J. Am. Chem. Soc. **1998,** *120,* 6443−6450

Photochemical Equilibration/Isomerization of *p*-, *m*-, and *o*-Methylbenzonitrile

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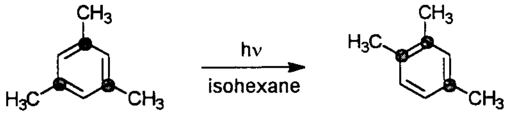
Received March 12, 1998

Abstract: The phototransposition reactions in acetonitrile of *p*-, *m*-, and *o*-methylbenzonitrile have been studied. Any one of the three is converted to the other two by either a 1,2- or 1,3-isomerization in a primary photochemical step. However, the reactivities are quite different with the relative values for *para*:*meta*:*ortho* = 32:4:1. For both the *para* and *meta* isomers, extended irradiations approach a calculated steady-state composition of *para*:*meta*:*ortho* = 3:20:77. Quenching of the excited triplet state of the *para* and *meta* isomers with 2,4-dimethyl-1,3-butadiene indicates that these reactions are occurring from the excited singlet state. Irradiation of selectively labeled 2,6-dideuterio-4-methylbenzonitrile demonstrates that only the cyano-substituted carbon undergoes migration.

Introduction

The photochemical transposition of substituents on benzene rings was first observed by Wilzbach and Kaplan[1] in 1964 for the gas-phase photochemical isomerization of *o*-xylene to *m*-xylene and of *m*-xylene to both *o*- and *p*-xylene. A quantum yield of 0.014 at 250 nm for the *ortho* to *meta* isomerization was reported; for isomerization of the *meta* isomer the value was about twice as high. Isomerization of the *meta* isomer in the pure liquid and in isohexane solution, with a lower quantum yield of 0.006, was also observed. This initial publication reported that photolysis of the *ortho* isomer in the gas phase and at very low conversions gave only the *meta* isomer. In a later paper,[2] the same observation was reported for *p*-xylene in the gas phase but in solution the yield of *para* from *ortho* was determined to be 7% that of *meta*. Therefore, at least in solution, both 1,2- and 1,3-shifts were occurring as primary photoreactions. Similar isomerizations resulting in photoequilibration of *o*-, *m*-, and *p*-di-*tert*-butylbenzenes to a photostationary state of *ortho*:*meta*:*para* = 0:1:4 were reported by Burgstahler and Chen in the same year.[3]

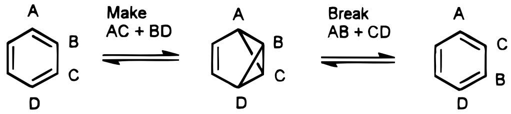
An important clue to the possible mechanism of these transpositions was provided by the observation that photolysis of 1,3,5-trimethylbenzene (mesitylene) specifically labeled with ^{14}C at C1, C3, and C5 gave 1,2,4-trimethylbenzene subsequently labeled at C1, C2, and C4, eq 1.[2] Therefore, the alkyl groups



(1)

are not detached from the ring during this isomerization, but rather the ring carbons themselves are transposed. A plausible mechanism for the isomerization reaction was then proposed invoking substituted tricyclo[3.1.0.0^{2,6}]hex-3-enes (benzvalenes) as intermediates.

For benzene itself there is, of course, only one benzvalene formed by two *meta* bondings in any set of four adjacent carbons; C_A to C_C and C_B to C_D are shown in eq 2.[4] Reversal



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of this process by breaking C_A to C_B and C_C to C_D will interchange C_B and C_C. In the absence of substituents, this interchange is an identity reaction. In the general case, for a polysubstituted benzene there are six possible benzvalene isomers. For a 1,2-disubstituted benzene, like *o*-xylene with two identical substituents, symmetry reduces the number of possible benzvalene isomers to four: 1,2-; 2,3-; 3,4-; and 1,6-dimethyltricyclo[3.1.0.0^{2,6}]hex-3-ene, **1**−**4**, Figure 1. The *ortho* to *meta* isomerization will only be observed from one of these four, the 1,2-dimethyl isomer **1**. Invisible carbon transpositions will occur from the other three. A similar analysis for *m*-xylene gives three benzvalene isomers with the 1,4-dimethyl form resulting in conversion to *p*-xylene and the 1,5-dimethyl form to *o*-xylene. For *p*-xylene, there are only two benzvalenes and the 1,3-dimethyl isomer results in *para* to *meta* conversions.

Phototranspositions have also been analyzed by a permutation approach.[5] For a six-membered aromatic ring, there are 12 possible permutations of the ring carbons, P_1−P_{12}, and nine of these will convert *o*-xylene to *m*-xylene. The benzvalene mechanism is one of the nine and is classified as P_2. In the absence of labels on the other four carbons, proving that this is the pathway occurring is not possible. However, the benzvalene

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[1] Wilzbach, K. E.; Kaplan, L. *J. Am. Chem. Soc.* **1964**, *86*, 2307−2308.

[2] Kaplan, L.; Wilzbach, K. E.; Brown, W. G.; Yang, S. S. *J. Am. Chem. Soc.* **1965**, *87*, 675−676.

[3] Burgstahler, A. W.; Chien, P.-L.; Abdel-Rahman, M. O. *J. Am. Chem. Soc.* **1964**, *86*, 5281−5290.

[4] The carbons are marked with upper case letters instead of numbers to avoid confusion with nomenclature numbers. For instance, A, B, C, and D are C1, C2, C3, and C4 in benzene but C2, C1, C6, and C5, respectively, in benzvalene.

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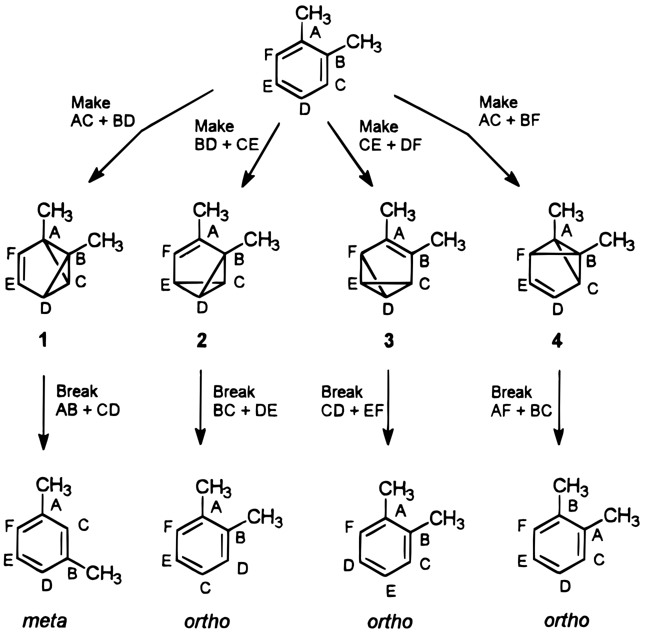
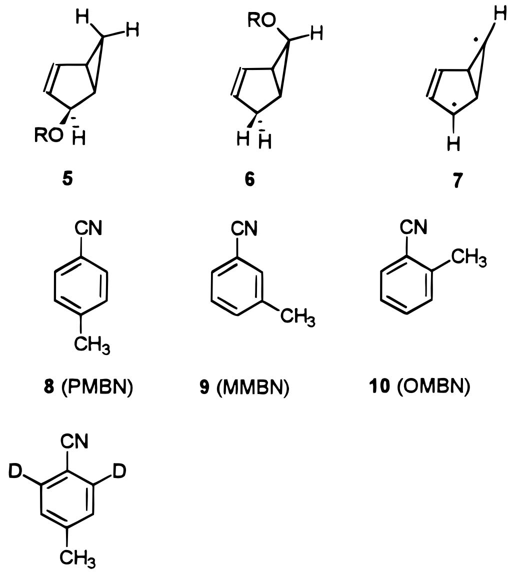


Figure 1. Pathways to the four possible benzvalenes, **1**−**4**, formed from *o*-xylene and the rearrangement to *m*-xylene for **1**.

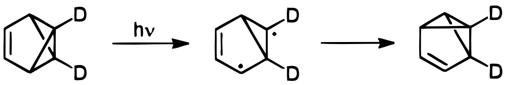
Chart 1



mechanism had already received considerable support after benzvalene was demonstrated to be formed (0.01% yield) by photolysis of liquid benzene at 254 nm.[6] The yield could be increased to 1% by irradiating benzene in dilute solutions of hydrocarbon solvents. Moreover, photolysis of benzene in solutions of acidic alcohols (HCl/CH_3OH and CF_3CH_2OH) or by treatment of benzene after irradiation with HCl/CH_3OH resulted in the formation of the addition products **5** and **6** (Chart 1).[7] When, after an independent synthesis was developed and benzvalene became available in "bounteous quantities",[8] these and other addition reactions were extensively studied.[9−11]

Several features of the proposed intermediacy of benzvalene derivatives in the phototransposition reactions were problematic. One of these was the observation of both 1,3- and 1,2-shifts as primary photochemical events. Other benzene isomers, Dewar and Landenburg benzene (prismane),[2] were therefore proposed as possible intermediates to explain the 1,3-shifts. Another question was how a substituted benzvalene, once formed, was converted back to a substituted benzene. The process for thermal return for benzvalene itself, with an activation enthalpy of 26 kcal/mol and a half-life of 48 h at 30 °C in ether,[11] is too slow. Appropriately substituted benzvalenes would likely have faster rates of return. A photochemical pathway for return is also possible although benzvalene absorption[6] ($\epsilon = 2500$ M^{-1} cm^{-1} at 225 nm) is rather weak at 254 nm and should not compete very effectively with that for benzene itself ($\epsilon = 215$ M^{-1} cm^{-1} at 255 nm)[12] which is at much higher concentration.

This two- or three-photon pathway could also lead to 1,3-phototranspositions because substituted benzvalenes are known to photoisomerize. By the permutation analysis,[5] these two successive P_2 permutations would be equivalent to a P_4 permutation. For instance, benzvalene selectively deuterated at C1 and C6 isomerizes by a vinylcyclopropane-type pathway to benzvalene deuterated at C1 and C2, eq 3, upon either direct



(3)

irradiation or by sensitization with triplet energy sensitizers of less than 63 kcal/mol.[13] In contrast, higher-energy sensitizers convert benzvalene back to benzene but in its excited triplet state. Thus a quantum chain process is initiated. This provides a mechanism for the return of benzvalene to benzene. Because benzene has both a reasonably high intersystem crossing efficiency ($\Phi_{ISC} = 0.25$) and a high triplet energy ($E_T = 84$ kcal/mol), a photochemical sequence is possible for the transposition reaction. Direct irradiation of benzene (or substituted benzene) creates benzvalene (or substituted benzvalene) from its excited singlet state. The triplet state of benzene then sensitizes the isomerization of benzvalene back to benzene. Again, this is a two-photon process, but because the second step is a quantum chain process, few secondary photons are required. Product analysis at very low conversions as a function of light absorbed could clarify whether the phototransposition reaction is a primary photochemical event or a two-photon process.

Another interesting feature of the photochemistry of benzene is that internal conversion from upper electronic states to S_1 is not rapid enough to preclude distinct photochemistry from S_2 or from upper vibrational levels of S_1. Thus, the quantum yield, in the gas phase, for formation of benzvalene from S_1 benzene increases, and the fluorescence intensity decreases as the wavelength decreases.[14] This observation suggests that there is a barrier to benzvalene formation on the S_1 surface. As well,

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Table 1. Photophysical Properties for PMBN, MMBN, and OMBN in Acetonitrile

	λ_{max} (nm)	$10^{-3}\epsilon$ ($M^{-1}\,cm^{-1}$)	λ_{max} (nm)	$10^{-4}\epsilon$ ($M^{-1}\,cm^{-1}$)	Φ_F	$E_{0,0}$ (kcal/mol)	$10^9\tau_S$ (s)	$k_Q\tau_S$[a] (M^{-1})	$10^{-10}k_Q$ ($M^{-1}\,s^{-1}$)
PMBN	268	0.70	232	2.29	0.16	101	9.1	214	2.0
MMBN	276	1.91	228	2.00	0.22	99	7.0	105	1.5
OMBN	276	1.36	228	1.09	0.35	99	7.1	143	2.0

[a] Stern−Volmer slope of fluorescence quenching by 2,3-dimethyl-1,3-butadiene.

excitation of liquid benzene to S_2 results in formation of Dewar benzene along with benzvalene and fulvene.[15]

A recent theoretical study[16] on benzene at the MC-SCF level has characterized the minima and transition states for these conversions on all three of the S_0, S_1, and S_2 surfaces. The conclusion reached for the formation of benzvalene is that there is a barrier separating the symmetrical excited-state minimum on the S_1 surface of benzene from a prefulvene biradical, **7**, located on the ground-state surface. A conical intersection connects these two surfaces. The biradical then partitions between return to benzene and closure to benzvalene.

Similar phototranspositions have been observed for both the monomethyl and the dimethylbiphenyls.[17,18] In both cases, the 2(or *o*)-methyl-substituted compounds isomerized efficiently to the 3(or *m*)-methyl isomers. The 3-methyl isomers isomerized less efficiently to the 4(or *para*)-methyl isomers, and the 4-methyl isomers were relatively inert. The authors attributed these observations to 1,2-shifts through benzvalene intermediates. Two explanations were presented for the higher reactivity of the *ortho* isomers. Either the *o*-methyl groups prevent rotation of the rings of the biphenyl chromophore to the unreactive coplanar geometry expected for the excited singlet state or the steric repulsion of adjacent methyl groups in the benzvalene intermediate(s) force the isomerizations away from *ortho* products. In addition to alkyl-substituted benzenes, phototranspositions have also been observed for 1-fluoro-2-, 1-fluoro-3-, and 1-fluoro-4-trifluoromethylbenzenes[19] and inefficiently for 2-tritioanisole[20] (but oddly, not for 3- or 4-tritioanisole which, except for the tritium label, are the same compound). Phototranspositions were not observed for deuterium-substituted chlorobenzenes.[21] Therefore, little is known about how substituents affect the efficiency and selectivity of these processes. As stated in a recent review,[22] the photochemical transposition reactions of substituted benzenes attracted considerable interest when first observed in the 1960s and 1970s, but have received little attention since that time. In contrast, there have been many studies reporting on photoisomerizations and phototranspositions in aromatic heterocycles.[23−25]

Our interest in these isomerization reactions was stimulated by our observations on the photochemistry of 3-cyanobenzyl acetate in methanol.[26] For this substrate the usual ester photochemistry involving benzylic carbon-to-oxygen bond cleavage was very inefficient. However, 4-cyanobenzyl acetate was an obvious photoproduct. To focus on the transposition reaction, we chose to examine *p*-, *m*-, and *o*-methylbenzonitrile (PMBN, MMBN, and OMBN), **8−10**, in acetonitrile solvent.

Results and Discussion

Photophysical Properties of *p*-, *m*-, and *o*-Methylbenzonitrile (8−10). All three isomers have the usual L_b and L_a bands in the UV spectrum with the former one being at a longer wavelength and with a higher molar absorptivity (ϵ). All three isomers also have fluorescence spectra that overlap with the absorbance bands at the expected 0,0 transition. Photophysical data are given in Table 1. As well, fluorescence quenching studies were done using 2,3-dimethyl-1,3-butadiene, chosen because its absorbance in the UV begins at shorter wavelengths than for most dienes, thereby avoiding any problem of competitive absorbance. Good linear Stern−Volmer plots were obtained for the methylbenzonitriles and the quenching rate constants are, within experimental error, at the diffusional limit in acetonitrile (1.8×10^{10} M^{-1} s^{-1})[27] for all three, Table 1.

Attempts were made to detect the triplet states of the three isomers in acetonitrile by laser flash photolysis (LFP) in order to make estimates of their lifetimes in solution at room temperature. A transient absorbance between 350 and 600 nm previously observed for benzonitrile in EPA glass at 77 K with a lifetime of 3.5 s has been assigned to the triplet state.[28] However, only very weak transient signals were observed at room temperature for the methylbenzonitriles, and these could not be assigned to triplet states with any confidence.

Photochemical Interconversions of *p*-, *m*- and *o*-Methylbenzonitriles (8−10). Plots for the phototranposition (Vicor-filtered 450 W medium-pressure Hanovia Hg lamp) of PMBN, MMBN, and OMBN (∼200 mg) in acetonitrile (280 mL) at 25 °C are shown in Figures 2, 3, and 4, respectively, at both high and low conversion. The yields are reported in percent normalized to 100% for the sum of all three. However, the overall mass balances were excellent, and the sum of the yields for all three isomers at the end of the photolysis reactions was still 80% based on the original starting isomer; at 50% conversion of PMBN and MMBN the total mass balance was over 90%. Therefore, other processes are inefficient relative to the phototransposition reactions.

Three major conclusions are obvious from these plots. First, the rate of isomerization is clearly isomer-dependent. For instance, to reach 20% disappearance of the starting material requires 75 min for the *para* isomer (PMBN), 330 min for the *meta* isomer (MMBN), and >6000 min for the *ortho* isomer (OMBN). These relative efficiencies were confirmed more

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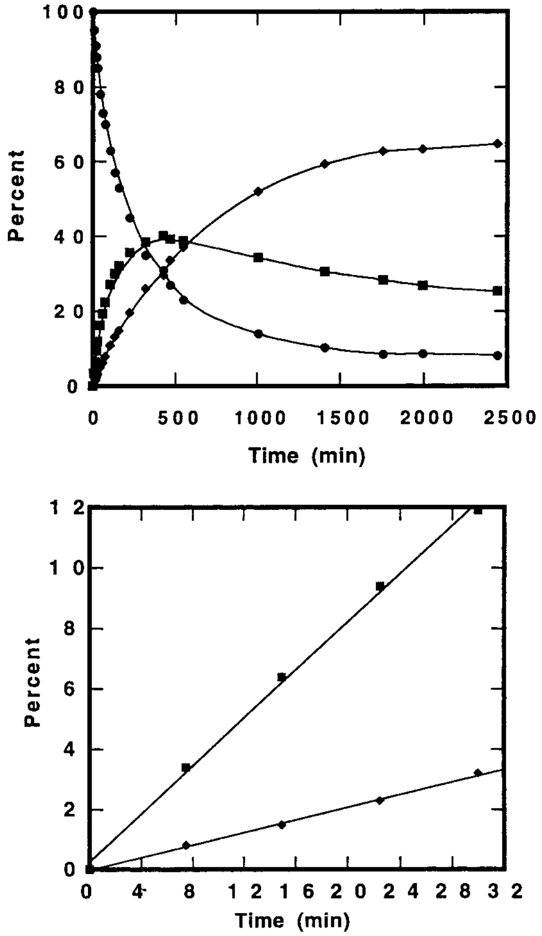

Figure 2. Plots at high and low conversion for the phototransposition reaction of PMBN (**8**) in acetonitrile: PMBN (●), MMBN (■), OMBN (♦).

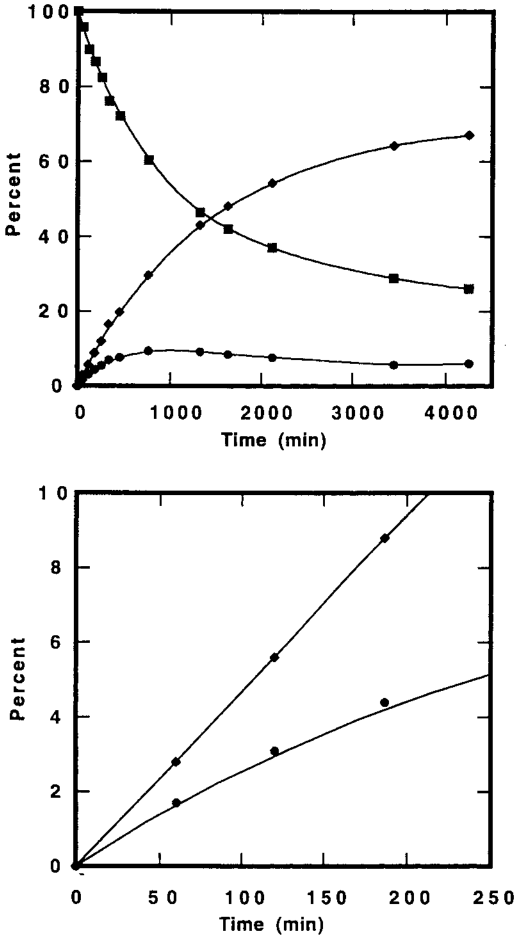

Figure 3. Plots at high and low conversion for the phototransposition reaction of MMBN (**9**), in acetonitrile: PMBN (●), MMBN (■), and OMBN (♦).

quantitatively for the *para* and *meta* isomers, giving quantum yields of disappearance (at less than 3% conversion) of 0.025 ± 0.001 and 0.003 ± 0.001, respectively. The *ortho* isomer was too unreactive to measure its quantum yield reliably. The previous studies on alkyl benzenes[3] and methylbiphenyls[17] suggested that one of the driving forces for phototranspositions was relief of steric strain in the *ortho* isomers. For the methylbenzonitriles studied here, this is not the case because the *ortho* isomer is the least reactive and the *para* the most. Clearly, electronic effects are the dominant factor.

Second, the low conversion plots for PMBN and OMBN show that both 1,2- and 1,3-transpositions are occurring as primary photochemical events. No delay of formation of the 1,3-transposition products is observed as would be expected if they are formed from the 1,2-transposition product by secondary photochemistry. At low conversion, for the *para* isomer, the limiting ratio of *meta*:*ortho* is 4.2:1; for the *meta* isomer, the ratio of *ortho*:*para* is 1.7:1; and for the *ortho* isomer, the ratio of *meta*:*para* is 7.1:1.

Third, for the more efficiently reacting *para* and *meta* isomers (Figures 2 and 3), a photostationary state is approached at high conversions. Because both 1,2- and 1,3-transpositions are occurring, the isomers are equilibrating through a triangular pathway as shown in Figure 5. Estimates for the efficiency of each of these six conversions can be made from the relative reactivity (at low conversion) of each isomer *para*:*meta*:*ortho* = 32:4:1; their molar absorptivities (ϵ) at $\lambda_{\max}$ (Table 1) *para*:*meta*:*ortho* = 784:1911:1363; and the relative yield (at low conversion) of the isomers from each substrate, vide supra. These relative efficiency values for each conversion are shown by the reaction arrows in Figure 5, with the least efficient process (OMBN to PMBN) assigned a value of one. Values of the isomer composition at complete photoequilibration can be calculated using the steady-state approximation: PMBN, 3%; MMBN, 20%; OMBN, 77%. These values are in reasonable agreement with the product composition plots for the *para* (Figure 2) and *meta* (Figure 3) isomers which gave a PMBN:MMBN:OMBN ratio of 7:26:67 when the irradiations were stopped. Longer irradiation times result in yellowing of the solutions leading to decreased absorbance by the benzonitriles and therefore lower reactivity as well as decreased mass balance. Consequently, the steady-state composition was not reached experimentally.

Reaction Multiplicity. The multiplicity of the excited state responsible for the phototransposition for both PMBN and MMBN was determined by doing simultaneous quenched and unquenched irradiations in a merry-go-round apparatus at 25° C using a Rayonet reactor and 254 nm lamps. The quencher used was 2,3-dimethyl-1,3-butadiene. Using the Stern−Volmer slopes determined from fluorescence quenching, Table 1, the percentage of the singlet-state excited states quenched can be calculated, Table 2. Higher quencher concentrations decrease the efficiency of the phototransposition reaction presumably because of the known photochemical cycloaddition reactions[29] of this diene with the methylbenzonitriles. The mechanism for

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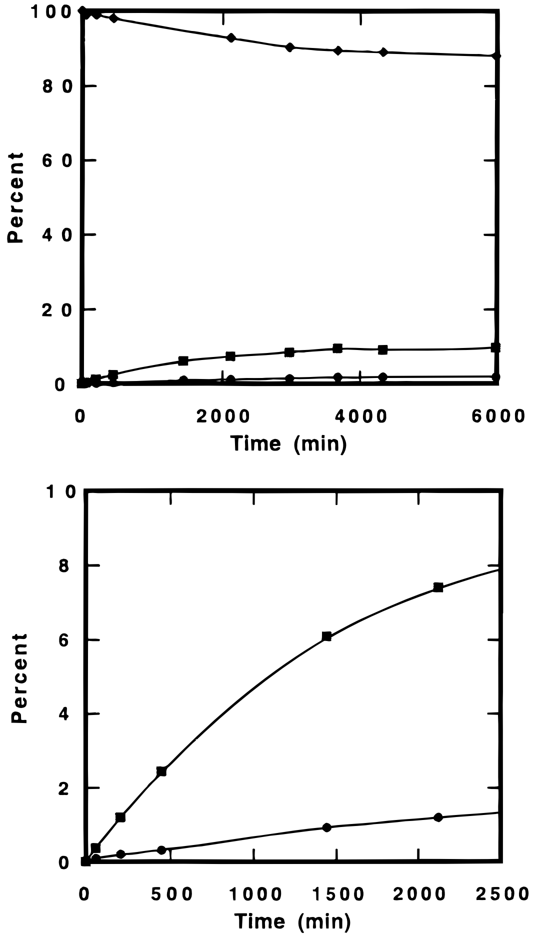


Figure 4. Plots at high and low conversion for the phototransposition reaction of OMBN (**10**) in acetonitrile: PMBN (●), MMBN (■), and OMBN (♦).

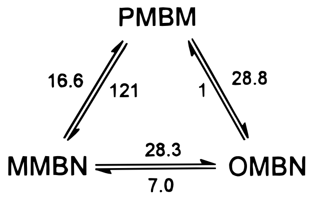


Figure 5. Efficiencies for the photoequilibration of PMBM, MMBN, and OMBN.

Table 2. Photolysis of PMBN and MMPN in the Presence of 2,3-Dimethyl-1,3-butadiene

substrate	t (min)[a]	Q (M × 10^3)[b]	% conv		% S_1[c]	% T[d]
				meta/*ortho*		
PMBN	15	0	6.6	4.25	0	0
	15	1	4.0	4.23	20	95
	30	0	8.2	3.93	0	0
	30	1	7.4	3.75	20	95
				ortho/*para*		
MMBN	60	0	6.6	1.74	0	0
	60	0.1	6.1	1.64	2	67
	120	0	12.1	1.86	0	0
	120	0.1	12.2	1.88	2	67

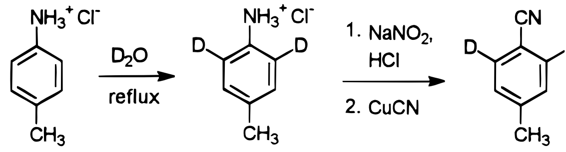
[a] Irradiation time. [b] 2,3-Dimethyl-1,3-butadiene. [c] Percentage of excited singlet states quenched. [d] Percentage of the excited triplet states quenched assuming a triplet lifetime of 1 μs and a rate constant for triplet quenching of 2 × 10^{10} M^{-1} s^{-1}, the diffusional rate.

this quenching is suggested to be by way of a polarized intermediate formed between S_1 of the arene and S_0 of the diene but not by electron transfer between the addends. Because the triplet excited states of the methylbenzonitriles could not be detected by LFP, their lifetimes could not be measured but they are certainly expected to be longer lived than the singlets. Assuming triplet lifetimes of 1 μs and diffusional quenching of the triplet state, the percentage of triplet states quenched can also be estimated, Table 2. Because the triplet states are likely longer lived than 1 μs, the actual % T values are likely higher.

As can be seen from the phototransposition results in Table 2, the presence of the quencher decreases the rate of conversion slightly for PMBN as expected because at a diene concentration of 10^{-3} M, 20% of the singlet states are being quenched. For MMBN at 10^{-4} M diene, essentially no singlet quenching results. For both substrates, the ratio of products is independent of the quencher, the classic "fingerprint" method[30] for comparing direct and quenched or direct and sensitized irradiations.

The conclusion reached from this section is that for the methylbenzonitriles, as for previously studied substates where multiplicity was examined, the excited singlet state is the reactive one in the phototransposition reactions.

Photolysis of 2,6-Dideuterio-4-methylbenzonitrile (11). This known[31] deuterated isomer was synthesized by the pathway shown in eq 4 with the idea that the deuterium labeling might provide important information on the mechanism for the phototranspositions of the methylbenzonitriles. For the *para* isomer, there are four possible *meta* bondings which lead to a prefulvene biradical and then, possibly, to a benzvalene. For illustrative purposes, only two of these four possibilities are shown: in eq 5 (Scheme 1), *meta* bonding occurs between C2 and C6 and the cyano group is on the single-carbon bridge of the prefulvene biradical; in eq 6 (Scheme 1), the *meta* bonding is between C3 and C5 and the methyl group is situated on the bridge. The first pathway will then lead to 5,6-dideuterio-3-methylbenzonitrile (specifically labeled MMBN) and then to 4,5-dideuterio-3-methylbenzonitrile (specifically labeled OMBN), whereas the second will give the isomeric 2,6-dideuterio-3-methylbenzonitrile (specifically labeled MMBN) and then 3,6-dideuterio-2-methylbenzonitrile (specifically labeled OMBN). Of course, if both these and the other two possible pathways (not shown) are occurring simultaneously, then a complex mixture of labeled isomers will be formed.



(4)

The position of the deuterium labels in the three isomers was determined by ^1H, ^2H, or ^{13}C NMR spectra. All three methods gave the same result, but because of the increased dispersion, the ^{13}C NMR spectra provide the clearest proof of the pathway(s) occurring. As shown in Figure 6a, a ^{13}C NMR spectrum of a mixture of the three isomers (41% *para*, 34% *meta*, and 25% *ortho*) gives 10 signals in the region that corresponds to the aromatic carbons which are hydrogen substituted; four of these belong to the *ortho* isomer, four to the *meta* and two to the *para*. Of the 10, eight can be assigned on the basis of literature spectra,[32] but the choice of assignment of C5 and C6 for the signals labeled **2** and **3** in Figure 6a at δ 128.9 and 129.2 for MMBN is not known and proved to be inconsequential. The

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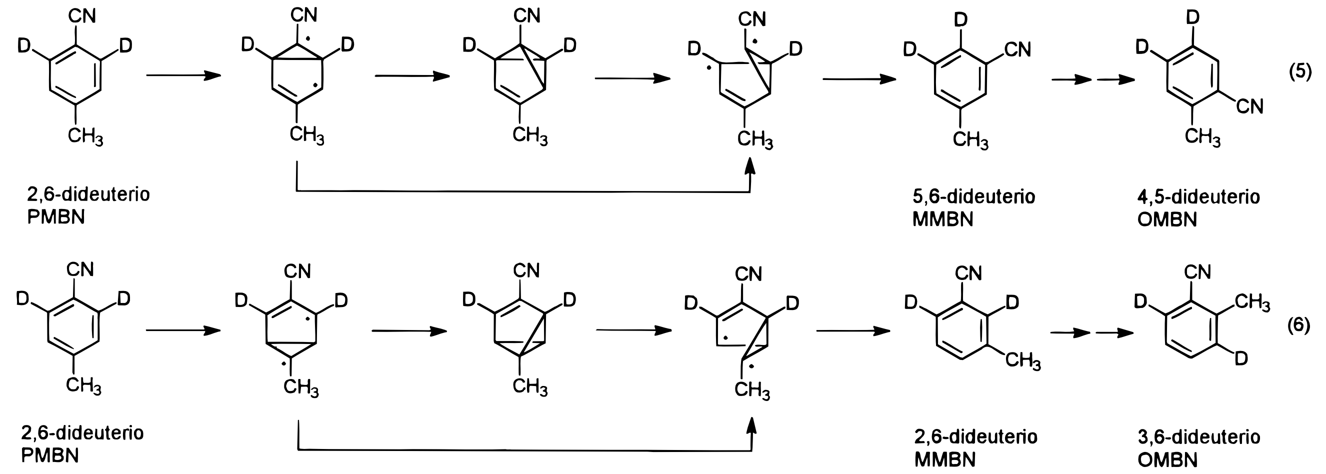
[30] Zimmerman, H. E. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 1−11.

[31] Ripka, W. C.; Applequist, D. E. *J. Am. Chem. Soc.* **1967**, *89*, 4035−4039.

[32] Haupt, E. T. K.; Leibfritz, D. *Spectrochim. Acta* **1989**, *45A*, 119−121.

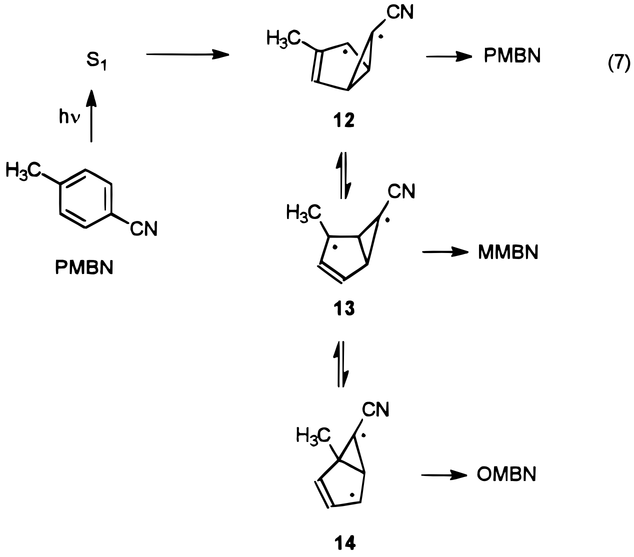
Scheme 1



spectrum for **11**, the selectively dideuterated *para* isomer, gives only one strong signal at δ 129.7; the replacement of hydrogen with deuterium at C2 and C6 greatly reduces the NOE of the carbon signals so that the one at δ 131.9 is considerably weaker. The expansion, Figure 6b, shows that the carbon signal can still be observed as a weak triplet (slightly isotope shifted) because of coupling to the deuterium; the even weaker signal for the residual C−H is also apparent. Figure 6c is a ^{13}C NMR spectrum of a sample of **11** that has been irradiated to a composition of 36% *para*, 35% *meta*, and 29% *ortho*. Only five strong signals are present: one from the starting *para* isomer and two each from *meta* and *ortho*. These signals correspond to those carbons which are hydrogen-substituted. Only very weak signals, scarcely above the noise level, can be seen at other chemical shifts. The transposition is obviously highly selective and gives a deuterium distribution identical to that expected from eq 5.

An important observation to make is that by this extent of irradiation, significant amounts of *meta* and *ortho* isomers have been formed from the starting *para* compound. Therefore, photoequilibration has commenced so that some *para* and *ortho* isomers are formed from the *meta* isomer. Thus, the product composition also reflects the photochemistry of a selectively labeled *meta* isomer. Nevertheless, the *para* isomer remains essentially exclusively labeled as it began, that is, 2,6-dideuterated. Hence the phototransposition reactions of at least two of the methylbenzonitrile isomers (*para* and *meta)* only involve migration of the cyano-substituted carbon. Moreover, there is no evidence that *ortho* reactivity, which is very low relative to the other isomers, involves migration of other than the cyano carbon.

Mechanistic Conclusions. The most probable mechanism for these phototransposition reactions can be summarized in Figure 7 and eq 7. Excitation of PMBN in the L_b band gives the reactive excited state, S_1. This is clearly a minimum on the surface because fluorescence is observed. A barrier separates this state from the biradical **12**, which results from remarkably selective *meta* bonding between C2 and C6. On the basis of the theoretical calculations for benzene,[16] this barrier is a result of a conical intersection and **12** is a ground-state biradical. For both 1,2- and 1,3-transpositions to be explained as primary photochemical events, **12** must isomerize by migration of the cyano-substituted carbon to **13** and **14**, which then collapse back to MMBN and OMBN. In permutation analysis,[5] the mechanism proposed is P_2 for the 1,2-transposition and P_4 for the 1,3-transposition. The energetics of the barriers and minima on the surface connecting **12**, **13**, and **14** are not easy to predict. Using ground-state arguments, **13** should be the most stable of the three minima and the other two might be of comparable stability. The structures **12**, **13**, and **14** are shown as biradicals, but obviously, as ground-state singlets, they could have considerable zwitterionic character. In that case, the cyano-substituted carbon would be negative and the allyl moiety would be positive.



Similarly, irradiation of MMBN and OMBN produce **13** and **14**, respectively, in the primary photochemical event from their S_1 states. Thus, any one of the isomers can produce the other two. However, the trajectory for arriving at the **12**/**13**/**14** surface may be very dependent on the starting material, and experimentally, the barrier on the excited-state surface is much higher for OMBN than for PMBN or MMBN. High-level MO calculations might be used to probe the details of this surface. Substituted benzvalenes have not been included as intermediates in these reactions both because of the observation of simultaneous single-photon 1,2- and 1,3-transpositions and because there is no need to include them. Possibly, they are formed but not detected because of their high reactivity.

These results also have a bearing on the mechanism of the photochemical cycloaddition of alkenes and dienes to substituted benzenes. Thus PMBN, MMBN, and OMBN have all been shown to react with *trans*-1,2-dichloroethene,[33] furan,[33] and 2,3-dimethyl-1,3-butadiene.[29] The products for PMBN are shown

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(33) Cornelisse, J. *Chem. Rev.* **1993**, *93*, 615−669.

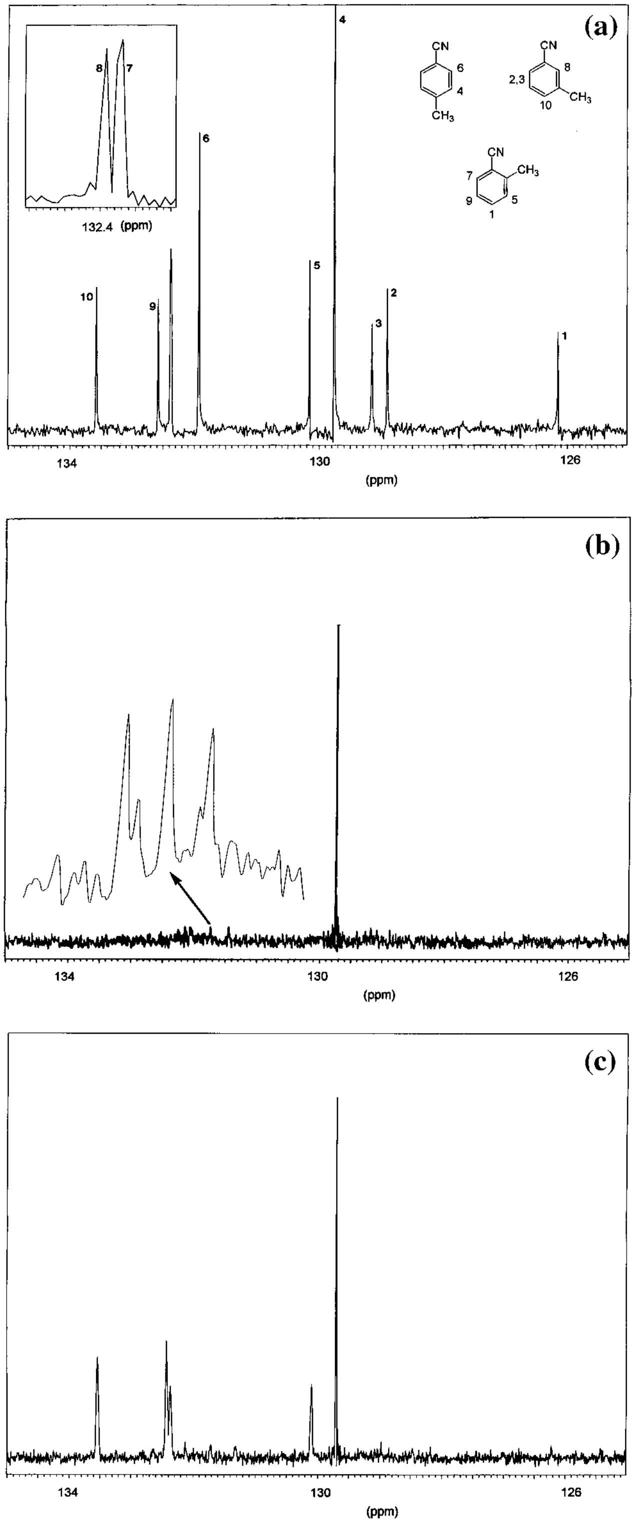


Figure 6. (a) ^{13}C NMR spectrum of aromatic C$-$H carbons for a mixture of PMBN, MMBN, and OMBN. (b) ^{13}C NMR spectrum of the aromatic C$-$H/C$-$D carbons of 2,6-dideuterio-4-methyl benzonitrile (**11**). The inset is an expansion of C2$\equiv$C6. (c) ^{13}C NMR spectrum of the aromatic C$-$H/C$-$D carbons for the mixture of PMBN, MMBN, and OMBN obtained from photolysis of **11** in acetonitrile.

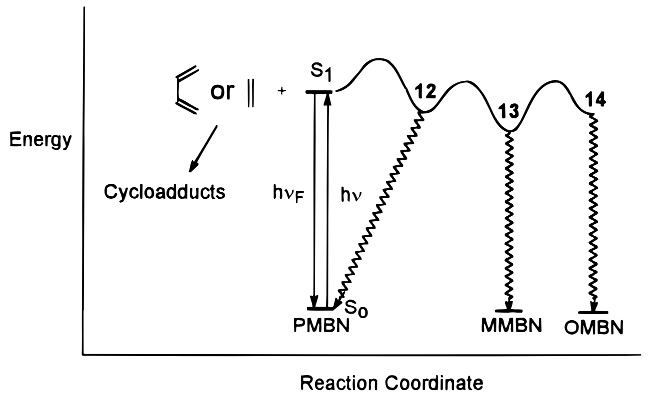
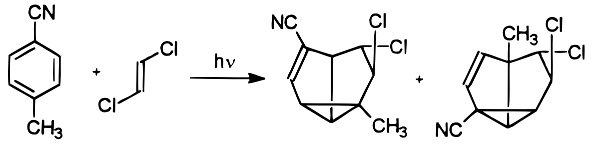
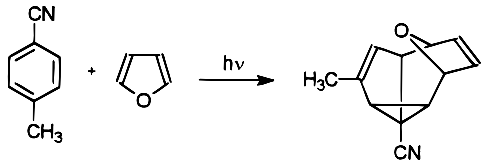


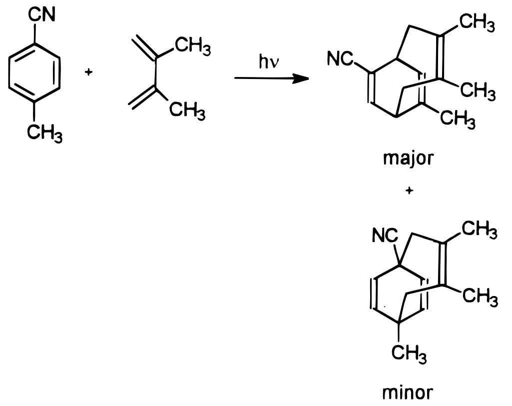
Figure 7. Energy versus reaction coordinate for the photochemical equilibration and cycloaddition reactions of PMBN.



(8)



(9)



(10)

for each in eqs 8, 9, and 10. For the alkene and furan additions, *meta* photocycloadditions are observed but the products are not those that would result from the prefulvene biradicals **12**, **13**, and **14**, because the cyano group is not at the single-carbon bridgehead position. For the diene addition, eq 10, 1,4-adducts are observed, again not from **12**, **13**, and **14**. Similar observations were made for the adducts from MMBN and OMBN. Because the phototransposition reactions demonstrate that the preferred biradical from the excited singlet state of the benzonitriles has the cyano group on the single-carbon bridge, these results support previous mechanistic conclusions that the cycloadditions occur by direct reaction of the excited singlet state of the aromatic with the unsaturated compound and not from a preformed biradical.[29,33]

Finally, the effect that other substituents have on the efficiency and selectivity of these transposition reactions is obviously of interest. We have confirmed and extended the previous observations for the xylenes and are currently examining other cases. At the moment, we have no clear idea as to why *meta* bonding in the methylbenzonitriles should be so selective for the cyano-substituted carbon. Preliminary results for the irradiation of PMBN in 2,2,2-trifluoroethanol indicate that a complex set of addition products are formed that are analogous in structure to **5** and **6**. Their structures should give valuable information on the prefulvene biradicals **12**, **13**, and **14** and/or the substituted benzvalene intermediates. Results on these studies will be reported soon.

Experimental Section

Chemicals. *P*-, *m*-, and *o*-methylbenzonitrile (Aldrich) were bulb-to-bulb distilled before use. GC analyses were performed on a Perkin-Elmer Autosystem using a Supelco Alpha-Dex column, 30 m × 0.25 mm, at 185° C using He as gas carrier (split) and FID detection. The retention time and purity of each isomer was PMBN, 5.04 min ($<$0.05% *meta*, $<$0.05% *ortho*); MMBN, 4.93 min (0.48% *ortho*, 0.80% *para*); and OMBN, 4.51 min (1.77% *meta*, 0.31% *para*). Naphthalene (retention time, 5.93 min) was used as an internal standard, and calibration plots for all three isomers were linear. Acetonitrile (OMNISolv HPLC, Spectrophotometry and Gas Chromatography grade) was used without further purification. For quenching studies, 2,3-dimethyl-1,3-butadiene (Aldrich) was distilled immediately before use.

2,6-Dideuterio-4-methylbenzonitrile was prepared as described previously[31] by exchange of the protons *ortho* to the ammonium group in *p*-toluidine hydrochloride with D_2O followed by conversion, after diazotization, to the nitrile with cuprous cyanide. Mass spectral analysis gave the molecular ion for $C_8H_5D_2N$, and ^{1}H NMR showed less than 2% protons at C2 and C6.

Photolyses. Product ratio studies were carried out using either a Rayonet reactor with 254 nm low-pressure mercury lamps or an immersion well with a 450 W Hanovia medium-pressure mercury lamp and a Vycor filter. Samples to be irradiated ($\sim 10^{-2}$ M in acetonitrile) were purged with nitrogen before and during photolysis. For the Rayonet reactions, the sample was thermostated at 25° C with a circulating water cooling tube centered in the 100 mL quartz reactor. For both reactors, the process of photolysis was monitored by GC after adding the standard naphthalene solutions (10 μL into 1 mL of sample). Percentage yields were corrected for the small amount of isomeric impurities in *o*- and *m*-methylbenzonitrile.

Fluorescence measurements were made with either an Aminco-Bowman Spectrofluorimeter or a Perkin-Elmer MPF 66 fluorescence spectometer. All samples were degassed by three freeze−pump−thaw cycles. For quantum yield measurements, fluorescence intensities relative to toluene ($\Phi_F = 0.13$)[34] were measured using solutions of equal absorbance at 254 nm.

Quantum Yield Measurements for PMBN were done using the Rayonet reactor at 25° C and ferrioxalate (0.06 M) actinometry.[35] To account for the very unequal absorbances of the substrate and the ferrioxalate actinometer, the previously proposed[36] correction method using three simultaneously irradiated samples in concentric quartz tubes was used, as follows: Sample 1, outer tube (acetonitrile), inner tube (PMBN); sample 2, outer tube (acetonitrile), inner tube (ferrioxalate actinometer); and sample 3, outer tube (PMBN), inner tube (ferrioxalate actinometer). The dimensions of the tubes were as follows: inner, 4 mm i.d. × 17 cm tall, 2 mL volume; outer, 13 mm i.d. × 17 cm tall, 15 mL volume. The concentration of PMBN was adjusted so that the absorbance was between 2 and 3. The difference in the ferrioxalate conversion between sample 2 and sample 3 was used as the light absorbed by the PMBN in sample 1. The quantum yield for MMBN was measured relative to that for PMBN.

Acknowledgment. We thank NSERC of Canada for financial support. P.J.M. thanks Dalhousie University for a graduate fellowship and NSERC of Canada and the Killam Foundation for scholarship awards. K.A.T. thanks the Dalhousie University Department of Chemistry for an undergraduate summer research scholarship.

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(35) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London* **1956**, *235A*, 518−536.

(36) Bunce, N. J. In *Handbook of Organic Photochemistry*, Scaiano, T., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. I, pp 241−259.