Photochemistry of Dibenzo-1,4-dioxin: Formation of 2,2′-Biphenylquinone as an Observable Intermediate

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Photolysis of dibenzo-1,4-dioxin **1**, which is the parent ring system of the well-known environmental contaminant 'dioxin' and 2,3,7,8-tetramethyldibenzo-1,4-dioxin **2**, in aqueous solution results in a novel intramolecular rearrangement, giving rise to intermediate 2,2′-biphenylquinones, which are observable by UV–VIS spectrophotometry.

The mechanism of photodegradation of chlorinated dibenzo-1,4-dioxins is a topic of great interest in environmental chemistry.[1–5] The most well-known member of this class of compounds is 2,3,7,8-tetrachlorodibenzo-1,4-dioxin (TCDD), commonly known as dioxin; TCDD and related contaminants are found in many industrial wastes. Owing to their much publicized high toxicity in laboratory animals, research into the environmental fate of TCDD and related compounds has attracted considerable interest. The majority of such studies have concentrated on the photodechlorination pathway, *i.e.* loss of chlorine atom followed by hydrogen abstraction from the solvent. Very little is known with respect to how the ring system itself is actually transformed on photolysis although it is clear that upon complete dechlorination, photochemical transformations involve the parent dibenzo-1,4-dioxin **1**. The few reports of the photochemistry of **1** available[1,2,5] suggest that the primary photochemical step is simple ring opening by aryl–oxygen bond homolysis, followed by reduction of the radical pair to give 2-phenoxyphenol **3**, which is transformed to 2,2′-biphenylphenol **4** on further photolysis. Here, we show that this mechanistic scheme is incorrect and that in fact a novel photorearrangement of **1** takes place, to give observable 2,2′-biphenylquinones, which are then reduced to give 2,2′-biphenylphenols as the ultimate products.

Photolysis of **1** ($\approx 10^{-3}$ mol dm^{-3}; Rayonet RPR 100 photochemical reactor; 300 nm; quartz; ≈12 °C; 15–60 min; deaerated) in MeCN, 1 : 1 H_2O–MeCN, 1,4-dioxane, tetrahydrofuran, MeOH or propan-2-ol gave **4** as the major product (>40%; mass balance >60%). No trace of **3** could be detected by GC/MS in low conversion runs. At high conversions (>50%), only ~2% of **3** was observed. In the non-hydroxylic solvents, a significant yield (15–25%) of 1-hydroxydibenzofuran **5** was also observed. The structure of this photoproduct was confirmed by comparing its ^{1}H NMR spectrum with that of an independently synthesized authentic sample. Photolysis of **2** in all of the above solvents gave biphenylphenol **6** as the only product.

The following observations provided crucial data as to the actual mechanism of the photoreaction. When samples of **1** and **2** were irradiated in 1 : 1 H_2O–MeCN in the presence of ≈0.01 mol dm^{-3} $NaBH_4$, the yields of the corresponding phenols **4** and **6** increased several fold with a similar improvement in mass balance (>90%). For **1**, we measured $\Phi = 0.016$ and 0.063 (in 1 : 1 H_2O–MeCN) in the absence and presence of $NaBH_4$, respectively. A slight (≈10%) enhancement in yield of these phenols was observed when $NaBH_4$ was added after photolysis. Control experiments showed that the substrates were unreactive towards to $NaBH_4$ in the dark. When UV–VIS spectra were taken of samples of **1** and **2** immediately after photolysis, two distinct absorption bands at long wavelengths† were observed, which decayed within several minutes (**1**: λ_{max} 340 and 532 nm; **2**: λ_{max} 345 and 556 nm) When $NaBH_4$ was present in solution, these long wavelength bands were not observed on photolysis.

The observed long wavelength absorptions were assigned to 2,2′-biphenylquinones **7** and **8**. Several stable but highly substituted 2,2′-biphenylquinones have been reported in the literature,[6–10] all of which have λ_{max} in the 350–380 and 550–600 nm regions. To our knowledge, the absorption spectrum of the parent 2,2′-biphenylquinone has not been previously reported.

Formation of **5** may arise from rearrangement of **7**. Such a rearrangement of a 2,2′-biphenylquinone has been reported.[6] However, it is not clear whether this reaction requires photolysis and why it was observed only in non-hydroxylic solvents.

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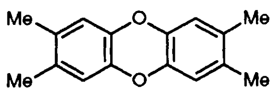
† The solutions developed a pale-pink colour on photolysis which disappeared after several minutes. Use of a laser resulted in a more pronounced development of this colour.



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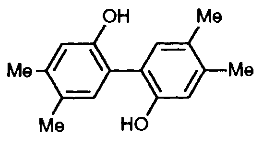

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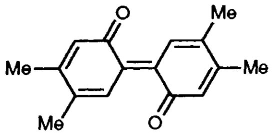

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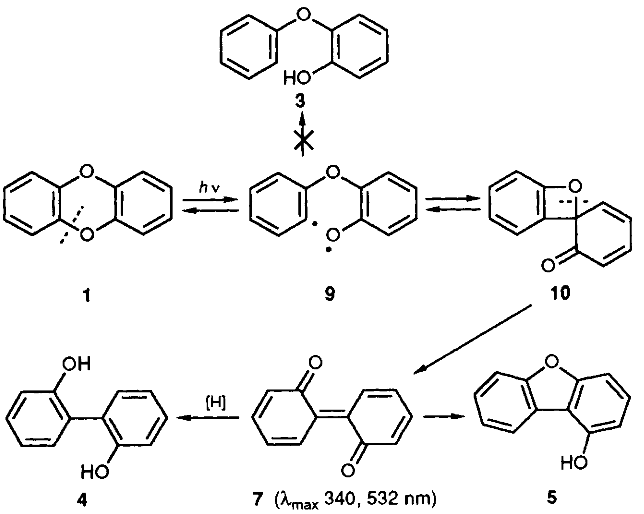

Scheme 1

A proposed mechanism of reaction which is consistent with the above observations is shown in Scheme 1. Photolysis of **1** results in aryl–oxygen bond homolysis, giving rise to biradical **9**. This species may return to substrate or react *via ipso* coupling, to give the spiro derivative **10**. Reduction of **9** by solvent (to give **3**) is at best a very minor pathway. This implies that the biradical **9** reacts *via* an intramolecular pathway essentially exclusively. Subsequent ring opening of **10** gives the observable 2,2′-biphenylquinone **7**. In the presence of $NaBH_4$, **7** is efficiently reduced to **4** in high yield (hence mass balance >90%). In its absence, **7** is reduced by solvent to give **4**, but in lower yield. Since the mass balance is much lower in this case, a significant fraction of **7** decomposes to products which were not characterizable and believed to be polymeric in nature. A significant decrease in yield of **4** was observed when CD_3CN was used as the organic solvent,[‡] consistent with solvent acting as the hydrogen donor to **7** in the absence of $NaBH_4$.

The results of this work show that the dibenzo-1,4-dioxin ring system is readily transformed to a 2,2′-dihydroxybiphenyl system *via* an intramolecular photorearrangement in which the medium acts as the reducing source for the overall conversion, *i.e.* the dibenzo-1,4-dioxin ring system photodecompose to give a reactive oxidizing intermediate in all of the sovlents used. The same photoreaction offers a unique way for photogenerating 2,2′-biphenylquinones which is amenable to laser flash photolysis studies. The implications of these results to the study of photodegradation of 'dioxins' is currently being investigated.

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[‡] The rate of decay of the 532 (or 340) nm band assigned to **7** was slower in CD_3CN than in MeCN (k_H/k_D = 1.16 ± 0.06), consistent with the proposal that hydrogen abstraction from the solvent by **7** is involved in its decay, resulting in overall reduction to give observed **4**. Correspondingly, the yield of **4** was higher in MeCN than in CD_3CN.