts only by homolytic cleavage, k^{s}_{hom}. If S_1 also reacts by heterolytic cleavage, then k^{s}_{het} would also be in the sum of rate constants for decay of S_1 in the denominator. For the photochemical reaction of the ethers described in this report, the results presented below indicate that $k^{s}_{hom} \gg k^{s}_{het}$.

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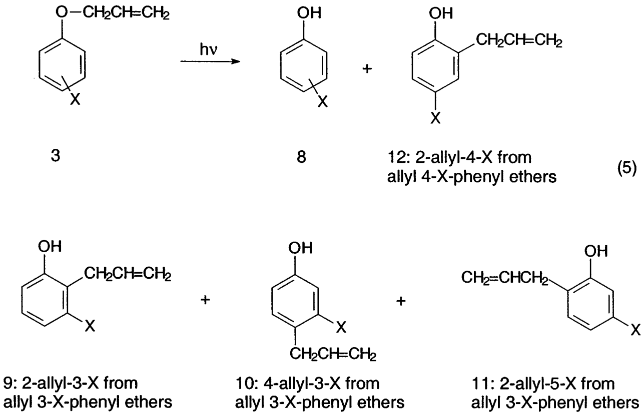
with allyl bromide using potassium carbonate in acetone; **3a**: X = H and **3b**: X = 4-CH_3O are available from Aldrich. As expected from previous reports and shown in eq 5, the major products in both methanol and cyclohexane are the corresponding phenols **8** and the rearranged allyl substituted phenols 2-allyl-3-X, 4-allyl-3-X, and 2-allyl-5-X (**9**, **10**, and **11**) for the 3-substituted substrates and only 2-allyl-4-X (**12**) for the 4-substituted cases. Many of these products have been characterized previously from studies of substituent effects on the rates of thermal Claisen rearrangements: **12** for X = 4-CH_3O, 4-CH_3, and 4-CN;[17,18] **9** and **11** for X = 3-CH_3O, 3-CH_3, and 3-CF_3.[19,20] The GC/FID yields, taken at low conversions (10−20%), are reported in Table 1. At these conversions the mass balance was always above 90%; the yields reported are normalized to 100%. The photochemistry of **3a**: X = H and **3d**: X = 4-CH_3 in both methanol and cyclohexane for the former, but only in cyclohexane for the latter, has been reported previously;[21] as indicated in Table 1, agreement with the literature yield values is good. For **3c**: X = 3-CH_3O, literature values are available in ethanol.[22] At higher conversions, the product allyl ethers all react by secondary photochemistry to give cyclopropyl derivatives, as in eq 6. These were identified as isomers by GCMS and as cyclopropyl derivatives by their high field signals in ^1H NMR. These cyclopropyl derivatives, expected from the aryl version of the photochemical di-π-methane rearrangement,[23] were not characterized completely but could easily be seen increasing in yield at the expense of the corresponding allyl compounds by GC/FID.

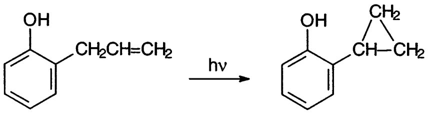


3 8 12: 2-allyl-4-X from allyl 4-X-phenyl ethers (5)

9: 2-allyl-3-X from allyl 3-X-phenyl ethers

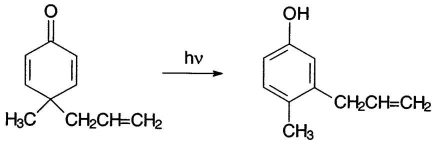
10: 4-allyl-3-X from allyl 3-X-phenyl ethers

11: 2-allyl-5-X from allyl 3-X-phenyl ethers



(6)

For **3d**: X = 4-CH_3 one of the products was found to be 3-allyl-4-methylphenol (**12**), expected from secondary photochemistry[24] of the cyclohexadienone **13**, eq 7. This product was also observed previously on photolysis in methanol.[21] In this case, the initially formed photo-Claisen product cannot enolize to the phenol. Similar 2,5-cyclohexadienone derivatives have always been proposed as the primary photoproducts in Claisen reactions and have been isolated from irradiations of substituted allyl aryl,[21] benzyl aryl,[25] and aryl naphthylmethyl[26] ethers. Products analogous to **12** are probably formed from others of the para-substituted compounds **3**, but if so, we were unable to isolate them.



13 **12** (7)

Table 1. Product Yields for the Photolysis of the Allyl Aryl Ethers **3a**−**j** in Methanol and Cyclohexane

Compound	X	Solvent[a]	8	9 or 12	10	11	
3a	H	M	4(11)[b]	50(45)[b]	46(41)[b]		
3a	H	C	28(21)[b]	33(38)[b]	39(41)[b]		
3b	4-OCH_3	M	11	89			
3b	4-OCH_3	C	44	56			
3c	3-OCH_3	M	8(18)[c]	16(22)[c]	40(31)[c]	36(28)[c]	
3c	3-OCH_3	C	23	12	28	37	
3d	4-CH_3	M	8(11)[b]	75(70)[b]	17(14)[b,d]		
3d	4-CH_3	C	41	53	6		
3e	3-CH_3	M	8	28	25	40	[e]
3e	3-CH_3	C	28	21	21	28	
3f	4-F	M	12	88			
3f	4-F	C	18	82			
3g	3-F	M	4	27	29	41	[e]
3g	3-F	C	4	28	30	39	
3h	4-CF_3	M	9	91			
3h	4-CF_3	C	23	77			
3i	3-CF_3	M	3	35	32	30	
3i	3-CF_3	C	21	23	32	23	
3j	4-CN	M	21	79			
3j	4-CN	C	16	84			

[a] M is methanol, C is cyclohexane. [b] Literature values, ref 21. [c] Literature values, ref 22. [d] Actually, 3-allyl-4-methylphenol as shown in eq 7. [e] Isomer assignment not certain, see Experimental Section.

Finally, the 3-cyano compound **3k** proved to be so unreactive photochemically that, by the time reasonable conversion of the starting material had occurred, the product mixtures were complicated by high yields of secondary photoproducts. These mixtures could not be separated, and therefore the photoproducts were not characterized. ^1H NMR spectra of the crude reaction mixtures indicated mainly cyclopropyl derivatives.

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Table 2. Absorbance and Fluorescence Data for the Allyl Aryl Ethers **3a**−**k** and the Anisoles **4a**−**k** in Methanol and Cyclohexane

compd	X	solvent[a]	$\lambda_{\max}$,[b] nm	ϵ,[b] M^{-1} cm^{-1}	$\lambda_{0,0}$,[c] nm	E_{S_1},[d] kcal/mol	Φ_f[e]	τ^s,[f] ns
4a	H	M	271	1680	281	102	0.24[g]	7.58 ± 0.06
3a	H	M	271	1600	282	101	0.012	
4a	H	C	271	1930	281	102	0.29[h]	7.8 ± 0.1
3a	H	C	272	1860	281	102	0.0056	
4b	4-OCH$_3$	M	290	2820	305	94	0.11	2.68 ± 0.02
3b	4-OCH$_3$	M	290	2730	305	94	0.0069	
4b	4-OCH$_3$	C	289	3200	304	94	0.12	3.02 ± 0.06
3b	4-OCH$_3$	C	288	2990	304	94	0.0054	
4c	3-OCH$_3$	M	274	2200	285	100	0.076	2.42 ± 0.02
3c	3-OCH$_3$	M	274	2250	286	100	0.0095	0.63 ± 0.04
4c	3-OCH$_3$	C	274	2220	284	101	0.093	2.48 ± 0.01
3c	3-OCH$_3$	C	274	2240	284	101	0.0095	
4d	4-CH$_3$	M	279	1880	289	99	0.22	6.37 ± 0.07
3d	4-CH$_3$	M	278	1660	290	99	0.0065	
4d	4-CH$_3$	C	279	2170	290	99	0.33	7.48 ± 0.07
3d	4-CH$_3$	C	279	1900	288	99	0.0053	
4e	3-CH$_3$	M	273	1660	283	101	0.27	8.0 ± 0.1
3e	3-CH$_3$	M	273	1540	285	100	0.0088	
4e	3-CH$_3$	C	273	1810	282	101	0.37	8.79 ± 0.05
3e	3-CH$_3$	C	273	1630	283	101	0.0074	
4f	4-F	M	280	2670	291	98	0.15	3.72 ± 0.04
3f	4-F	M	279	2460	291	98	0.020	
4f	4-F	C	281	2900	290	99	0.18	3.86 ± 0.03
3f	4-F	C	281	2690	290	99	0.014	
4g	3-F	M	269	1590	279	103	0.0077	
3g	3-F	M	269	1450	280	102	0.0055	
4g	3-F	C	269	1650	278	103	0.022	0.8 ± 0.01
3g	3-F	C	269	1590	278	103	0.0081	
4h	4-CF$_3$	M	270	1060	279	103	0.093	4.47 ± 0.05
3h	4-CF$_3$	M	269	860	280	102	0.028	1.47 ± 0.02
4h	4-CF$_3$	C	270	1100	280	102	0.13	5.05 ± 0.06
3h	4-CF$_3$	C	270	1060	280	102	0.021	0.93 ± 0.01
4i	3-CF$_3$	M	277	2310	288	99	0.11	3.16 ± 0.02
3i	3-CF$_3$	M	277	2250	289	99	0.067	2.03 ± 0.01
4i	3-CF$_3$	C	267	2440	289	99	0.16	3.41 ± 0.03
3i	3-CF$_3$	C	276	2300	288	99	0.064	1.63 ± 0.01
4j	4-CN	M	271 (sh)	2030	286	100	0.075	3.37 ± 0.04
3j	4-CN	M	272 (sh)	2250	286	100	0.048	2.38 ± 0.05
4j	4-CN	C	274	1310	286	100	0.11	5.88 ± 0.09
3j	4-CN	C	274 (sh)	1480	287	100	0.044	2.45 ± 0.02
4k	3-CN	M	290	2960	305	94	0.14	3.60 ± 0.04
3k	3-CN	M	290	2870	305	94	0.10	3.10 ± 0.04
4k	3-CN	C	288	2980	300	95	0.20	4.83 ± 0.03
3k	3-CN	C	288	2840	301	95	0.16	3.90 ± 0.04

[a] M is methanol, C is cyclohexane. [b] Obtained from absorption spectra. [c] Obtained from the overlap of the absorption and fluorescence spectra. [d] Calculated from $E_{S_1} = 2.86 \times 10^4/\lambda_{0,0}$. [e] Quantum yield of fluorescence relative to anisole in methanol (0.24) and cyclohexane (0.29), estimated error ± 10%. [f] Singlet lifetime by nanosecond single photon counting. The errors given are the standard deviation of the fit to the experimental counts. No value indicates that the lifetime was less than 0.5 ns. [g] Reference 27. [h] Reference 28.

The conclusion from these observations is that these substituted aryl allyl ethers behave as expected according to the well-established radical pair mechanism for the photo-Claisen rearrangement.[13]

Photophysical Properties for the Allyl Aryl Ethers 3 and the Corresponding Anisoles 4. The absorbance spectral data ($\lambda_{\max}$, ϵ for the long-wavelength S_1 band) and fluorescence emission data ($\lambda_{0,0}$, E_S (calculated from $\lambda_{0,0}$), Φ_f, and τ^s) are given in Table 2 for the two complete sets of allyl aryl (**3a**−**k**) and aryl methyl (**4a**−**k**) ethers in both methanol (M) and cyclohexane (C). The quantum yields of fluorescence (Φ_f) were determined relative to literature values for anisole **4a**: X = H in methanol (0.24)[27] and cyclohexane (0.29).[28] The singlet lifetimes are too short to measure with our nanosecond system for many of the allyl ethers **3** in both solvents. This fact will be discussed in more detail below.

The absorbance spectra support the proposal that the anisoles are good models for the allyl ethers. First, the absorbance maximum ($\lambda_{\max}$) and molar absorptivity (ϵ) are essentially the same for both compounds in either solvent for all substitutents. The ϵ values for each compound are slightly, but consistently, higher in cyclohexane than in methanol. The exception is for the 4-cyano compounds, but their spectra are complicated because of the strong conjugative interaction between the alkoxy and cyano substitutents which shifts the S_2 band to longer wavelengths so that it overlaps with the S_1 band. To strengthen the case for similarity of the absorption spectra for the allyl and methyl ethers, normalized absorption spectra comparing the S_0 to S_1 band for the allyl aryl ethers **3** (dashed lines) and the anisoles **4** (solid lines) for each substituent are included in the Supporting Information, Figures S1 (methanol) and S2 (cyclohexane). In all cases, the spectra are essentially superimposable considering the 1 nm resolution of the spectrometer. The 4-trifluoromethyl compounds show the largest difference at the short-wavelength end of the S_0–S_1 transition.

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(27) Kohler, G.; Kittel, G.; Getoff, N. *J. Photochem.* **1982**, *18*, 19−27.
(28) Berlman, I. B. In *Handbook of Fluorescence Spectra of Aromatic Molecules*; Academic Press: New York, 1971; p 139.

The fluorescence emission spectra also support the reliability of the anisole model. This comparison of the fluorescence spectra is critical in evaluating the excited-state properties of **3** and **4**. The anisole model requires that any interaction between the aromatic chromophore and the allyl group (relative to methyl) is small so as not to interfere with the postulate that leads to eqs 3 and 4 and reliable estimates of k^{s}_{hom}. First, the 0,0 bands (from the overlap of absorbance and fluorescence spectra) and derived excited singlet state energies (E_S) are essentially the same for all substituents in either solvent. Second, complete normalized spectra comparing the two ethers **3** and **4** for each substituent are given in the Supporting Information, Figures S3 (methanol) and S4(cyclohexane). The deviations observed in the comparison of the spectra are small and are only significant for the allyl ethers with very low quantum yields of fluorescence, Φ_f (Table 2). The major reason for these deviations is that the spectra of these very weakly emitting allyl derivatives are perturbed by the superposition of the relatively intense Raman scattering band.

A third fluorescence method in support of the anisole model is through excitation spectra. These are shown as a function of emission wavelength in the Supporting Information in Figures S5a/5b (**3a** and **4a** in methanol/cyclohexane, X = H), S6a/S6b (**3f** and **4f** in methanol/cyclohexane, X = 4-F), S7a/S7b (**3j** and **4j** in methanol/cyclohexane, X = 4-CN), S8a/S8b (**3a**/**4a** in cyclohexane, X = H), S9a/S9b (**3f**/**4f** in cyclohexane, X = 4-F), and S10a/S10b (**3j**/**4j** in cyclohexane, X = 4-CN). These compounds were chosen because they span the complete range of reactivity for the allyl ethers. All of these excitation spectra show essentially identical intensity versus wavelength dependence, independent of the wavelength of observation. This equivalence of the intensity of the vibrational modes helps to establish that the S_1 minima for the allyl and methyl ethers are very similar.

In contrast to the identical wavelength dependence of the fluorescence spectra, the fluorescent quantum yields are consistently lower for the allyl aryl ethers **3** than the methyl ethers **4** in both solvents. As indicated by eqs 1 and 2, this is a consequence of the reaction itself, k^{s}_{hom}, increasing the total rate of decay of S_1. In agreement with this conclusion, in all cases where the singlet state lifetimes could be obtained, the allyl ethers have shorter lifetimes (τ^s) than the methyl ethers (τ^s_M).

For all but one (**4g**: X = 3-F) of the substituted methyl ethers, and for the less reactive allyl ethers (**4h**: X = 4-CF_3, **4i**: X = 3-CF_3, **4j**: X = 4-CN, and **4k**: X= 3-CN) excited singlet state lifetimes and fluorescence quantum yields can be used to obtain other rate constants for that state, namely k_f and $k_d = 1/\tau^s - k_f$. The exception **4g**: X = 3-F has an unusually short lifetime, almost at the limit of the time resolution (0.5 ns) of our flash lamp lifetime equipment in cyclohexane (0.8 ns) and too short to measure in methanol (~0.3 ns). Table 3 gives these k_f and k_d values for the other methyl ethers. In all cases, $k_d > k_f$. Likely k_d, the radiationless decay of the excited singlet state, is dominated by intersystem crossing to the triplet state. For instance, the quantum yield of intersystem crossing ($\Phi_{isc} = 0.64$)[29] for anisole **4a**: X = H along with the singlet lifetime ($\tau^s = 7.6$ ns, Table 2) gives $k_{isc} = \Phi_{isc}/\tau^s = 8.4 \times 10^7$ s^{-1}, in good agreement with our experimental value in cyclohexane, $k_d = 9.7 \times 10^7$ s^{-1}. The very short singlet lifetime for the anisole **4g**: X = 3-F is a result of a very high value for $k_d = 120 \times 10^7$ s^{-1}, a factor of 3−17 higher than any of the other substrates. The reason for this is unknown.

For the less reactive allyl ethers (**4h**: X = 4-CF_3, **4i**: X = 3-CF_3, **4j**: X = 4-CN, and **4k**: X =3-CN), k_f values can also be obtained experimentally; see Table 3. In all cases, the agreement between the value for the allyl ethers and the model compounds, the methyl ethers **3**, is very good. The largest deviation is for the **4i**: X = 3-CF_3/**3i** in cyclohexane and **4k**: X = 3-CN/**3k** in methanol equal to 3.9 ns/3.2 ns or 1.22.

The conclusion from this section is that the unreactive anisoles **4** serve as excellent models for the reactive allyl ethers **3**. Presumably, the excited-state potential energy minimum is essentially the same for both except that the activation barrier for oxygen−carbon bond cleavage is lower and consequently the reaction occurs faster for the weaker oxygen to allyl, compared to oxygen to methyl, bond.

Calculation of Fluorescent Rate Constants, k_f, for the Ethers 3a−k and 4a−k in Methanol and Cyclohexane. The theoretical relationship between the radiative lifetime ($\tau_f = 1/k_f$) and the absorbance spectrum is given in eq 8,[30,31]

$$k_f = 2.88 \times 10^{-9} n^2 \langle \bar{\nu}_f^{\,-3} \rangle^{-1} \int \epsilon \ln \bar{\nu} \qquad (8)$$

where n is the refractive index of the solvent,[32,33] ν_f is the expectation value for the frequency of the fluorescence spectrum, and the final term is the integrated absorbance spectrum. The constant gives k_f in units of s^{-1} if the frequency values are expressed in wavenumber (cm^{-1}) and molar absorptivity ϵ in the usual units (M^{-1} cm^{-1}). This equation is derived on the basis of the oscillator strength model and the assumption that the excited singlet state and the ground state have similar geometries. It has been used successfully in the past for simple aromatic compounds such as benzene, toluene, and σ-xylene.[34]

Calculated values of k_f for all compounds, except the 4-cyano and 4-trifluoromethyl ones are given in Table 3. Values of k_f for the 4-CF_3 and 4-CN compounds were not calculated because the absorption spectrum for the S_0 to S_1 transition could not be integrated due to an overlap with the more intense S_0 to S_2 transition. Also given in parentheses in the same column are ratios of k_f(experimental)/k_f(calculated) in cases where experimental values could be obtained. The average of these ratios is 0.96 ± 0.13, an indication of a random distribution about a value of 1. These calculations give us considerable confidence that good estimates of k_f can be made even in cases where fluorescence lifetimes are too short to be measured. These calculated values of k_f can then be used to estimate $k_{dt} = 1/\tau^s$ values using the measured quantum yields of fluorescence because $k_{dt} = k_f/\Phi_f$. These values of k_{dt}, in parentheses, along with experimental ones are in Table 3.

Calculation of k^{s}_{hom} Values for the Allyl Aryl Ethers, 3a−k, in Methanol and Cyclohexane. Using eq 3 or 4 and the

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[29] Murov, S. L.; Carmichael, T.; Haig, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993; p 13.

[30] Strickler, S. J.; Berg, R. A. *J. Chem. Phys.* **1962**, *37*, 814−822.

[31] Birks, J. B.; Dyson, D. J. *Proc. R. Soc. A* **1963**, *275*, 135−148.

[32] The value of n = 1.34 for methanol was estimated for 330 nm by extrapolation from seven refractive index values from 656 to 404 nm; Wood, S. E.; Langer, S.; Battino, R. *J. Chem. Phys.* **1960**, *32*, 1389−1393.

[33] The value of n = 1.45 for cyclohexane was taken from ref 28, Appendix 7.2, p 422.

[34] Cundall, R. B.; Pereira, L. C. *J. Chem. Soc., Faraday Trans.* **1972**, *68*, 1152−1163.

Table 3. Excited-State Rate Constants for the Alkyl Aryl Ethers **3a**−**k** and the Anisoles **4a**−**k** in Methanol and Cyclohexane

compd	X	solvent[a]	k_{dt} (s^{-1})/10^7 = 1/τ^s [b]	k_f (s^{-1})/10^7 = Φ_f/τ^s	k_f (s^{-1})/10^7 from eq 9[c]	k_d (s^{-1}) /10^7 = $k_{dt} - k_f$[d]	k^s_{hom} (s^{-1})/10^7 from eq 5	k^s_{hom} (s^{-1})/10^7 from eq 4[e]
4a	H	M	13.2	3.2	2.4 (1.33)	10		
3a	H	M	(270)		2.5	(17)		250
4a	H	C	12.8	3.7	3.6 (1.03)	9.7		
3a	H	C	(660)		2.9	(7)		650
4b	4-CH$_3$O	M	37.3	4.0	4.3 (0.93)	33		
3b	4-CH$_3$O	M	(580)		4.1	(46)		530
4b	4-CH$_3$O	C	33.1	3.9	5.5 (0.71)	29		
3b	4-CH$_3$O	C	(720)		5.1	(25)		690
4c	3-CH$_3$O	M	41.3	3.1	3.1 (1.00)	38		
3c	3-CH$_3$O	M	(330)		3.1	(37)		290
4c	3-CH$_3$O	C	40.3	3.8	3.5 (1.09)	36		
3c	3-CH$_3$O	C	(400)		3.7	(46)		350
4d	4-CH$_3$	M	15.7	3.5	3.1 (1.12)	12		
3d	4-CH$_3$	M	(530)		2.9	(17)		510
4d	4-CH$_3$	C	13.4	4.4	3.9 (1.13)	8.9		
3d	4-CH$_3$	C	(830)		3.2	(7.7)		820
4e	3-CH$_3$	M	12.5	3.4	2.8 (1.21)	9.1		
3e	3-CH$_3$	M	(380)		2.3	(7.6)		370
4e	3-CH$_3$	C	11.3	4.2	3.4 (1.24)	7.1		
3e	3-CH$_3$	C	(570)		2.8	(0)		570
4f	4-F	M	26.8	4.0	4.1 (0.98)	23		
3f	4-F	M	(200)		3.8	(26)		170
4f	4-F	C	25.9	4.6	4.9 (0.94)	21		
3f	4-F	C	(330)		4.7	(25)		300
4g	3-F	M	(300)		2.3	(300)		
3g	3-F	M	(418)		2.3	(300)		(120)
4g	3-F	C	125	2.9	2.9 (1.00)	120		
3g	3-F	C	(345)		2.8	(132)		210
4h	4-CF$_3$	M	22.3	2.1		20		
3h	4-CF$_3$	M	68	1.9		21	46	51
4h	4-CF$_3$	C	19.8	2.6		17		
3h	4-CF$_3$	C	108	2.3		18	88	100
4i	3-CF$_3$	M	31.6	3.5	3.7 (0.95)	28		
3i	3-CF$_3$	M	49.2	3.3	4.0 (0.83)	28	18	20
4i	3-CF$_3$	C	29.3	3.2	4.4 (0.73)	26		
3i	3-CF$_3$	C	61.3	3.9	4.0 (0.98)	25	32	44
4j	4-CN	M	29.6	2.2		27		
3j	4-CN	M	42.0	2.0		27	12	16
4j	4-CN	C	17.0	1.9		15		
3j	4-CN	C	40.8	1.8		15	24	26
4k	3-CN	M	27.8	3.9	4.5 (0.87)	24		
3k	3-CN	M	32.2	3.2	4.6 (0.70)	24	6	11
4k	3-CN	C	20.3	4.1	5.1 (0.80)	16		
3k	3-CN	C	25.6	4.1	4.6 (0.89)	17	6	11

[a] M is methanol, C is cyclohexane. [b] Values in parentheses are obtained from k_f(eq 8)/Φ_f. [c] Values in parentheses are k_f(experimental)/k(calculated). [d] Values in parentheses are calculated from $k_{dt} - k_f - k_{hom}$. [e] Estimated error ± 20%.

appropriate fluorescence quantum yields or lifetimes, respectively, leads to an estimation of k^s_{hom}, the rate constant for homolytic cleavage for S_1 of the allyl ethers. These values are also given in Table 3. As discussed in the Introduction, triplet-state reactivity or internal return by collapse of radical pairs will not complicate these values because these values, determined by fluorescence data, are a measure of only excited singlet state reactivity.

In cases where fluorescence lifetimes are available experimentally, eq 4 is probably more reliable. Quantum yields of fluorescence, required for eq 3, are inherently more difficult to measure accurately because they are obtained by comparison of the relatively weak fluorescence spectra of the allyl aryl ethers with a standard (anisole) using solutions of matched absorbance. Very small amounts of the more strongly fluorescent corresponding phenols, which are the synthetic precursors for the allyl ethers, will significantly enhance these weak emissions. However, as seen for the substituted ethers of lower reactivity, where both eqs 3 and 4 can be applied, the two methods are in good agreement. Of course, in these cases the quantum yields of fluorescence are also higher and therefore more reliable. For the allyl ethers of higher reactivity and consequently singlet lifetimes too short to measure, only the relative fluorescence quantum yields and eq 3 can be used to obtain k^s_{hom}.

Finally, the self-consistency of this method of obtaining k^s_{hom} values by using the unreactive model can be assessed by examining k_d values for the excited singlet state. These are now obtained from eq 9

$$k_d = k_{ic} + k_{isc} = k_{dt} - k_f - k^s_{hom} \tag{9}$$

using measured values for the less reactive allyl ethers and calculated values, in parentheses, for the more reactive substrates where k_f (calculated from eq 8) and Φ_f lead to $k_{dt} = 1/\tau^s$. These can then be compared to experimental k_d values obtained for the unreactive methyl ethers. The agreement is again very good, validating the basic assumption of the method. *The excited singlet state properties of the reactive allyl aryl ethers and the unreactive aryl methyl ether model compounds are essentially*

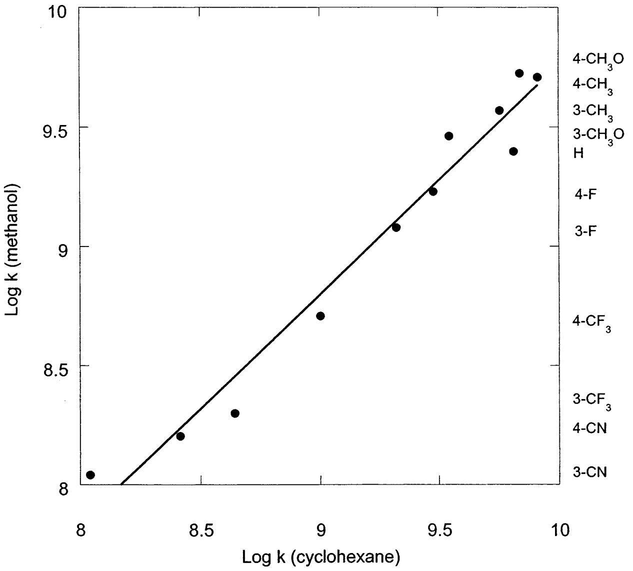


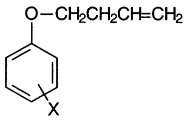
Figure 1. Plot of log k^s_{hom}(methanol) versus log k^s_{hom}(cyclohexane) for the photo-Claisen reaction of the allyl aryl ethers **3a**−**k**.

the same in all respects except for the inclusion of an additional process, k^s_{hom}, *for the reactive compounds.*

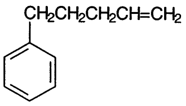
Compound **3g**: X = 3-F is particularly interesting in this regard. Although the model compound **4g** is too short-lived in methanol to measure its singlet lifetime, its lifetime can be reliably estimated using Φ_f and k_f (calculated from eq 8). Then eq 3 can be used to calculate $k^s_{hom} = 120 \times 10^7$ s^{-1} (in parentheses in Table 3 because it is not obtained by direct experiment). As will be shown below, this value is in good agreement with correlations of rate constants for the other substrates.

Several general observations concerning these rate constants can be made. First, due to the experimental errors in determining Φ_f and k_f, these values are probably accurate only to about ±20%, particularly for the reactive ethers. Therefore, all rate constants are reported to only two significant figures. Second, the effect of the substituents is unusually large for a photochemical reaction, spanning almost 2 orders of magnitude. Third, the trend in the rate constants as a function of substitutents is the same in methanol and cyclohexane. This observation is reinforced by Figure 1, a linear log/log plot of the rates in methanol versus cyclohexane. This is an important observation because it demonstrates that ion pair intermediates are not formed directly from S_1 in methanol. The slope of 0.96 indicates that the rate constants are greater in cyclohexane than in methanol as is seen numerically in Table 3 for **3a**−**k**. The similarity in yields in methanol and cyclohexane (Table 1) also indicates that ion pairs are not formed at a later stage after the excited-state chemistry is finished, i.e., k_{et} (Scheme 1).

Photophysical Properties for the Aryl 4-Butenyl Ethers, 14. At a conference presentation of these results,[35] the valid question was raised as to whether the allyl ethers are reliably modeled by the anisoles. The point was made that a decrease in fluorescence intensity or lifetime for the allyl ethers could reflect an excited singlet state interaction (exciplex formation) that does not lead to cleavage of the carbon−oxygen band but is invisible because the excimer is nonemissive. Therefore, this would be another process for internal conversion. The homologous aryl 4-butenyl ethers **14** were proposed as a better choice for a model as they cannot undergo the photo-Claisen reaction but do have a second vinyl functional group.



14



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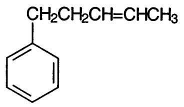

16

The problem with compounds **14** as models is that now interaction between the two chromophores is essentially guaranteed according to the $n = 3$ rule for the number of saturated atoms that separate the two chromophores. This fact was first demonstrated for 1,ω-diphenylalkanes where the localized emission ($I_f = 4$) was strongly quenched in cyclohexane and excimer emission was observed for 1,3-diphenylpropane but not for 1,2-diphenylethane ($I_f = 105$) or 1,4-diphenylbutane ($I_f = 100$).[36] This rule has been found to be not rigorously followed. For instance, for 1,ω-dipyrenylalkanes excimer emission was observable for a whole range ($n = 2-16$) of insulating (CH$_2$)$_n$ linkers.[37] However, even in these cases, the ratio of excimer to monomer emission was high (>15) for $n = 3$ and low (<0.5) for $n = 2$. Moreover, the emission was blue shifted for the $n = 2$ case relative to both the $n = 3$ and the intermolecular pyrene cases, suggesting that the excimer was of higher energy because the shortness of the chain prevented a geometry that allowed maximum interaction between the two chromophores.

Morrison and co-workers[38] were the first to report a similar effect for ω-arylalkenes. Thus, in cyclopentane, the fluorescence (relative intensity $I_f = 0.05$) of **15** ($n = 3$) was strongly quenched at room temperature relative to phenylhexane ($I_f = 0.90$) whereas that for **16** ($n = 2$) was essentially the same ($I_f = 0.88$). Moreover, this rapid formation of an exciplex for **15** was followed by intramolecular cycloaddition, a process (meta photocycloaddition) which has since been observed for many tethered alkenes and aromatics for $n = 3$.[39] To our knowledge, there are no examples for $n = 2$. We conclude that interaction between the aryl and the vinyl group in the compounds **14**, as a consequence of exciplex formation, should be much greater than for the allyl ethers **3**.

We have synthesized and measured fluorescence quantum yields and singlet lifetimes in both methanol and cyclohexane for three butenyl ethers **14a**: X = H, **14b**: X = 4-OCH$_3$, and **14j**: X = 4-CN. These were chosen to span the range of fluorescence quenching observed for the allyl ethers **3**. For instance, fluorescence is strongly quenched relative to the corresponding anisole **4** for **3a**: X = H, $\Phi^4_F/\Phi^3_F = 20$ and **3b**: X = 4-OCH$_3$, $\Phi^4_F/\Phi^3_F = 16$, and quenched only slightly for **3j**: X = 4-CN, $\Phi^4_F/\Phi^3_F = 1.6$ (values are in methanol as solvent). The three butenyl ethers also span the range of electron-donating (X = 4-OCH$_3$) to electron-withdrawing (X = 4-CN) groups to test for any electron transfer component to exciplex formation. The results are given in Table 4.

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(35) Presented at the IAPS Conference, Arizona State University, Tempe, AZ, January 2002.

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(37) Zachariasse, K.; Kuhnle, W. *Z. Phys. Chem. Neue Folge* **1976**, *101*, 267−276.

(38) Ferree, W.; Grutzner, J. B.; Morrison, H. *J. Am. Chem. Soc.* **1971**, *93*, 5502−5512.

(39) Cornelisse, J. *Chem. Rev.* **1993**, *93*, 615−670.

Table 4. Absorbance and Fluorescence Data for the Aryl 4-(1-Butenyl) Ethers **14**

compd	X	solvent[a]	$\lambda_{0,0}$,[b] nm	$E_{S_1,}$[c] kcal/mol	Φ_f[d]	τ^s,[e] ns
4a	H	M	281	102	0.24[f]	7.58 ± 0.06
14a	H	M	281	102	0.043	1.64 ± 0.01
4a	H	C	281	102	0.29[g]	7.8 ± 0.1
14a	H	C	280	103	0.050	1.73 ± 0.02
4b	4-OCH_3	M	305	94	0.11	2.68 ± 0.02
14b	4-OCH_3	M	304	94	0.10	2.58 ± 0.02
4b	4-OCH_3	C	304	94	0.12	3.02 ± 0.06
14b	4-OCH_3	C	304	94	0.13	2.96 ± 0.02
4j	4-CN	M	286	100	0.075	3.37 ± 0.04
14j	4-CN	M	286	100	0.035	1.38 ± 0.02
4j	4-CN	C	286	100	0.11	5.88 ± 0.09
14j	4-CN	C	286	100	0.061	3.40 ± 0.03

[a] M is methanol, C is cyclohexane. [b] Obtained from the overlap of the absorption and flurorescence spectra. [c] Calculated from $E_{S_1} = 2.86 \times 10^4/\lambda_{0,0}$. [d] Quantum yield of fluorescence relative to anisole in methanol (0.24) and cyclohexane (0.29), estimated error ± 10%. [e] Singlet lifetime by nanosecond single photon counting. The errors given are standard deviations of the fit to the experimental counts. [f] Reference 27. [g] Reference 28.

Reports on intramolecular photocycloadditions have appeared for two of these compounds, **14a**: X = H and **14c**: X = 4-CN. In the former case,[40] the process in cyclohexane was described as "very inefficient; excessive polymer formation";[39] much better yields have been obtained in dioxane as solvent, giving a mixture of products derived from ortho and meta cycloadducts.[41] In the 4-CN case, high yields of intramolecular ortho cycloadducts were obtained on irradiation in all sovents used.[42] For this substrate, the cycloaddition products have been shown to arise from the triplet state, first by Gilbert and co-workers[42] and later by Wagner and Smart.[43]

No reports on intramolecular photoadducts for the butenyl ether **14b**: X = 4-OCH_3 are available (SciFinder). In agreement with this fact, the quantum yields of fluorescence and singlet lifetimes in both cyclohexane and methanol are essentially identical to those of the anisole **4b**: X = 4-OCH_3 (Table 4). In contrast, for the allyl ether **3b**: X = 4-OCH_3, the fluorescence quantum yield is highly reduced, relative to the corresponding anisole or butenyl ether. This is a consequence of its high reactivity from the excited singlet state via homolytic bond cleavage leading to photo-Claisen products. This observation is particularly important because it is the very reactive compounds like **3b** that are critical in establishing the correlation shown in Figure 3 (see below).

For the two other butenyl ethers **14a**: X = H and **14j**: X = 4-CN, modest quenching of the fluorescence relative to the anisole is observed, by a factor of about 4−5 for the former and only about 2 for the latter. Because fluorescence quantum yield and singlet lifetimes are decreased in a parallel fashion, the k_f values remain similar, as expected. Again, exciplex formation should be much more favorable for the $-OCH_2CH_2-$ linker ($n = 3$) in the butenyl ethers **14** than for the $-OCH_2-$ ($n = 2$) linker in the allyl ethers **3**. Therefore, the small changes for the butenyl ether indicate that the changes observed for the allyl ethers, which are larger for X = H and slightly smaller for X = 4-CN, are a consequence of singlet-state deactivation by bond cleavage, not exciplex formation.

Table 5. Quantum Yields and Derived Rate Constants for the Photo-Claisen Reaction of Allyl Aryl Ethers **3**

compd	X	solvent[a]	Φ_r[b]	k^r_{hom} (s^{-1})/10^{-7} [c]	k^s_{hom}/k^r_{hom}
3a	H	M	0.20 ± 0.02	54	5
3a	H	C	0.14 ± 0.03	92	7
3b	4-CH_3O	M	0.29 ± 0.01	170	3
3b	4-CH_3O	C	0.21 ± 0.01	150	5
3c	3-CH_3O	M	0.17 ± 0.02	56	5
3c	3-CH_3O	C	0.08 ± 0.01	28	12
3d	4-CH_3	M	0.18 ± 0.02	95	5
3d	4-CH_3	C	0.13 ± 0.01	110	8

[a] M is methanol, C is cyclohexane. [b] Quantum yield at 25 °C, average of two determinations for disappearance of allyl aryl ether. [c] Obtained from $\Phi_r k_{dt}$.

Quantum Yields (Φ_r) of Reaction for the Allyl Aryl Ethers 3a−k. Before discussing the trends in rate constants obtained for singlet-state reactivity of the substituted allyl aryl ethers **3**, a brief discussion of measured quantum yields of reaction is required. These are given in Table 5 for a few of the more reactive ethers. The often invoked caution of using quantum yields as a measure of excited-state reactivity certainly applies here. For instance, **3d**: X = CH_3 has a relatively low quantum yield of reaction ($\Phi_r = 0.14$) in cyclohexane, but the highest rate constant of reaction ($k^s_{hom} = 690 \times 10^7\ s^{-1}$). Moreover, the quantum yields of reaction are lower in cyclohexane but the rate constants of reaction are higher for all cases studied.

These Φ_r values can be used to calculate an operational value[10] of $k^r_{hom} = \Phi_r k_{dt}$ using the k_{dt} values, also given in Table 3. In all cases, the k^r_{hom} values (Table 5) calculated in this way are significantly smaller than those obtained from the fluorescence method described above. The ratio of k^s_{hom}/k^r_{hom} averages 4.5 ± 0.7 in methanol and 8.0 ± 2.0 in cyclohexane. Because of the observation that the rate constants parallel each other in methanol and cyclohexane (Figure 1), ion pairs are not involved. Therefore, the left-hand protion of Scheme 1 can be ignored and only complications arising from k_{isc}, potentially followed by triplet reactivity (k^T_{hom}), and singlet radical pair recombination (k_{rcom}) need consideration. The fact that the rate constants (k^r_{hom}) obtained from quantum yield results are lower than those (k^s_{hom}) obtained from the S_1 fluorescence measurements indicates, not surprisingly, that k_{rcom} is an important process. Thus, a significant fraction of the singlet radical pairs generated undergo recombination to starting material. This fact has been previously demonstrated for the photo-Claisen reaction both by CIDNP studies[25,44] and by the observation of 1,3-migration in

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unsymmetrical (deuterium- or methyl-substituted) allyl derivatives.[21] Such migrations do not occur in the concerted thermal Claisen rearrangement.[45]

The observation of lower rate constants of reaction by the quantum yield measurements as opposed to the fluorescence method also suggests that the triplet states of these ethers are not reactive. If k_{isc} followed by k^{T}_{hom} were an important process, then quantum yields of reaction would be expected to lead to the determination of rate constants greater than those obtained by the fluorescence method which monitors only the reactivity of S_1. In effect, products would be formed more efficiently than expected on the basis of only excited singlet state reactivity. In support of this conclusion, photo CIDNP reults[25] indicate that the excited singlet state is the precursor to homolytic bond cleavage for **3a**: X = H. We have also determined, by diene quenching studies, that triplet states are not reactive for the aryl *tert*-butyl ethers **1**.[8]

Substitutent Effects on k^{s}_{hom} for the Photo-Claisen Reaction of the Allyl Aryl Ethers 3a−k. The substitutent effects on k^{s}_{hom} are substantial, the ethers with electron-donating groups (methoxy, methyl) reacting considerably faster than those with electron-withdrawing groups (trifluoromethyl, cyano). In all cases and in both solvents, the para and meta isomers react at comparable rates although the para isomers are more reactive for all substitutents in both solvents. Obviously, the photochemical meta effect[7,46] which predicts enhanced reactivity of meta isomers relative to para is not operative here. For instance, in one of the pioneering studies of the meta effect,[47] 3-cyanophenyl trityl ether was found to react with a higher quantum yield (0.68) than its 4-cyano analogue (0.30). However, these reactions are probably occurring by excited-state heterolytic cleavage to form ion pairs.

The data give a reasonable correlation with σ_{ex},[2] the σ values obtained from the excited-state pK_a's of substituted phenols.[48,49] Figure 2 shows the plot for cyclohexane as solvent; $\rho = -0.81$ ($r = 0.93$). As expected on the basis of the parallel reactivity in methanol and cyclohexane (Figure 1), the σ_{ex} plot (not shown) for the rate constants in methanol is similar; $\rho = -0.87$ ($r = 0.92$). Surprisingly, this substitutent effect is in the opposite direction of that for the defining phenol pK_a[50] values, even though both might be expected to have similar polarities; $O^{-}\cdots H^{+}$ for the phenols and $O^{\delta-}\cdots C^{\delta+}$ for the allyl ethers.

A possible reason for this order of reactivity for the allyl ethers became apparent while examining reported substitutent effects on the rate constants for the thermal Claisen reaction of a similar set of allyl aryl ethers. For the 4-substituted cases,[15,18] the rates were found to correlate very well with σ^{+}; $\rho = -0.61$ ($r = 0.994$), indicating again that electron-donating substituents accelerate the reaction. The total span (a factor of about 20: $k = 1.03 \times 10^{-5}$ and 21.3×10^{-5} s^{-1} for 4-NO_2 and 4-CH_3O, respectively, in carbitol as solvent at 181 °C) of the rate constants is considerably less than that for the photochemical reactions. Because the transition state for this thermal reaction would be expected to have a polarity with $O^{\delta-}\cdots C^{\delta+}$, this correlation was also rather surprising. Rather convoluted arguments were developed to explain this observation.

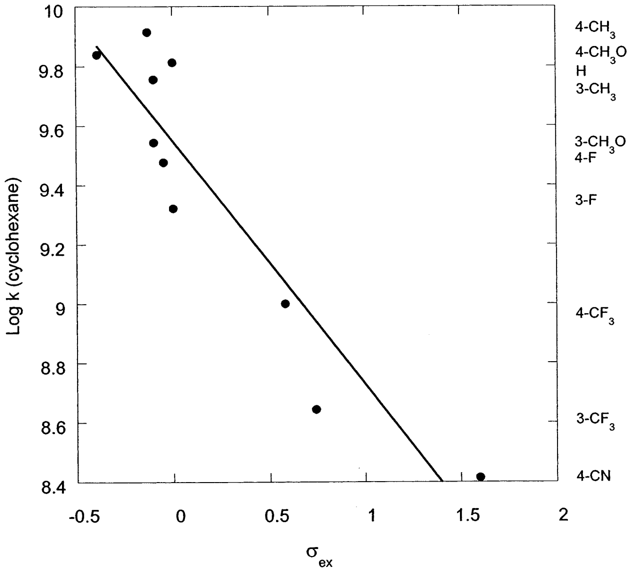

Figure 2. Plot of log k^{s}_{hom}(cyclohexane) versus σ_{ex} for the photo-Claisen reaction of the allyl aryl ethers **3a−k**.

Since the first report in 1988,[51] the bond dissociation energy (BDE, kJ/mol) in phenols has been shown to be strongly dependent on substitutents. This topic has been investigated extensively and recently reviewed.[52] The values are very well correlated with σ^{+}; $\rho = +28.1$ ($r = 0.990$) for ΔBDE (kJ/mol), the change in bond dissociation energy relative to phenol, for both para- and meta-substituted cases.[52] This means that electron-donating groups weaken the bond (ΔBDE = −22 kJ/mol for 4-methoxy) and electron-withdrawing ones strengthen the bond (ΔBDE = +18 kJ/mol for 4-cyano). Although there has been considerable discussion about the reasons behind this effect, i.e., changes in stability of the substituted phenols or changes in the stability of the substituted phenoxy radicals, the current arguments are strongly in favor of the latter factor. Moreover, this effect has been clearly shown to hold true for substituted alkyl aryl ethers such as anisoles and benzyl 4-X-aryl ethers.[53] For instance, $X-C_6H_4O-CH_2Ph$ BDEs have been estimated by DFT calculations (46.7, 52.8, and 55.8 kcal mol^{-1}) and pyrolysis kinetics experiments (47.6, 53.1, and 56.3 kcal mol^{-1}) for X = 4-CH_3O, H, and 4-CF_3, respectively. The previous observation of the correlation of the rate constants of the thermal Claisen rearrangement for allyl 4-X-aryl ethers with σ^{+} now becomes obvious. The electron-donating substitutents weaken the bond and increase the rate, as expected for a thermal reaction.[54]

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(48) There is no σ_{ex} value available for the 3-CN substituent.

(49) Not surprisingly, the correlation with the parallel[3] but differently scaled σ^* value is similar; $\rho = -0.34$ ($r = 0.92$). Therefore the ρ value is lower but still negative.

(50) There is some confusion about the sign of ρ values in σ_{ex} correlations. Baldry[2] set $\rho = -3.10$ but plotted p$K_a^* = -\log K_a^*$ rather than $\log K_a^*$. The defining reaction for ground-state Hammett correlations, the ionization of substituted benzoic acids, has $\rho = +1$ using $\log K_a$, not pK_a. This double reversal of sign means that the σ^* values have the normal sign, positive values for electron-withdrawing groups and negative for electron-donating ones. Therefore, Baldry's negative ρ should be positive whereas ours is negative. Shim and co-workers[3] set $\rho^* = +1$ for the excited-state ionization of benzoic acids, using $\log K_a^*$ and found $\rho^* = 1.28$, i.e., positive for the excited-state ionization of phenols as expected.

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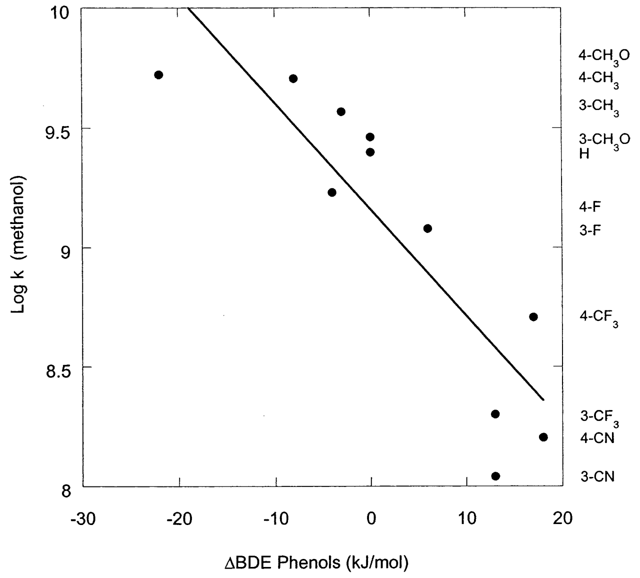

Figure 3. Plot of log k^{s}_{hom}(methanol) versus ΔBDE (kJ/mol) for the allyl aryl ethers **3a**−**k**.

Because the rate constants for the thermal Claisen reaction show the same trend in substitutent dependence as our photochemical ones, we were forced to consider the effect of ΔBDEs on the photochemical values. In fact, a plot of log k^{s}_{hom} versus ΔBDE (kJ/mol) for phenols,[52] Figure 3, shows a fair correlation: $\rho = -0.04$ ($r = 0.87$), which should perhaps best be described as a strong trend. We therefore propose that changes in BDEs may be having a major effect on the photochemical rate constants. This effect may dominate the other more usual substituent effects (electron density changes on excitation, resonance, inductive, etc.) for the σ bond cleavage reactions of phenolic ethers because it is particularly large for $XC_6H_4Y{-}Z$ cases when Y = O and Z = H or C. For other cases where Y = C and X = H, C, or halogen,[55] the substituent has only a minor effect on the BDE. In those cases, the other effects of the substituent may dominate.

In our previous study[8] of the substituted aryl *tert*-butyl ethers **1a**−**j** in methanol, we did not notice the dominance of the effect of the BDEs. However, in that case we used the quantum yield method for obtaining the excited-state rate constants. We now know this is not a reliable method of obtaining k^{s}_{hom} because of the radical pair recombination problem. Using the fluorescence lifetime method and eq 4, the k^{s}_{hom} values for these *tert*-butyl ethers span only a very narrow range of a factor of 6. Moreover, we obtained evidence that some of the products were ion pair derived in methanol, at least for the adamantyl analogue **2**. We did not study these substrates in cyclohexane. We are in the process of making a set of substituted 1-adamantyl aryl ethers in order to complete a similar study as is reported here in order to probe the very different reactivities of the allyl versus *tert*-alkyl ethers.

Conclusion

The rate constants for the homolytic cleavage from the excited singlet state of the substituted allyl aryl ethers **3a**−**k** in both methanol and cyclohexane have been determined by a fluorescence (static and dynamic) comparison method with the unreactive anisoles **4a**−**k**. These values exhibit an unusually large substituent effect for an excited-state reaction that follows the same trend in both solvents. This effect is rationalized by the similar large change in bond dissociation energy for the carbon−oxygen bond that breaks in the rate-determining step of this photo-Claisen rearrangement. This conclusion is surprising because the excitation energy available to the excited-state S_1 of these allyl ethers is some 45−50 kcal mol^{-1} (Table 2) above the bond dissociation energy of ∼50 kcal mol^{-1}, estimated with the usual assumption that an allyl and benzyl ether will have similar BDE values.[56] To our knowledge, such an effect is unprecedented in excited-state homolytic cleavage reactions.

Experimental Section

Preparation of the Allyl Aryl Ethers 3a−k. The ethers **3a**: X = H and **3b**: X = 4-CH_3O were available from the Aldrich Chemical Co. The others were all synthesized by a standard literature procedure from the substituted phenol (Aldrich) using allyl bromide and potassium carbonate in acetone. They were purified by flash chromatography on silica gel followed by bulb-to-bulb distillation. They have all been previously reported, some of them many times, but spectral data are not in general available; ^1H and ^{13}C NMR, GCMS, and HRMS data are given in the Supporting Information. The literature references given are taken from publications where several of the ethers were prepared: **3c**: X = 3-CH_3O,[19] **3d**: X = 4-CH_3,[15,57] **3e**: X = 3-CH_3,[19] **3f**: X = 4-F,[57] **3g**: X = 3-F,[20] **3h**: X = 4-CF_3,[57] **3i**: X = 3-CF_3,[58] **3j**: X = 4-CN,[15] **3k**: X = 3-CN.[19]

The aryl 4-butenyl ethers **14** were synthesized by the same method using 4-bromo-1-butene and also purified by flash chromatography and bulb-to-bulb distillation. NMR spectra obtained were identical to those reported previously: **14a**: X = H,[41] **14b**: X = 4-OCH_3,[59] and **14j**: X = 4-CN.[42]

Irradiation of Ethers. A solution of 0.5−0.7 g of the ether in 280 mL of methanol or cyclohexane was purged with nitrogen and then irradiated with a Hanovia 450 W mediumpressure Hg lamp. The progress of the reaction was monitored by GC/FID. In most cases, flash chromatography on silica gel did not result in separation of the isomeric allyl phenols and the cyclopropyl phenols (secondary photoproducts) into analytically pure compoumds. However, the primary photoproducts, the allyl phenols **9**, **10**, **11**, and **12**, were easily identified by GC/MS and quantified by GC/FID. In most cases, their structures could be determined by ^1H NMR analysis of the partially separated mixtures. The assignment of the positional isomers of the products **8**−**11** was done by analyses of the coupling pattern of the aromatic hydrogens in ^1H NMR spectra. However, for the substrates **3e**: X = 3-CH_3 and **3g**: X = 3-F the three allyl ethers **9**, **10**, and **11** could not be completely separated, and therefore their aromatic hydrogens could not be analyzed because of overlapping signals. In Table 1, the individual yields are given but the assignments are not known. Because the product yields are close to equal, the lack of individual assignments is not a concern.

Absorbance Measurements. Absorbance spectra were recorded at 1 nm resolution using a Cary 100 UV−vis spectrometer thermostated

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(54) The explanation previously given for the substitutent effect on the thermal Claisen reaction for meta or allyl 3-X-aryl ethers was even more convoluted. This is not surprising because the substitutent will have an effect on the BDE of the O−C bond that is breaking but also will likely have a strong effect on the C−C bond that is forming at the ortho position (ortho or para to X) in this concerted process.

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at 25 °C. The integrated spectra needed for eq 8 were obtained by summing the 1 nm incremental areas (the absorbance values converted to ϵ by dividing by the molar concentration) over the complete absorption band. These areas are somewhat uncertain at the short-wavelength end because of overlap with the long-wavelength tail of the S_2 band so that the absorbance does not reach zero. The wavelength for the minimum in absorbance was used as the cutoff point for the S_1 band. For **3** and **4h**: $X = CF_3$ and **3** and **4k**: $X =$ 4-CN, this overlap was too extensive to allow integration of the S_1 band.

Fluorescence Measurements. All samples were degassed by three freeze−pump−thaw cycles and then thermostated at 25 °C. The substituted anisoles used for comparison were all commercial samples (Aldrich) and were distilled before use. Fluorescence intensity measurements were done using a PTI-210M fluorescence spectrometer with dual Model 101 monochromators, a 75 W xenon lamp, and a Model 814 photomultiplier detector. Corrected spectra were obtained. Fluorescence quantum yields were determined using solutions of matched absorbance by comparison with the known fluorescence quantum yield of 0.24[27] for anisole in methanol and 0.29[28] in cyclohexane. The expectation values necessary for eq 8 were obtained by summing the 1 nm incremental areas over the complete emission band.[28] Singlet lifetimes were measured by monitoring fluorescence decay using a PRA time correlated single photon counting apparatus with a hydrogen flash lamp of pulse width about 1.8 ns.

Quantum Yield Measurements. The quantum yields of reaction for the ethers were determined by irradiation at 270 nm using an optical bench equipped with a 450 W high pressure Osram Hg/Xe lamp focused onto open slits of a SPEX 1670 monochromator giving a band pass of 20 nm. The beam was split (approximately 12:1) into cylindrical sample (5 cm long, 24 mL) and reference (9 mL) cells. The concentration of the ether was adjusted to give absorbance values >2, and the cell was thermostated at 25 °C. Ferrioxolate actinometry[60] was used both to measure the splitting ratio and to determine light intensity into the reference cell during ether photolyses. Both the ferrioxalate actinometer and the allyl ether solutions were purged with nitrogen and sealed before photolysis. The disappearance of the ethers was determined by GC/FID by duplicate injections on triplicate samples using naphthalene as an internal standard. Percentage conversions were approximately 10%. The values given are the average of two determinations.

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Supporting Information Available: ^{1}H and ^{13}C NMR, GCMS, and HRMS spectral data for compounds **3c**−**3k** and absorbance, fluorescence, and fluorescence excitation spectra for selected examples of **3** and **4**. (PDF) This material is available free of charge via the Internet at http://pubs.acs.org.

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