Photolysis of a series of α-brominated *ortho*-xylenes in apolar solvents

Daisy de B. Rezende, Ivan P. de Arruda Campos, Vicente G. Toscano and Luiz H. Catalani *
Instituto de Química, Universidade de São Paulo, C.P. 26.077, 05599-970, São Paulo, SP, Brazil

The α-brominated *ortho*-xylenes have been subjected to 254 nm irradiation in deaerated benzene, isooctane and benzene–cyclohexene. The product analysis revealed that homolysis of the C–Br bond is followed by a series of hydrogen abstraction and radical recombination reactions resulting in xylenes more and less brominated than the starting compound. The less brominated products are formed with higher quantum yield when cyclohexene is present, due to hydrogen abstraction by the *o*-benzyl radical formed initially, together with cyclohexene dimers. Additionally, the formation of 2-bromo-2,4,4-trimethylpentane is observed when isooctane is the solvent. The quantum yields observed for the photolysis of **1** and **2** are higher in benzene than in isooctane, suggesting sensitization by benzene. A biradical intermediate of the type *o*-quinodimethane was expected in the case of (*a*) photolysis of the *o*-benzyl radical formed (biphotonic process) or (*b*) intramolecular hydrogen abstraction. However, the addition of cyclohexene failed to produce the expected Diels–Alder adduct. The synthesis of the novel α,α-dibromo-*o*-xylene **3** is reported.

Introduction

Since the pioneering work of Zimmerman[1] on the photolysis of several benzyl derivatives, including halides and ammonium salts, a great deal of work has been accomplished in this field. Special attention has been given to the competition between homolytic and heterolytic processes in polar solvents.[2] Conclusions were drawn to provide a general mechanism for the heterolysis of the carbon–heteroatom bond, including the nature of the leading excited state. In contrast, only very few studies were done in apolar solvents.[3]

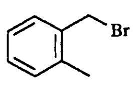
The behaviour of α-halogenated xylenes under UV irradiation is scarcely known. The recent work of Platz and co-workers,[4a] on the search for biradical species from the photolysis of α,α′-dichloro-xylene *ortho* and *meta* isomers remains a landmark. From these compounds the authors reported the preparation of *ortho*- and *meta*-xylylene in a matrix at 77 K, but very few experiments were done in solution with no clear results.

Platz and co-workers[4b] also demonstrated that mesitylylene biradical is produced in the photolysis of matrix-isolated mesitylene through a biphotonic process. Interestingly, the two photons are used to produce the mesitylene monoradical first *via* a T_n state of mesitylene. The nascent hydrogen formed reacts within the matrix cage to form the mesitylylene and H_2, most likely through thermal activation. These findings make α-halogenated *ortho*-xylenes good candidates for the monophotonic generation of xylylenes.

The intermediacy of an *ortho*-xylylene in the production of 1,2-dibromobenzocyclobutene by thermal reduction of α,α,α′,α′-tetrabromo-*o*-xylene **5** was recognized as early as 1957 by Cava *et al.*[5] The importance of *ortho*-xylylenes (or *ortho*-quinodimethanes) in Diels–Alder reactions is attested by the great number of routes for their preparation (including photochemical methods) and of applications in intramolecular cycloaddition reactions as a synthetic approach to polycyclic ring systems.[6]

Finally, Tournier *et al.*[3a] reported high quantum yields of HCl formation when benzyl chloride is photolysed in saturated hydrocarbon solution, and that this yield depends on solvent viscosity. As hydrogen halide photogenerating systems are of great value to photoresist applications, such molecules may be of industrial interest.

We report here the results of a study of the photochemical and photophysical behaviour of a series of α-halogenated xylenes in apolar solvents, where homolysis is expected to be the main event after light absorption. The compounds investigated are α-bromo-*o*-xylene **1**, α,α′-dibromo-*o*-xylene **2**, α,α-dibromo-*o*-xylene **3**, α,α,α′-tribromo-*o*-xylene **4** and α,α,α′,α′-tetrabromo-*o*-xylene **5**. The solvents chosen, benzene, isooctane and benzene–cyclohexene mixture, are representative non-polar solvents of different hydrogen donor abilities.



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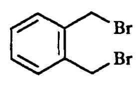

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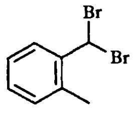

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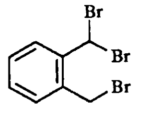

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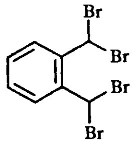

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Results

Photolysis in benzene

Compounds **1**–**5** were subjected to photolysis in deaerated benzene at 254 nm (low pressure mercury lamp). The reaction mixtures were analysed by GC–MS and the product identification was confirmed by co-injection with authentic samples. The reaction profiles, following either reagent consumption or product formation, are linear up to five hours irradiation, when they start to level out. Table 1 shows the product distribution relative to the total number of moles of the consumed starting compound. These values were calculated from the linear regression of the reaction profiles at 150 min.

The first observation in Table 1 is that the photolysis of these compounds leads to others of similar structure, but with higher and lower degrees of bromination at the α-position. Aldehyde and carboxylic acid functionalities are derived from hydrolysis of geminal dibromo and tribromo derivatives, respectively (most probably as a result of thermal reactions). No ring-

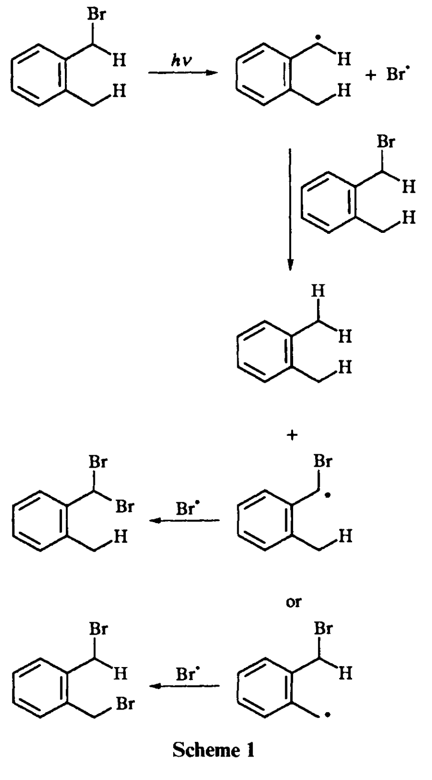
Table 1 Product distribution on the photolysis of **1**–**5** in benzene[a]

Product	**1**	**2**	**3**	**4**	**5**
o-Xylene	38.4	nf[b]	nf[b]	nf[b]	nf[b]
1	—	16.6	5.4	nf[b]	nf[b]
2	11.4	—	3.7	4.0	nf[b]
3	5.1	3.2	—	2.9	nf[b]
4	nf[b]	18.4	22.7	—	6.3
5	nf[b]	nf[b]	nf[b]	12.5	—
9[c]	16.3	—	1.8	6.1	3.5
Other products[c]	9.8 of **10**[d]	5.6 of **11**	18.4 of **12** 5.3 of **13**[d]	3.7 of **12** 11.6 of **13**[d]	12.1 of **14**[d] 2.5 of **15**[d]
Recover[e]	81	43.8	57.3	40.8	24.4
Total conversion[f]	9.4	20.3	18.4	12.0	3.8

[a] In percent relative to the number of moles of reagent consumed after 150 min irradiation. [b] Not found. [c] **9** *o*-tolualdehyde, **10** α-bromo-*o*-tolualdehyde, **11** α-bromo-α′-phenyl-*o*-xylene, **12** *o*-toluic acid, **13** α,α,α-tribromo-*o*-xylene, **14** α-bromo-*o*-toluic acid, **15** α,α-dibromo-*o*-tolualdehyde. [d] Tentative structure (proposed on the basis of MS data; see Experimental section). [e] The sum of all products found (in percent relative to reagent consumed). [f] The percentage of converted starting material.

brominated product was found. It must also be emphasized that this list is restricted by the analytical methods used, which preclude the determination of higher oligomers.

It is expected that in an apolar solvent such as benzene, homolysis of the C–Br bond is the leading photolytic step, forming an *ortho*-substituted benzyl radical (hereafter, called α-xylyl radical) as an intermediate species. As the starting material is the only possible hydrogen atom donor in the system, the 'scrambling' of bromine atoms must occur at its expense, reacting with the nascent α-xylyl radical. This thermal reaction gives rise to a reduced product and a second radical which can then react with the extruded bromine atom producing an *o*-xylene derivative with a higher number of bromo substituents. Moreover, in the non-symmetrical xylenes as **1**, **3** and **4**, there are two different α hydrogens (with different abilities to react with the α-xylyl radical) therefore leading to two different types of radicals (in different proportions). A representation of these processes is shown in Scheme 1 for the case of compound **1**; all other compounds undergo analogous reactions.



Scheme 1

The total concentration of products with higher numbers of bromine atoms is very similar to the concentration of products with a lower number. The apparent exception is **3** and this may be due to its extreme sensitivity towards hydrolysis, which prevented a precise determination of its product distribution. This bromine atom balance is consistent with the observation that Br_2 is not a major product.

Another interesting observation in Table 1 is that the recovery of the photolysed material (that is, the sum of moles of the products found) decreases from **1**→**5**. A possible explanation is that the decrease in the number of abstractable hydrogens in the series might lead to a concurrent reaction of the α-xylyl radical resulting in products not detected by our analytic method, for example, oligomers. One could also argue on energetic grounds that the increase of the number of bromine substituents may provide a lower intrinsic quantum yield due to differences in energy levels. However, (*i*) as we will see below, if the solvent sensitizes the reaction, energy transfer from excited benzene to compounds **1**–**5** is exothermic in all cases (see Table 3); (*ii*) the S_1 and T_1 energy levels measured for compounds **1**, **2**, **4** and **5** are essentially identical; (*iii*) we found that the quantum yield of consumption of **2** is higher than that of **1** in the three solvents tested, including neat isooctane, therefore opposite to the decrease of recovered material.

Photolysis in benzene–cyclohexene mixture

To show that homolysis of the C–Br bond was the primary photolytic process responsible for the products found in benzene, we used other solvents of similar polarity and viscosity, but with enhanced hydrogen donating ability. Our expectation was to reduce the scrambling of bromine by quenching the first intermediate formed, presumably, the α-xylyl radical.

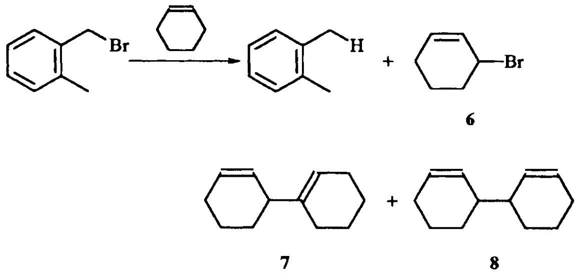
The first approach to reach optimal conditions to carry out this experiment was to exchange only partly the benzene with some solvent of enhanced hydrogen donating ability. Among all possibilities considered, 20% cyclohexene (2.0 mol dm^{-3}) was the best compromise in terms of (*i*) minor change in solvent physical properties, (*ii*) low light absorbance at 254 nm and (*iii*) a cyclohexene concentration competitive with that of the starting reagent (*ca.* 40-fold higher). Furthermore, with cyclohexene present we would have the chance to prove formation of an *ortho*-xylylene through a Diels–Alder type reaction. Although cyclohexene is not an ideal dienophile, it has been used with success as a trapping agent for *o*-xylylene.[7]

Table 2 summarizes the quantum yields in different solvents for (*i*) reagent consumption (Φ_{-RBr}) and (*ii*) formation of the reduced derivative (Φ_{RH}). Comparing benzene to mixed benzene–cyclohexene, the great increase in Φ_{RH} and the

Table 2 Quantum and chemical yields for the photolysis of **1**–**5**[a]

Reagents	Solvent	$\Phi_{\text{-RBr}}$	Φ_{RH}	η_{RH}[b]
1	Benzene	0.33	0.13	0.38
	Benzene–cyclohexene[c]	0.82	0.24	0.29
	Isooctane	0.22	0.08	0.35
2	Benzene	0.52	0.09	0.11
	Benzene–cyclohexene[c]	0.91	0.27	0.29
	Isooctane	0.32	0.07	0.22
3	Benzene	0.49	0.03	0.05
4	Benzene	0.25	0.02[d]	0.41[d]
5	Benzene	0.13	0.01	0.13

[a] $\Phi_{\text{-RBr}}$ is the quantum yield for consumption of starting material and Φ_{RH} and η_{RH} are the quantum and chemical yields for formation of first reduced product. [b] Determined by GC analysis relative to reagent consumption after 150 min irradiation (molar response corrections were applied in all cases). [c] [Cyclohexene] = 2 mol dm^{-3}. [d] Sum of formation of **2** and **3**.



Scheme 2

observed suppression of scrambling products when cyclohexene is present confirms our hypothesis. Accordingly, we found new products derived from cyclohexene: 3-bromocyclohexene **6**, and the dimers **7** and **8** (Scheme 2). Compound **6** may be a product of radical recombination, while compounds **7** and **8** are probably formed by an addition–elimination reaction of a cyclohexenyl radical on a cyclohexene molecule. We did not find any sign of a Diels–Alder adduct, which shows that formation of *o*-xylylene as an intermediate is very unlikely.

A close look at Table 2 gives rise to two new questions: (*i*) why does $\Phi_{\text{-RBr}}$ increase so abruptly if cyclohexene is acting in a post-photolytic step? and (*ii*) why is this increment in $\Phi_{\text{-RBr}}$ not mostly (if not totally) reflected in Φ_{RH}? The answers to these questions are rather connected: in the absence of a good hydrogen donor, recombination of the radicals originally formed may play an important role. In fact, bromine radicals are known to be stabilized in benzene as a π-complex prolonging the lifetime of the radical.[8] Addition of cyclohexene provides an important new pathway for α-xylyl radical deactivation, which is reduction. But it is not the only one possible: polymerization is definitely another path. Although we did not quantify or identify it, we did observe a film deposition of insoluble material onto the quartz wall of the photolysis cell in all three solvents.

Photolysis in isooctane

To test a total exchange of solvent we selected isooctane mainly because it is completely transparent at 254 nm, yet its physical properties are similar to that of benzene [relative permittivity (dielectric constant), ε = 1.940 and viscosity, η = 0.652 cP for benzene at 20 °C and ε = 2.284 and η = 0.507 cP for isooctane at 20 °C; ref. 9], which makes it a good solvent for comparison.

Isooctane proved to be a poorer donor of hydrogen atoms than the starting reagent, specially considering its 120-fold higher concentration. The photolysis of **1** and **2** in this solvent showed a set of products similar to that observed in benzene, plus one specific to this solvent, which is 2-bromo-2,4,4-trimethylpentane (data not shown), therefore characterizing the same scrambling of bromine. The role of benzene as sensitizer of the reaction is well represented by the drop in Φ_{RH} (the quantum yield for the formation of the first reduced product) when going from pure benzene to isooctane. In both cases—**1** and **2**— Φ_{RH} in isooctane is *ca.* 1.5 times smaller than in benzene. This is not surprising since most of the incoming light is taken up by the latter.[†]

Concerning the values of $\Phi_{\text{-RBr}}$—the quantum yield for starting material consumption—one consideration must be brought about: in benzene, the starting compound is the major (the only one at time zero) hydrogen donor. For each photon leading to the α-xylyl radical, two molecules of the original xylene are consumed—one by photochemical cleavage of C–Br bond and a second by thermal radical abstraction reaction. Hence, $\Phi_{\text{-RBr}}$ is overestimated by a factor close to two. In isooctane, hydrogen abstraction from the solvent competes with this process lowering this overestimation. When cyclohexene is present $\Phi_{\text{-RBr}}$ approaches its 'true' value, once there is no consumption of the starting xylene but by photochemical processes. Nonetheless, Φ_{RH}—the quantum yield for the formation of the first reduced product—is a reliable number for comparison.

Quantum yields and kinetics

The actinometry of our irradiating system was performed using malachite green leucocyanide according to literature.[10] This procedure has two advantages over the classic potassium ferrioxalate system: (*i*) malachite green leucocyanide does not absorb in the visible region, allowing the manipulations to be done without protection from ambient light; (*ii*) it absorbs in the same region as compounds **1**–**5** avoiding errors deriving from actinometer absorption of higher wavelengths light, not effective in the photochemical system in study, which would cause an apparent lowering in the determination of the quantum yields.

In conditions where all the light is directly absorbed by the reagent and where $\varepsilon_{254}(\text{reagent}) \cong \varepsilon_{254}(\text{product})$ in all cases, we have 'isosbestic' actinometric conditions as described by Bunce.[11] In other words, during the initial phase of the process the system behaves like Bunce's 'photobleaching' and absolute quantum yields are obtained employing eqn. (5) (see Experimental section). When benzene is the sensitizer of the reaction, eqn. (5) still applies and an 'apparent' quantum yield can be calculated if (*i*) most of excited benzene is quenched and (*ii*) the quenching rate constants are similar for reagent and product, conditions which are met here.[‡] Fig. 1 represents a kinetic profile of one of the reactions studied here. It is clear that the assumption of linearity is valid in this case. We observed linearity in all the other cases for reaction times up to three hours (or more in some cases). All the quantum yields presented in Table 2 were calculated according to eqn. (5) and they represent its limit to time zero.

Discussion

The photolysis of **1**–**5** in apolar solvents generated a series of products that can be rationalized in terms of a primary

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[†] Considering the concentrations used and the molar absorption coefficient for compounds **1**–**5** (of the order of 2000 at 254 nm), 99.9% of the light was totally absorbed in the first 0.15 mm of isooctane solution, while in benzene as solvent or co-solvent (ε_{254} = 200) this layer is of the order of 0.01 mm. The ratio for solvent/solute total absorbance is 11:1.

[‡] According to Table 3, all possible energy transfer processes from benzene to compounds **1**, **2**, **4** and **5** are exothermic by ≈8 kcal mol^{-1} (singlet-singlet) or ≈13 kcal mol^{-1} (triplet-triplet). Hence, ET rate constants must be close to diffusion (1 × 10^{10} dm^3 mol^{-1} s^{-1} for benzene).[12]

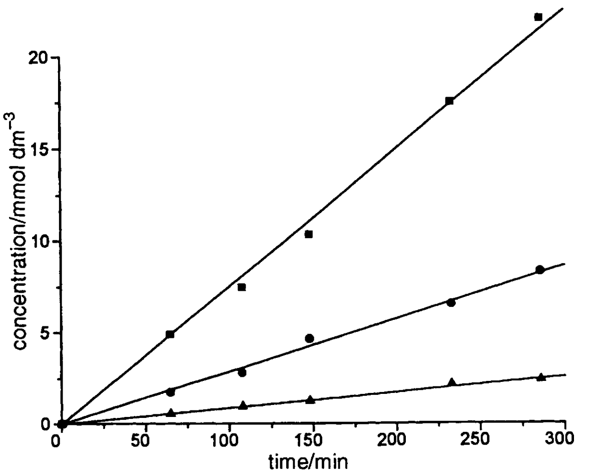

Fig. 1 Time-dependent product distribution for the photolysis of **1** in benzene: (■) $[\mathbf{1}]_0 - [\mathbf{1}]_t$; (●) [*o*-xylene]$_t$; (▲) $[\mathbf{2}]_t$

Table 3 Energy levels[a]

Compound	T_1	S_1	T_2
Benzene	84[b]	110[c]	105[b]
Toluene	83[c]	106[c]	—
o-Xylene	82[c]	105[c]	—
1	71	100	—
2	72	100	—
4	70	99	—
5	72	103	—
Benzyl chloride	73[c]	—	—

[a] All measurements were made in EPA matrix; T_1 energies were calculated from the highest energy vibrational band of phosphorescence emission spectra; S_1 energies were calculated from the crossing points of the normalized fluorescence excitation and emission spectra. [b] In crystal (ref. 13). [c] In non-polar solvents (ref. 12).

homolytic cleavage of C–Br bond, followed by thermally allowed radical reactions (Table 1). Our results show that either direct excitation or sensitization by benzene leads to the same type of chemistry. However, comparing the results in benzene and isooctane one sees *ca.* 50% enhancement of the Φ_{RH} quantum yields in the sensitized reaction (Table 2).

In the early 80s, as a result of his studies on the photosolvolysis of benzylic halides and benzylammonium salts, McKenna[2a,b] presented convincing arguments that ion pairs are derived from singlet excited states, while radical formation would come mostly from a triplet species formed from the singlet *via* intersystem crossing. This process should be facilitated by spin-orbit relaxation, enhanced here by the presence of bromine substituents. Using different quenching techniques, Cristol and co-workers[2e,f] showed the existence of two triplet states on benzyl chlorides. Contradicting McKenna, they stated that either an upper short-lived triplet or the first singlet state is responsible for formation of photosolvolysis products. In addition, they consider that T_1 does not lead to products.

In the present case benzene sensitizes the reaction when it is used as a solvent or co-solvent. Considering the low quantum yield of fluorescence and the short lifetime of benzene singlet state in non-polar solvents (6% and 34 ns, respectively)[12] both S_1 and T_1 excited states of benzene could be quenched with sufficient efficiency to produce the sensitized quantum yields observed in Table 2. Benzene's second triplet could also be at play, since its energy is somewhat lower than S_1 (see Table 3), but its lifetime is expected to be extremely short[13] constraining energy transfer from this state.

Many other groups have questioned the factors that regulate homolysis *versus* heterolysis of benzylic systems upon irradiation.[2,3] The simple fact that this competition has been looked at only in nucleophilic (polar) solvents already biases the observations, mainly because of the induced polarization of the carbon–halogen bond. On the basis of *ab initio* MO–CI and valence bond calculations, Larson and co-workers suggest that the initial triplet species undergoes dissociation into radical pairs 'unless there is an alternate decay mechanism'.[2d] In polar solvents, formation of an ion pair would be accomplished by a fast spin-inversion.. When examining the photolysis of alkyl iodides, Kropp and co-workers[14] were convinced that electron transfer, producing ion pairs, is a path of deactivation of the radical pair, competing with diffusion. This became known as the Kropp hypothesis. It should be noted that in our work, should ion pairs be formed, they would not be noticed once they have no other way of reaction but to collapse back to starting reagent. The only evidence we have for the presence of a carbocation is the formation of compound **11** (see Table 1) as a product of electrophilic substitution on a solvent molecule.

As in heterolysis, solvent participation in deactivating the unstable intermediates formed during photohomolysis determines the set of products obtained. The hydrogen donating ability of the solvent could limit or even totally abort the scrambling of bromo radicals, as was the case of benzene–cyclohexene presented here. The only few studies of similar systems in apolar solvents[3] also showed a determining participation of the media towards thermally activated radical chemistry.

We did not observe products coming from an *o*-xylylene intermediate. Even using 20% v/v of cyclohexene in the photolysis of **1** and **2**, the expected Diels–Alder adduct was not detected. Two possible ways for its formation were foreseen: (*i*) extrusion of HBr or Br_2 through a Berson type mechanism as suggested by Platz[4b] and (*ii*) stepwise homolysis of two C–Br bonds by a two-photon process. By the first mechanism, the bromine atom must react with its partner radical abstracting a hydrogen at α' position within the solvent cage. The low viscosity of the solvents used here must have prevented this mechanism from operating. We are presently testing its viability in solvents of very high viscosity. The second possibility was certainly precluded by the low light intensity of our system. Adam and Ouchi[15] observed that photolysis of 1,8-bis(bromomethyl)naphthalene produced acenaphthene by the stepwise homolysis of the two C–Br bonds, followed by intramolecular C–C bond formation. This was possible by using the laser-jet technique[16] in which a high intensity laser beam is concentrated into a very small area. Unfortunately, this technique failed to produce results in the photolysis of **2** in benzene when sensitized by acetophenone.[17]

Experimental

Instruments

All qualitative and quantitative chromatographic analyses were performed on a Shimadzu CG-14-A gas chromatograph, using a splitter injector (43:1; 230 °C), a 25 m × 0.25 mm × 0.22 μm Shimadzu CBP-1 column (polydimethylsilicone), helium as carrier gas (1.6 cm^3 min^{-1}), and a flame ionization detector (260 °C, nitrogen as make-up gas). Oven temperature program: 80 °C (4 min), 30 °C min^{-1} (up to 250 °C), 250 °C (2.7 min). Data were collected with a Shimadzu Chromatopac C-R4A electronic recorder/digital integrator. GC–MS analyses were done either on a Finnigan-MAT model ITD-800 ion trap mass spectrometer coupled to a Finnigan-MAT gas chromatograph with a DB-5 capillary column (30 m × 0.25 mm × 0.25 μm), or on a Finnigan-MAT INCOS-50 quadrupole mass spectrometer interfaced to a Varian 3400 gas chromatograph having a similar column, or on a Hewlett-Packard 5988A quadrupole mass spectrometer attached to a

5890 gas chromatograph having a HP1 (12 m × 0.25 mm × 0.25 μm) column; in all cases, the experimental conditions were those described for conventional GC. The high-resolution mass spectrum was obtained with a Finnigan Mat 90 instrument (in direct sample injection mode). ^{1}H NMR (200.13 MHz) spectra were recorded at 20 °C on a Bruker AC-200-F spectrometer. All measurements were performed in 5 mm o.d. tubes, using a deuterium lock. Absorption spectra were obtained on a Hitachi U-2000 spectrophotometer in hexane solutions, at room temperature. Fluorescence and phosphorescence spectra were determined on a SPEX-Fluorolog-2 FL 111 spectrofluorimeter in EPA matrix, at 77 K, with a 1934D phosphorimeter attachment being employed for all phosphorescence emission measurements.

Materials

All solvents employed in irradiations and spectroscopic measurements were of spectrophotometric grade (Aldrich Gold Label), used without further purification. α-Bromo-*o*-xylene[18a] (**1**) was prepared from *o*-xylene (Aldrich) and purified by fractional distillation in a 10 cm Hempel column, under vacuum. α,α′-Dibromo-*o*-xylene[18b] (**2**), α,α,α′-tribromo-*o*-xylene[18c] (**4**) and α,α,α′,α′-tetrabromo-*o*-xylene[18d] (**5**) were also prepared from *o*-xylene (Aldrich) by literature procedures and recrystallized from hexanes (light petroleum, **2**: 60–68 °C and **5**: 80–100 °C; **3**: hexane–benzene, 9:1 v/v), until colourless. *o*-Methylbenzaldehyde was obtained from α-bromo-*o*-xylene, through a Kornblum reaction,[18e] and twice distilled. The final purity attained for each one of these compounds was of, at least, 97% (by GC). Malachite green leucocyanide was prepared from malachite green oxalate (Carlo Erba) according to Calvert and Rechen.[19]

α,α-Dibromo-*o*-xylene (3). Boron tribromide (14.0 cm^3, 37.1 g; 0.15 mol; Aldrich, Gold Label) was added to 8.10 g of *o*-methylbenzaldehyde (0.07 mol), dissolved in 150 cm^3 of anhydrous chloroform, and stirred overnight under argon. The solvent was removed in the absence of oxygen and moisture, and the residual material pyrolysed under vacuum, at 150 °C/10 mmHg, during a bulb-to-bulb distillation. The crude product was then fractionally distilled (through a 5 cm Vigreaux column) and 10.2 g of compound **3** was obtained as a slightly yellowish liquid of bp = 104–106 °C/1 mmHg. Yield: 57%. Purity: 98% (by GC). Meaningful elemental analysis results for this compound could not be obtained, due to its prompt hydrolysis upon exposure to air moisture. High-resolution mass spectrometry, however, afforded a parent peak group with the required isotopic masses and distribution: *m*/*z* (rel. abundance) Found: 261.899 296 (51.4%), 263.897 292 (100), 265.895 288 (48.6); $C_8H_8Br_2$ requires: 261.899 296 (51.1%), 263.897 292 (100), 265.895 288 (48.9); $\delta_H(CDCl_3)$ 2.38 (s, 3 H), 6.86 (s, 1 H), 7.06 (dm, 1 H, J = 7.7 Hz), 7.18 (m, 1 H), 7.24 (m, 1 H) and 7.80 (dd, 1 H, J = 7.8, 1.2 Hz).

Preparative photolyses

Solutions of compounds **1** and **2** were irradiated using four circular ('doughnut' type) low pressure mercury lamps model PCQ-X1 from Ultra-Violet Products (18 W/lamp; $\lambda_{emission}$ = 254 nm). The solutions (25 cm^3; 0.1 mol dm^{-3}) were placed in a cylindrical quartz vial within the circumference of the lamps and purged with argon throughout the irradiation time. Samples were collected by means of a syringe every 30 or 60 min, depending on the system, and analysed by GC with n-hexadecane as internal standard. All products were identified by GC–MS spectrograms, and their identities confirmed by co-injection with authentic samples. The exceptions are compounds **10**, **13**, **14** and **15**, whose structures are proposed on the basis of the detailed interpretation of their mass spectra. The quantifications were performed by conventional GC, utilizing response factors determined in relation to n-hexadecane.

Mass spectral assignment of 10, 13, 14 and 15

C_8H_7BrO (**10**; 199 g mol^{-1}; on INCOS-50) *m*/*z* (assignment; rel. int.): 200 ($M^{\cdot+}$ [for ^{81}Br]; 20.08%), 198 ($M^{\cdot+}$ [for ^{79}Br]; 20.75), 119 ($M^{\cdot+}$ − $Br^{\cdot}$; 100.00), 118 [$M^{\cdot+}$ − HBr; 16.78), 91 ([119]$^+$ − CO; 87.62), 65 ([91]$^+$ − HC≡CH; 17.75). $C_8H_7Br_3$ (**13**; 343 g mol^{-1}; on INCOS-50) *m*/*z* (assignment; rel. int.): 346 ($M^{\cdot+}$ [for $^{81}Br_3$]; 0.30%), 344 ($M^{\cdot+}$ [for $^{81}Br_2{}^{79}Br$]; 0.93), 342 ($M^{\cdot+}$ [for $^{81}Br^{79}Br_2$]; 0.98), 340 ($M^{\cdot+}$ [for $^{79}Br_3$]; 0.35), 331 ([346]$^{\cdot+}$ − $^{\cdot}CH_3$; 0.08), 329 ([344]$^{\cdot+}$ − $^{\cdot}CH_3$; 0.24), 327 ([342]$^{\cdot+}$ − $^{\cdot}CH_3$; 0.25), 325 ([340]$^{\cdot+}$ − $^{\cdot}CH_3$; 0.09), 265 ($M^{\cdot+}$ − $Br^{\cdot}$ [for $^{81}Br_2$]; 54.58), 263 ($M^{\cdot+}$ − $Br^{\cdot}$ [for $^{79}Br^{81}Br$]; 74.01), 261 ($M^{\cdot+}$ − $Br^{\cdot}$ [for $^{79}Br_2$]; 60.51), 184 ([265 or 263]$^+$ − $Br^{\cdot}$; 37.68), 182 ([263 or 261]$^+$ − $Br^{\cdot}$; 35.90), 103 ([184 or 182]$^{\cdot+}$ − $Br^{\cdot}$; 100.00), 91 ($C_7H_7^+$; 18.66), 77 ([103]$^+$ − HC≡CH; 52.92), 63 ([103]$^+$ − MeC≡CH; 20.00). $C_8H_7BrO_2$ (**14**; 215 g mol^{-1}; on ITD-800) *m*/*z* (assignment; rel. int.): 216 ($M^{\cdot+}$ [for ^{81}Br]; 15.89%), 214 ($M^{\cdot+}$ [for ^{79}Br]; 17.33), 171 ([216]$^{\cdot+}$ − $^{\cdot}CO_2H$; 20.50), 169 ([214]$^{\cdot+}$ − $^{\cdot}CO_2H$; 22.36), 122 ($M^{\cdot+}$ − :CHBr; 27.33), 121 ($M^{\cdot+}$ − $^{\cdot}CH_2Br$; 33.23), 105 ($M^{\cdot+}$ − $^{\cdot}$Br − CH_2O; 64.91), 104 ($M^{\cdot+}$ − HBr − CH_2O; 49.36), 90 ([171 or 169]$^+$ − $^{\cdot}$Br; 20.50), 89 ([171 or 169]$^+$ − HBr; 17.39), 77 ([105]$^+$ − CO; 100.00), 63 ([89]$^+$ − HC≡CH; 24.84). $C_8H_6Br_2O$ (**15**; 278 g mol^{-1}; on INCOS-50) *m*/*z* (assignment; rel. int.): 280 ($M^{\cdot+}$ [for $^{81}Br_2$]; 1.27%), 278 ($M^{\cdot+}$ [for $^{81}Br^{79}Br$]; 2.41), 276 ($M^{\cdot+}$ [for $^{79}Br_2$]; 1.62), 199 ($M^{\cdot+}$ − $Br^{\cdot}$ [for ^{81}Br]; 46.83), 197 ($M^{\cdot+}$ − $Br^{\cdot}$ [for ^{79}Br]; 58.02), 171 ([199]$^+$ − CO; 6.02), 169 ([197]$^+$ − CO; 6.94), 118 ([199 or 197]$^+$ − $Br^{\cdot}$; 100.00), 90 ([118]$^{\cdot+}$ − CO; 67.29), 89([118]$^{\cdot+}$ − $^{\cdot}$CHO; 96.52), 64 ([90]$^{\cdot+}$ − HC≡CH; 9.58), 63 ([89]$^+$ − HC≡CH; 69.74), 62 ([90]$^{\cdot+}$ − $H_2C{=}CH_2$; 33.77).

The MS spectrum of **13** is similar to that obtained from authentic **4**, the main difference being that only the MS spectrum of **13** shows a multiplet arising from $M^{\cdot+}$ − $^{\cdot}CH_3$. This feature, also present in the MS spectrum of **3** but absent from that of **2**, is a strong evidence in favour of the proposed structure for **13**. Upon aging, *o*-toluic acid, the hydrolysis product of **13**, was identified and confirmed by co-injection of authentic sample. The same was observed for **15**, giving rise to *o*-bis(formyl)benzene.

Actinometry

The quantum yields of these photoprocesses were determined by performing the irradiation of solutions of compounds **1**–**5**, in a spinning merry-go-round apparatus surrounded by the lamps with room for six quartz tubes of 13 × 100 mm. The concentration used was 0.053 mol dm^{-3} for **2** in benzene–cyclohexene mixture, 0.016 mol dm^{-3} for **2** in isooctane and 0.100 mol dm^{-3} in every other case. The solutions were argon purged before being transferred to the tubes under inert atmosphere. The tubes to be analysed (as described above) were removed from the irradiating system at equal intervals, maintaining the lamps on. The photon flux in this irradiation system was determined using malachite green leucocyanide, according to Johns[10a] and the malachite green cation formation was monitored by measuring its light absorption at 618 nm.

These systems may be represented by the kinetic eqn. (1),

$$-V\frac{d[R]_t}{d(I_0 \times t)} = \Phi\frac{[R]_t}{[R]_0} \qquad (1)$$

adapted from Bunce,[11] V is the volume of irradiated solution, $[R]_0$ and $[R]_t$ are the concentration of solute at time zero and t respectively, I_0 is the photon flow (in Einstein min^{-1}) of light absorbed and Φ is the quantum yield of the reaction.

When integrated this equation becomes (2) which implies

$$\Phi = \frac{V}{I_0 \times t} [\mathrm{R}]_0 \ln\left(\frac{[\mathrm{R}]_0}{[\mathrm{R}]_t}\right) \tag{2}$$

that the solute is consumed exponentially with time and, therefore, quantum yield varies in the same way. Nevertheless, at sufficiently short time, this curve can be described as a straight line, represented by eqn. (3)

$$[\mathrm{R}]_t = [\mathrm{R}]_0 - k_0 t \tag{3}$$

which means that

as
$$\lim_{[\mathrm{R}]_t \to [\mathrm{R}]_0} \left\{ [\mathrm{R}]_0 \ln\left(\frac{[\mathrm{R}]_0}{[\mathrm{R}]_t}\right) \right\} = k_0 t \tag{4}$$

then
$$\Phi = \frac{k_0 V}{I_0} \tag{5}$$

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