

## Kinetics of *meta*-Photocycloaddition of Benzene to Cyclopentene

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The kinetics of *meta*-photocycloaddition of benzene to cyclopentene were investigated by means of fluorescence quenching measurements and quantum yield determination. All the results proved compatible with a mechanism involving a reaction in one step from the first excited singlet state of the arene and the ground-state alkene.

The *meta*-photocycloaddition of arenes to alkenes is a well known reaction: the photoadditions of several arenes (including benzene,<sup>1-3</sup> anisole,<sup>4,5</sup> toluene,<sup>6,7</sup> benzonitrile,<sup>8,9</sup> and fluoro-benzene<sup>10-13</sup>) have been examined. The effects of various substituents have been determined. A mechanism has been suggested which is in agreement with the observed regio- and stereo-selectivity<sup>13,14</sup> (see Scheme 1).

After photoexcitation the arene interacts with the alkene and the arene becomes polarized. The interaction intensifies and the bonds between the arene and the alkene are formed. Simultaneously formation of the three-membered ring begins. Finally the ring closes.

Some questions remain unanswered: does the reaction proceed from the singlet or the triplet state of the excited arene, is an exciplex involved, and is there an intermediate along the reaction pathway, for example the biradical (5)?

It has been generally assumed<sup>15-17</sup> that the reaction proceeds directly from the  $S_1$  state of the arene (being symmetry-allowed from this state) but this has only been proved for one or two specific cases.

The intramolecular *meta*-photocycloaddition of 6-phenylhex-2-ene has been investigated thoroughly.<sup>18</sup> The fluorescence of this arene is low as compared with that of phenylhexane, the quantum yield of the reaction is dependent on the wavelength of irradiation, and  $O_2$  (which accelerates intersystem crossing of the excited arene) quenches the addition reaction, while increasing the triplet-sensitized *cis/trans*-isomerization of the alkene moiety. All these observations are consistent with the reaction proceeding from the  $S_1$  state.

The photoaddition to 1,3-dioxoles has also been investigated extensively.<sup>19-21</sup> The fluorescence quenching of arenes by 1,3-dioxoles is efficient. Exciplex emission is observed in polar

solvents and this emission is quenched by triethylamine to the same extent that the *meta*-addition reaction is quenched. These results and many others indicate that this reaction proceeds from the  $S_1$  state of the arene, *via* the exciplex to the adduct. Exciplexes have not been detected in other cases.

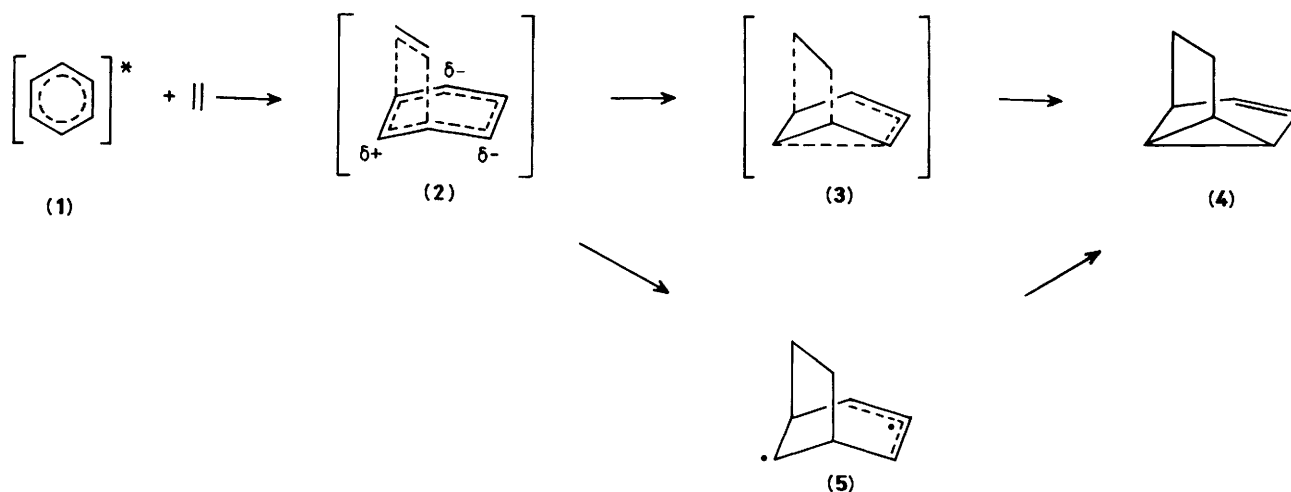
It has been argued that the fluorescence quenching of arenes by simple alkenes (such as *cis*-but-2-ene) in the vapour phase is too low to explain the efficient *meta*-photocycloaddition.<sup>22,23</sup>

Some work on the *meta*-photocycloaddition of benzene to cyclopentene has been published.<sup>3</sup> The dependence of the quantum yield of the reaction on the alkene concentration was determined: a linear relationship between the reciprocals was shown to exist. No reaction rate constants were determined.

In this paper we present the results of our investigations into the kinetics of this *meta*-photocycloaddition reaction in cyclohexane. Two adducts are formed, *exo*- and *endo*-tetracyclo-[6.3.0.0<sup>2,11</sup>.0<sup>3,7</sup>]undec-9-ene, in the ratio 12:88.

### Results and Discussion

The relative fluorescence of several solutions of benzene with cyclopentene in cyclohexane was determined. The lifetime of the  $S_1$  benzene in the absence of cyclopentene (11.1 ns) was determined by flash spectroscopic techniques. From a Stern-Volmer plot the fluorescence quenching rate constant of benzene by cyclopentene in the presence of oxygen was determined as  $8.3 \times 10^7 \pm 0.3 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ . The experiment was also performed without oxygen ( $\tau$  24.5 ns); the result ( $k_q = 7.9 \times 10^7 \pm 0.2 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ ) confirmed the value determined in the presence of oxygen. The fluorescence quenching rate was also determined with the help of picosecond laser spectroscopy in the absence of oxygen. The fluorescence



Scheme 1. Possible mechanism for the *meta*-photocycloaddition of benzene to ethene

**Table.** Quantum yields at 254 nm determined at various cyclopentene concentrations for the *meta*-photocycloaddition of benzene to cyclopentene in cyclohexane

[cp]/M	$\phi$	[cp]/M	$\phi$
1.120	0.214, 0.213	0.268	0.083, 0.082
1.118	0.197, 0.197	0.270	0.089, 0.089
0.887	0.175, 0.175	0.180	0.060, 0.059
0.890	0.180, 0.181	0.180	0.062, 0.061
0.895	0.184, 0.183	0.180	0.057, 0.057
0.542	0.153, 0.153	0.135	0.048, 0.046
0.537	0.146, 0.146	0.135	0.046, 0.047

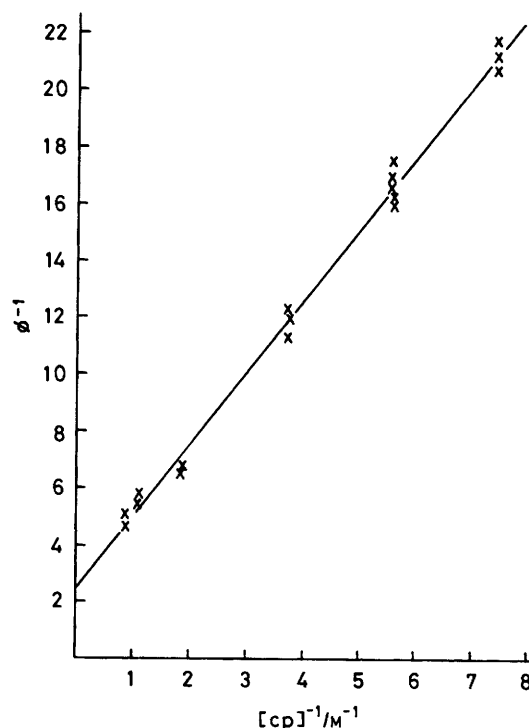
quenching rate constant determined under these circumstances was  $7.5 \times 10^7 \pm 0.2 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ , similar to the other values but less accurate as an unknown amount of cyclopentene is lost from the solution during the three freeze-pump-thaw cycles employed to remove the oxygen.

A similar fluorescence quenching rate constant was reported for the quenching in the vapour phase of benzene by *cis*-but-2-ene<sup>22</sup> ( $5.54 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ ) but this value was held to be too low for the *meta*-photocycloaddition to proceed directly from the  $S_1$  state of the arene.<sup>23</sup> It was of interest to compare our value with the kinetic information obtained from measurements of the dependence of the quantum yield of the reaction on the cyclopentene concentration. We therefore determined the quantum yield of the *meta*-photocycloaddition of benzene to cyclopentene under conditions similar to those used during the fluorescence quenching experiments in the presence of oxygen at 253.8 nm. The products of the irradiation do not absorb light above 230 nm and the amount of product formed had to be determined by capillary g.l.c. Ethyl octanoate was used as internal reference and the response factor of the adduct relative to ethyl octanoate on g.l.c. was determined. Solutions of benzene, cyclopentene, and ethyl octanoate in cyclohexane were prepared, irradiated for various lengths of time, and analysed by g.l.c. The amount of product formed was calculated and the light intensity on the cuvette during the irradiation was determined with an actinometer. The quantum yield was calculated for each cyclopentene concentration; the values found are shown in the Table.

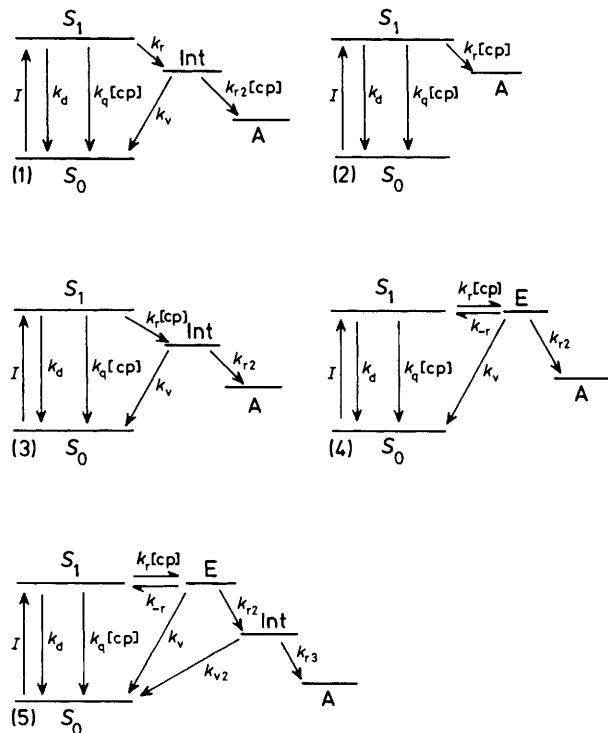
In Figure 1 the reciprocal of the quantum yield is plotted against the reciprocal of the cyclopentene concentration ( $[\text{cp}]/\text{M}$ ) and is shown together with the relationship  $\phi^{-1} = 2.54[\text{cp}]^{-1} + 2.48$ . The standard deviations of the slope and intercept are 0.03 and 0.13, respectively. The correlation coefficient is 0.998. From the intercept it can be calculated that the quantum yield will approach 0.40 at very high concentrations, in good agreement with the literature.<sup>3</sup>

Five candidates must be considered seriously for the mechanism of the *meta*-photocycloaddition reaction. For each a relationship can be derived for the quantum yield as a function of the rate constant and the cyclopentene concentration. These five mechanisms are shown in Scheme 2.

In mechanism (1) the alkene and the singlet excited arene do not undergo interaction leading directly to the adduct. The kinetic equation is:  $\phi^{-1} = k_v(k_r + k_d)k_r^{-1}k_{r2}^{-1}[\text{cp}]^{-1} + (k_vk_q + k_dk_{r2} + k_rk_{r2})k_r^{-1}k_{r2}^{-1} + k_qk_r^{-1}[\text{cp}]$ . If the term  $k_qk_r^{-1}[\text{cp}]$  is much smaller than the other two the relationship between  $\phi^{-1}$  and  $[\text{cp}]^{-1}$  could well appear linear in the concentration range used. The fact that a linear relationship is observed experimentally is not enough to discard this mechanism. At constant temperature there will be a constant ratio between  $k_v$  and  $k_{r2}$  and we may define  $k_v = ak_{r2}$ . The equation for  $\phi^{-1}$  is now simplified to  $\phi^{-1} = a(k_d + k_r)k_r^{-1}[\text{cp}]^{-1} + (ak_q + k_d + k_r)k_r^{-1} + k_qk_r^{-1}[\text{cp}]$ , and it can



**Figure 1.** The reciprocal of the quantum yield plotted against the reciprocal of the cyclopentene concentration shown together with the line corresponding to  $\phi^{-1} = 2.54[\text{cp}]^{-1} + 2.48$



**Scheme 2.** Five possible mechanisms for the *meta*-photocycloaddition reaction; A = adduct, Int = intermediate, E = exciplex, and  $[\text{cp}]$  = cyclopentene concentration

be rewritten as  $[\text{cp}]\phi^{-1}(k_r + k_d + k_q[\text{cp}])^{-1} = ak_r^{-1} + [\text{cp}]k_r^{-1}$ . For each concentration the left-hand term of the equation may be calculated, as we know the values of  $\phi$ ,  $k_q$  ( $8.3 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ ), and  $(k_r + k_d)$  ( $9.01 \times 10^7 \text{ s}^{-1}$ , the

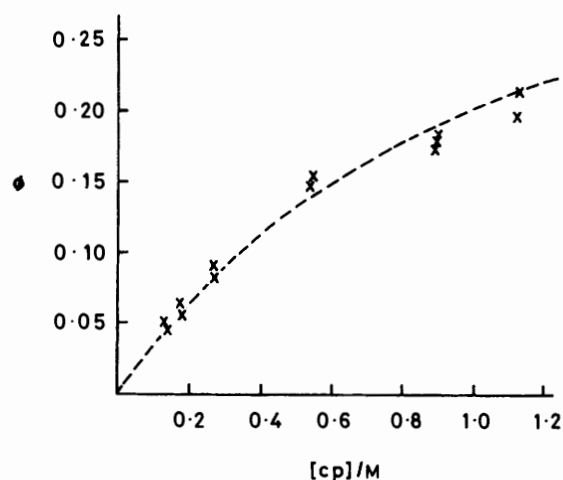


Figure 2. Quantum yield versus cyclopentene concentration shown together with the line corresponding to  $\phi = [\text{cp}] / (2.59 + 2.38[\text{cp}])^{-1}$

reciprocal of the  $S_1$  lifetime). This can then be plotted against the cyclopentene concentration, and if the reaction proceeds *via* this mechanism the plot should be linear with slope  $k_r^{-1}$  and intercept  $ak_r^{-1}$ . By the least-squares method we calculated the best fit, and the correlation was 0.21. Thus this mechanism may be discarded. The intermediate in this mechanism could be an isomer of the  $S_1$  excited benzene, such as  $T_1$  or  $T_2$ . In rejecting this mechanism we exclude the possibility of reaction *via* a  $T_1$  of  $T_2$  state. We may conclude that the reaction proceeds directly from the  $S_1$  state, or from a state which is formed reversibly from the  $S_1$  state.

In mechanism (2) there is an interaction between the two addends, leading directly to the adduct. There are no intermediates. There is a linear relationship between the reciprocals of the quantum yield and the cyclopentene concentration;  $\phi^{-1} = k_d k_r^{-1} [\text{cp}]^{-1} + (k_q + k_r) k_r^{-1}$ . From the slope ( $S$ ) and the intercept ( $I$ ), two independent values for  $k_r$  may be calculated:  $k_r = k_d S^{-1} = 3.54 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$  and  $k_r = (k_q + k_r) I^{-1} = 3.35 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ . The difference between these two values is 6%, which is within experimental error. The value of  $k_r = \phi \{k_r + k_q + k_d [\text{cp}]^{-1}\}$  can also be calculated for each cyclopentene concentration. The mean value of  $k_r$  thus determined is  $3.48 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$  with a standard deviation of  $0.17 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ .

All the rate constants in the expression of  $\phi$  as a function of  $[\text{cp}]$  are now known and the relation is  $\phi = [\text{cp}] / (2.59 + 2.38[\text{cp}])^{-1}$ . The function is represented graphically in Figure 2 together with the experimentally determined values of  $\phi$ . The kinetics of the photoaddition can therefore be satisfactorily described by mechanism (2) with  $k_d = 9.01 \times 10^7 \text{ s}^{-1}$ ,  $k_r = 3.48 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ , and  $k_q = 4.82 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ . We may conclude that formation of the *meta*-adduct *via* direct interaction between  $S_1$  benzene and cyclopentene is in agreement with the observed kinetics. Under these circumstances rather more than half of the  $S_1$  benzene molecules undergoing interaction with cyclopentene revert to the ground state, and rather less than half carry on to form the adduct.

Mechanism (3) is more complicated. Cyclopentene reacts with the excited arene yielding an intermediate (biradicaloid or zwitterionic) which can either decay to the ground state of the starting material or proceed to the adduct. As  $k_v$  and  $k_{r2}$  are constant, their ratio is also constant and we may define  $b = k_{r2} / (k_v + k_{r2})^{-1}$ . The relation between  $\phi^{-1}$  and  $[\text{cp}]^{-1}$  is:  $\phi^{-1} = \{k_d + (k_q + k_r)[\text{cp}]\} (bk_r [\text{cp}])^{-1}$ , which can be rewritten as  $bk_r = \phi (k_r + k_q + k_d [\text{cp}]^{-1})$ . Calculation of  $bk_r$  yields of course the same value as that obtained for  $k_r$  in mechanism (2):

$bk_r = 3.48 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ . The relationship between  $\phi$  and  $[\text{cp}]$  is kinetically equivalent to that for mechanism (2) (the difference being the constant factor  $b$ ) and no distinction between the two can be made on kinetic grounds: they are equally likely. The value of  $k_r$  cannot exceed that of  $(k_q + k_r)$  ( $8.3 \times 10^7$ ) and the minimum value of  $b$  is therefore 0.42. If interaction between  $S_1$  benzene and cyclopentene produces an intermediate, at least 42% of that intermediate will yield the adduct.

Mechanisms (4) and (5) are again more complicated. Both involve an exciplex and mechanism (5) also involves an intermediate. The relationships between  $\phi^{-1}$  and  $[\text{cp}]^{-1}$  are as given in equations (i) and (ii), respectively. Both equations contain too many unknowns, and cannot be solved.

$$\phi^{-1} = (k_{-r} + k_v + k_{r2}) k_{r2}^{-1} \{k_d k_r^{-1} [\text{cp}]^{-1} + (k_q + k_r) k_r^{-1}\} - k_{-r} k_{r2}^{-1} \quad (\text{i})$$

$$\phi^{-1} = (k_{v2} + k_{r3}) k_{r3}^{-1} \{ (k_{-r} + k_v + k_{r2}) k_{r2}^{-1} \{k_d k_r^{-1} [\text{cp}]^{-1} + (k_q + k_r) k_r^{-1}\} - k_{-r} k_{r2}^{-1} \} \quad (\text{ii})$$

In mechanisms (2) and (3) the quotient of slope ( $S$ ) and intercept ( $I$ ) of the linear relationship between  $\phi^{-1}$  and  $[\text{cp}]^{-1}$  is equal to  $k_d (k_r + k_q)^{-1}$ . The experimentally determined value of  $S I^{-1}$  is 1.01, and the value of  $k_d (k_r + k_q)^{-1}$  obtained from the rate constant of quenching and the lifetime of the excited state is 1.09, in agreement allowing for experimental error. In mechanisms (4) and (5) the value of  $S I^{-1}$  is larger than  $k_d (k_r + k_q)^{-1}$  because of the negative term in the intercept. For mechanism (4),  $S(I + k_{-r} k_{r2}^{-1}) = k_d (k_r + k_q)^{-1}$ . The term  $k_{-r} k_{r2}^{-1}$  is positive and its introduction will lower the value of  $1.01 (S I^{-1})$  and remove it further from the value determined for  $k_d (k_r + k_q)^{-1}$  (= 1.09). At first sight this mechanism seems therefore less satisfactory than mechanism (2) or (3) but, allowing for experimental error in the determination of  $S$  and  $I$ , a value of  $k_{-r}$  of  $0.01 k_{r2}$  can still be said to be in agreement with the experimental evidence. This value is low and if the reaction were to proceed *via* this mechanism a vast majority of the exciplex molecules would continue to the adduct and a small minority would return to the excited arene and cyclopentene. (This is of course in agreement with the fact that a monoexponential decay is observed for  $S_1$  benzene in the presence of cyclopentene.) With such a value of  $k_{-r} / k_{r2}$  the difference between mechanisms (3) and (4) becomes, in kinetic terms, merely semantic. However, as a mechanism it is nonetheless possible and cannot be discarded.

Mechanism (5) is kinetically equivalent to mechanism (4) [as are mechanisms (2) and (3)] and is on kinetic grounds equally feasible.

Another possible mechanism would be one similar to mechanism (1) but in which the intermediate is formed reversibly from the excited arene. On kinetic grounds alone this mechanism cannot be excluded. An indication against such a mechanism is however that the decay of the singlet excited arene in the presence and absence of cyclopentene is monoexponential, which would not be the case if there were an equilibrium between the excited arene and an isomer.

It can be concluded that the most likely mechanism for the *meta*-photocycloaddition of benzene to cyclopentene involves interaction between the singlet excited arene and the adduct. A mechanism involving reaction between cyclopentene and an isomer of the  $S_1$  state of the arene (formed reversibly from the  $S_1$  state of the arene) cannot be excluded on kinetic grounds, but would seem unlikely on the basis of the flash spectroscopic experiments. It is not impossible that the reaction proceeds *via* an intermediate or an exciplex (or an exciplex and an intermediate) but no indications could be found on kinetic

grounds for the existence of such species. All attempts to detect the presence of an intermediate or an exciplex in the *meta*-photocycloaddition of benzene to cyclopentene with the help of nanosecond laser spectroscopy were unsuccessful.

One thing is clear: the experimentally determined fluorescence quenching rate of  $8.3 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$  is certainly not too low for the reaction to proceed from the  $S_1$  state of the arene.

## Experimental

**Solvents and Reagents.**—Benzene was obtained commercially (Aldrich Chemicals N.V., Belgium) and purified by means of distillation and preparative gas chromatography before use. Cyclopentene was obtained commercially (E. Merck Nederland B.V., The Netherlands) and was purified immediately before use by means of repeated reaction with tetracyanoethylene and distillation under  $N_2$ . Cyclohexane was obtained commercially (J. T. Baker Chemicals B.V., The Netherlands) and purified prior to use, as follows. Cyclohexane (1 l) was stirred with concentrated  $H_2SO_4$  (150 ml) for 3 h. The  $H_2SO_4$  was removed and the process was repeated twice. The cyclohexane was then washed three times with water, three times with aqueous 4N-NaOH, three times with saturated alkaline  $KMnO_4$ , and five times with distilled water. The cyclohexane was dried ( $CaSO_4$ ) and distilled.

**Fluorescence Quenching Experiments.**—With a fluorescence spectrophotometer. The fluorescence quenching experiments were performed in the presence and in the absence of oxygen. For the experiments in the presence of oxygen solutions were prepared of benzene ( $4.5 \times 10^{-2} M$ ) and cyclopentene (0, 0.08, 0.1, 0.2, 0.4, 0.8, 1.0, and 1.5M) in cyclohexane. These solutions were prepared in triplicate from fresh stock solutions. For the experiments in the absence of oxygen, oxygen was removed from cyclohexane and from the alkene with three freeze-pump-thaw cycles, and the solutions were then prepared in a glove-box under He atmosphere. For these solutions the benzene concentration was  $4.5 \times 10^{-2} M$  and the cyclopentene concentrations 0, 0.1, 0.2, 0.4, 0.8, and 1.0M.

The standard deviation in the concentrations of alkene and arene was calculated to be less than 1%.

The fluorescence intensity was determined with a Spex Fluorolog 2 111C spectrophotometer. The spectral band widths used for excitation and for detection of the emission were 3.6 and 2.4 nm, respectively. Fluorescence was determined in the front face mode in a cuvette which was maintained at  $25 \pm 1^\circ C$ . The fluorescence was monitored throughout the day; the values for a reference solution remained constant within 2%. As excitation wavelengths we chose 243 and 253.8 nm. Fluorescence intensity was determined over a wavelength range of 265–340 nm with steps of 0.5 nm and an integration time of 0.5 s. The fluorescence was integrated over this wavelength range and the baseline noise (determined with a cyclohexane sample) was subtracted. Each solution was measured at both excitation wavelengths in quadruplicate. The relative value of  $\phi_0\phi_{alk}^{-1}$  was calculated for each cyclopentene concentration at 253.8 nm and plotted against the concentration. The slope and intercept of these linear relationships were then calculated. The quenching rate constants could be calculated as  $(8.3 \pm 0.3) \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$  for the measurements in the presence of oxygen and  $(7.9 \pm 0.2) \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$  for the measurements in the absence of oxygen. The correlation coefficients were 0.995 and 0.9997, respectively. The quenching rate constants determined from the experiments performed at 243 nm were also calculated and proved (within experimental error) identical with those determined at 253.8 nm.

**With nanosecond flash spectroscopy.** For the flash photolysis experiments solutions were prepared of benzene ( $4.5 \times 10^{-2} M$ )

and cyclopentene (0, 0.2, 0.4, 0.8, 1.0, and 1.5M) in cyclohexane. In all solutions the standard deviation in the concentration of the arene and the alkene was less than 1%. Samples of these solutions were prepared and oxygen was removed from the solution in the cuvette immediately before use with three freeze-pump-thaw cycles.

For the experiments a single laser pulse was subtracted from a passively-mode-locked Nd-YAG laser. The fourth harmonic (265 nm) was used and the pulse width was 25 ps. Fluorescence was collected on a vacuum photodiode (ITL) and recorded on a transient digitizer (Tektronix). The signals were fitted to mono- and di-exponential functions. In all cases the fit to the monoexponential function was excellent. The lifetime of the fluorescence was calculated for each cyclopentene concentration and the reciprocal was plotted against the concentration of cyclopentene. The quenching rate constant could be calculated from the slope of the line as  $(7.5 \pm 0.2) \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ . The correlation coefficient was 0.996.

**Quantum Yield Measurements.**—For the irradiations use was made of a Hanau NK 25/7 low-pressure mercury lamp and two filters: 1 cm of Kasha's filter<sup>24,25</sup> at a concentration of 200 mg  $l^{-1}$  in water and 2 cm of a solution of nickel and cobalt sulphate<sup>26,27</sup> ( $CoSO_4 \cdot 7H_2O$  at 76.96 g  $l^{-1}$  and  $NiSO_4 \cdot 6H_2O$  at 400.74 g  $l^{-1}$  in water). The resulting light intensity on the cuvette was of the order of  $9.5 \times 10^{-6}$  einstein  $l^{-1} \text{ min}^{-1}$  and the light had a monochromatic purity of 94.6% at 254 nm with a band of 4.3% at 265 nm. As our actinometer we chose the potassium ferrioxalate system.<sup>28</sup> The analyses of the irradiated solutions were performed with the help of on-column g.l.c. [Carlo Erba 4160, fused silica column (Hewlett Packard) 25 m  $\times$  0.32 mm, SE-30, carrier gas  $H_2$ ]. The column was calibrated for these conditions with the help of solutions of ethyl octanoate ( $4.8 \times 10^{-5} M$ ) and *endo-meta*-adduct (0,  $1.55 \times 10^{-5}$ ,  $3.09 \times 10^{-5}$ ,  $4.64 \times 10^{-5}$ ,  $6.19 \times 10^{-5}$ , and  $7.73 \times 10^{-5} M$ ) in cyclohexane. These solutions were all prepared in duplicate. Over the concentration range used a linear relationship was observed between the response factor and the concentration. The error in the calibration line was calculated to be 0.5%.

Solutions were prepared of benzene ( $4.5 \times 10^{-2} M$ ), cyclopentene, and ethyl octanoate ( $4.8 \times 10^{-5} M$ ) in cyclohexane. The cyclopentene concentrations were 0.135, 0.180, 0.268, 0.537, 0.890, and 1.12M. The standard deviations in the concentrations of benzene, ethyl octanoate, and cyclopentene were calculated to be 0.7, 1.2, and 0.7%, respectively. These solutions were irradiated for various lengths of time between 15 min and 4 h [always corresponding to a maximum formation of *endo-meta*-adduct of  $8.5 \times 10^{-5} M$  (0.2% conversion relative to the arene)].

The intensity of the light was determined before and after irradiation with the help of the actinometer. This was averaged and corrected for light of wavelengths greater than 300 nm.

The irradiated solutions were analysed by g.l.c. and the concentration of the *meta*-adduct formed was determined with the help of the calibration graph. The quantum yield for the *meta*-addition was calculated for each irradiation for each cyclopentene concentration. For each cyclopentene concentration the concentration of product formed was plotted against the light (einstein  $l^{-1}$ ) absorbed by the solution during the irradiation. The plot revealed a linear relationship, the slope of which was equal to the quantum yield. The quantum yields were thus determined at various concentrations of cyclopentene in duplicate and (the reciprocals of) these values were plotted against (the reciprocals of) the cyclopentene concentrations. The plot of the reciprocals yielded a linear relationship:  $\phi^{-1} = 2.54[cp]^{-1} + 2.48$  (see Figure 1). The standard deviations calculated for the slope and the intercept were 0.03 and 0.13, respectively. The quantum yields determined for the various cyclopentene concentrations are shown in the Table.

### Acknowledgements

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