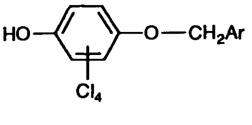
Photoinduced Electron Transfer Reactions of Chloranil with Benzodioxoles

Bao-Zhen Yan,[b] Zhao-Guo Zhang,[a] Han-Cheng Yuan,[b] Long-Cheng Wang[a] and Jian-Hua Xu*[,a]
[a] *Department of Chemistry, Nanjing University, Nanjing 210093, China*
[b] *Department of Applied Chemistry, Beijing Institute of Chemical Technology, Beijing, 100029, China*

Photoinduced reactions of chloranil (CA) with benzodioxoles **3–12** give triaryl orthoformate products **13–22** in 88–98% yields *via* a single electron transfer (SET) mechanism. Photo-CIDNP measurements show that ion radical pairs such as $(CA^{\bullet -}–3^{\bullet +})$ are formed in acetonitrile and neutral semiquinone–benzodioxol-2-yl radical pairs (RP) are formed in benzene as evidenced by the emissive and abnormally enhanced absorptive polarizations of the methylenedioxy protons ($–O–CH_2–O–$) in the regenerated benzodioxoles in CD_3CN and C_6D_6, respectively. Abnormally enhanced absorptions for the methine proton (2-H) in products **13**, **15**, **17** and **20** are also observed in C_6D_6 in accord with the formation of a radical pair (RP) intermediate *en route* to the product.

Photoinduced reactions of the high potential quinone chloranil (2,3,5,6-tetrachloro-*p*-benzoquinone, CA) with donor compounds have been widely investigated.[1] These reactions often involve a single electron transfer (SET) process from the donor to $^3CA^*$. Solvent polarity has a profound effect on the intermediates formed and on their fate in subsequent chemical reactions. In polar solvents such as acetonitrile, CA has often been used as an acceptor to generate cation radicals of the donor compounds for the investigation of their properties and reactivities by transient techniques such as photochemically induced dynamic nuclear polarization (photo-CIDNP)[2] and transient absorption spectra.[3] In these reactions, back electron transfer and further dissociation of the triplet ion radical pairs prevail and, as a result, CA is used as a sensitizer which does not participate in net chemical reactions. Intermolecular reactions between CA and donor compounds are more prone to take place in nonpolar solvents where the ionization of the polar exciplex and the further dissociation of the contact ion radical pairs (CIP) are disfavoured. These photochemical reactions in which CA is not used as a sensitizer but takes part in bond-forming chemical reactions as a partner are currently of interest[1,4–9] because it has been found that the reaction modes are more diverse than those of the unsubstituted parent benzoquinone (BQ). In photoinduced reactions with alkenes, BQ invariably gave spirooxetane products in accord with an $n\pi^*$ triplet state.[10] However, photoreactions of CA with alkenes can afford either cyclobutane or spirooxetanes, depending on the structure and oxidation potential of the alkenes.[4,6,7,9] For aromatic compounds with benzylic hydrogens and alkenes with allylic hydrogens, electron transfer followed by proton transfer and subsequent coupling of the resulting semiquinone radical with the benzylic (allylic) radical leads to the formation of phenol ether type products. Examples of the latter reaction modes are found in photoinduced reactions of CA with toluene derivatives[8] and a few cycloalkenes[9a] which gave products **1** and **2**, respectively. During our investigations on the different reaction modes and mechanistic origin of the selectivity in photoinduced reactions of CA with a variety of electron donors, we have found that photoinduced reactions of CA with benzodioxole derivatives **3–12** gave the triaryl orthoformate derivatives **13–22** in high yields *via* an SET mechanism (Scheme 1). Photo-CIDNP measurements were carried out to investigate the different reaction intermediates and mechanisms in the reactions in benzene and in acetonitrile.



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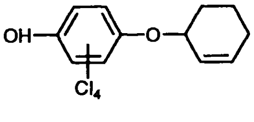

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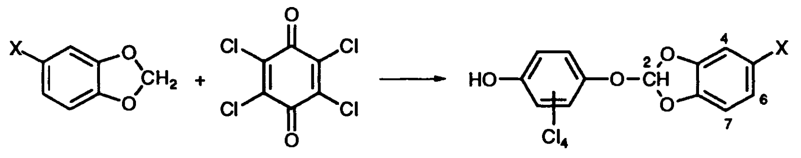
Results and Discussions

Photolysis of a benzene solution of CA (0.05 mol dm^{-3}) with 1,3-benzodioxole 3 (0.1 mol dm^{-3}) under an argon atmosphere with light of $\lambda > 400$ nm gave the triaryl orthoformate product **13** in 93% yield (based on consumed CA). Irradiation under the same conditions in acetonitrile also gave **13** in 94% yield. Photoinduced reactions of CA with 1,3-benzodioxole derivatives **4–12** were investigated and the results are given in Table 1. In each case, photolysis of CA with the benzodioxole derivative in benzene under the above conditions leads to the formation of the corresponding triaryl orthoformate product (**14–22**, respectively) in high yield (Table 1).

The structures of products **13–22** were fully characterized by their spectral data (IR, ^1H NMR and mass) and elemental analysis. In the IR spectrum, the carbonyl stretching absorption at 1680 cm^{-1} in CA is replaced by an H-bonded hydroxy band at ~3350 cm^{-1}. In the mass spectrum, the base peak is from the elimination of a CA semiquinone radical from the molecular ion radical ($M^+ - 245$). In the ^1H NMR spectra of these products, the methine proton (2-H) from the methylenedioxy group of the starting benzodioxoles moved downfield from $\sim\delta$ 6 to above 7 to become hidden in the absorptions of the aromatic protons. For example, δ (2-H) is at 7.62 in **18** and at 7.93 for **21**.

It is found that, although photoinduced cycloadditions of the carbonyl or ethene double bond of CA with alkenes are commonly observed, and α,β-unsaturated carbonyl compounds including chalcone and (*E*)-4-phenylbut-3-en-2-one derivatives gave spirooxetane products with CA,[9b] similar products are not formed in photoinduced reactions of CA with the methylenedioxy substituted chalcone **11** and (*E*)-4-phenylbut-3-en-2-one **12**. The only products are **21** and **22**, respectively in which the carbon–carbon double bond is untouched. In the ^1H NMR spectrum of **21**, the two olefinic protons resonate at δ 7.75 and 7.92 with a coupling constant of 15 Hz, which is identical to that in the starting compound **11**, indicating that the *E*-configuration of the double bond is retained.

Benzodioxoles are good electron donors, the oxidation potentials of **3–12** were measured in acetonitrile solution by cyclic voltammetry with tetrabutylammonium perchlorate as the supporting electrolyte *vs.* a saturated calomel electrode. The



CA

3 X = H
5 X = CN
7 X = COMe
9 X = CO_2Et
11 X = CH=CHCOPh

4 X = Br
6 X = NO_2
8 X = CO_2Me
10 X = $CH_2CH{=}CH_2$
12 X = CH=CHCOMe

13 X = H
15 X = CN
17 X = COMe
19 X = CO_2Et
21 X = CH=CHCOPh

14 X = Br
16 X = NO_2
18 X = CO_2Me
20 X = $CH_2CH{=}CH_2$
22 X = CH=CHCOMe

Scheme 1

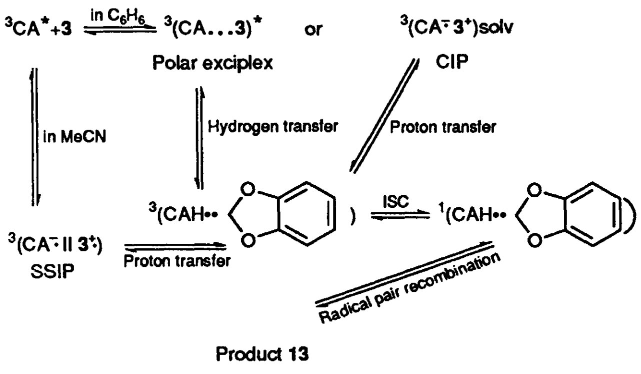
Table 1 Photoinduced reactions of CA with benzodioxoles

Compound	$E(D/D^{\cdot+})^a$ V	Solvent	$\Delta G_{ET}{}^b$ kcal mol^{-1}	Reaction scale (mmol) CA	Benzodioxoles	Irrad. time (h)	Conversion (%)	Product (% yield)
3	1.45	C_6H_6	−6.2	5	10.3	5	100	**13** (93)
	1.45	MeCN	−16.4	5	10.5	5	100	**13** (94)
4	1.59	C_6H_6	−3.0	5	10.4	5.5	100	**14** (93)
5	1.73	C_6H_6	+0.2	5	10.1	4.5	100	**15** (98)
6	1.75	C_6H_6	+0.7	5	10.9	4.5	92	**16** (88)
7	1.68	C_6H_6	−0.9	5	10.4	3	94	**17** (95)
8	1.65	C_6H_6	−1.6	5	9.0	4.5	100	**18** (93)
9	1.64	C_6H_6	−1.8	5	7.8	5.5	100	**19** (95)
10	1.40	C_6H_6	−7.4	5	9.4	8	100	**20** (94)
11	1.50	C_6H_6	−5.1	4	8.4	3.5	64	**21** (96)
	1.50	MeCN	−15.2	4	8.4	3.5	67	**21** (95)
12	1.45	C_6H_6	−6.2	3	6.0	5	100	**22** (91)

[a] *Vs.* SCE. [b] Calculated by Weller equations;[12] in benzene, $\Delta G_{ET} = 23.06\,[E(D/D^{\cdot+})\text{-}E(A/A^{\cdot-}) + 0.38] - E_T$; in acetonitrile, $\Delta G_{ET} = 23.06\,[E(D/D^{\cdot+})\text{-}E(A/A^{\cdot-})\text{-}0.06] - E_T$, where $E(D/D^{\cdot+})$ is the oxidation potential of the donor, $E(A/A^{\cdot-})$ is the reduction potential of CA (0.02 V, SCE),[13] and E_T is the triplet energy of CA (2.12 eV, 49 kcal mol^{-1}).[14] 1 cal = 4.184 J.

electrolytic oxidations are irreversible in all cases. The halfwave oxidation potentials are obtained by subtracting 0.028 V from the peak potentials[11] measured and are listed in Table 1. The free energy change for electron transfer (ΔG_{ET}) between $^3GA^*$ and the benzodioxoles in acetonitrile and in benzene solutions can be estimated by Weller equations[12] and the results are also included in Table 1. The ΔG_{ET} values are almost all negative. These ΔG_{ET} values and the formation of the phenol ether type products strongly suggest that SET processes are involved in these reactions and products **13–22** are proposed to be formed by the mechanism shown in Scheme 2.

An electron transfer interaction between $^3CA^*$ and the donor resulted in the formation of a polar exciplex or contact ion radical pairs (CIP) in benzene and the formation of solvent separated ion radical pairs (SSIP) in acetonitrile.[3,8,15] Hydrogen transfer in exciplex and proton transfer in CIP and SSIP leads to the semiquinone–benzodioxolyl radical pairs (RP) which give the product by radical pair recombination.



Scheme 2

Table 2 Formation constants and molar absorption coefficients of charge transfer complexes between CA and benzodioxoles

Donor	Solvent	λ_{CT}	K_{CT}	ε_{CT}	γ^a	S^b
3	CCl_4	498	0.735	772	0.999	0.24–0.45
4	CCl_4	487	0.398	918	0.999	0.15–0.32
9	$CHCl_3$	460	0.776	323	0.998	0.15–0.33
10	CCl_4	532	0.961	781	0.999	0.24–0.50

[a] Linear correlation coefficient in 1/[donor] *vs.* $[CA]/A_{CT}$ plot. [b] Saturation $S = K_{CT}[\text{donor}]/(1 + K[\text{donor}])$.[19]

Charge transfer complex (CTC) formation between CA and donor compounds are common and have been widely investigated.[16] To assess the extent to which CTC excitation is involved in the photoreactions of CA with the benzodioxoles, electronic spectra of these CA–benzodioxole systems have been measured. For the stronger donors **3**, **4**, **9** and **10**, a new absorption band caused by CTC appears in the long wavelength region upon the addition of the donors into a solution of CA in $CHCl_3$ or CCl_4. In these cases the CTC formation constants and the molar absorption coefficients (ε_{CT}) at the absorption maxima (λ_{CT}) are calculated by the Benesi–Hildebrand treatment[17] and related methods[18] (see Experimental section). The results are shown in Table 2. In these CA–benzodioxole systems, irradiation with light at a wavelength longer than 400 nm is well into the CTC absorption band. When a solution of CA (0.05 mol dm^{-3}) and **3** (0.1 mol dm^{-3}) is photolysed, the CA monomer absorbs $>70\%$ and the CTC absorbs $<30\%$ of the incident light as estimated by comparing the ε values of CA and the CTC at $\lambda > 400$ nm and the relative concentrations of the uncomplexed CA monomer and the CTC formed. The result of direct excitation of the CTC is the formation of very short lived ion radical pairs of singlet manifold.[3b,3d,8] Proton transfer in the singlet ion radical pairs followed by radical pair coupling also gives the products although this is a minor contribution to the overall reaction pathway. For the solid benzodioxoles **11** and **12** and for the less electron donating benzodioxoles **5–8** (where formation of the CTC in appreciable concentration demands the addition of a large concentration of the donor), their limited solubilities prevented them from being added in concentrations large enough for accurate CTC absorption measurements. However, it was found that the addition of **5–8** in the small excess used in the preparative photolyses ([CA]/[benzodioxole] ~ 1:2) did not cause any significant spectral change in the region used for irradiation (>400 nm). In these preparative photolyses, CA monomer is the principal absorbing species and is selectively excited.

Photoinduced reactions between CA and donor alkenes in acetonitrile often fail to give a cross adduct when an SET process is involved. For example, although photoinduced cycloaddition of CA with stilbene derivatives in benzene gave oxetane products in good yield, photolysis under similar conditions in acetonitrile resulted only in the *E–Z* isomerization of the stilbenes without oxetane product formation.[9b] In contrast with this, the benzodioxoles give coupling products in high yields in photoinduced reactions with CA in acetonitrile (see the results for **3** and **11** in acetonitrile in Table 1). The strong acidity of the C–H bond of the cation radicals of **3–12** and their quick deprotonation which effectively inhibits back electron transfer and further dissociation of the ion radical pairs are probably the reason for the efficient product formation.

The mechanism and the intermediates involved in the photoreactions of CA with the benzodioxole derivatives in benzene and in acetonitrile have been investigated further by photo-CIDNP studies. Strong nuclear polarization of the methylene proton (2-H) and some of the aromatic protons in the starting benzodioxoles are observed on irradiation of a solution of CA with the corresponding benzodioxole in CD_3CN. The ^1H NMR spectra of CA (~0.02 mol dm^{-3}) and **3** (~0.02 mol dm^{-3}) in CD_3CN in the dark and during the irradiation are shown in Fig. 1. The methylene protons in **3** at δ 5.93 show a strong emission peak. This polarization is in agreement with the mechanism proposed in Scheme 2 in which the cation radical of **3** is formed. The main factors that decide the polarizations[20] are: (1) the methylene protons in the cation radical of **3** have a positive hyperfine splitting constant with the unpaired electron;[21] (2) the *g* value of $\mathbf{3}^{\cdot+}$ is 2.0039[21] which is smaller than that of $CA^{\cdot-}$ (2.0062);[21] (3) electron transfer between $^3CA^*$ and **3** resulted in the formation of triplet radical ion pairs, and the nuclear polarized **3** was formed by in-cage back electron transfer from $CA^{\cdot-}$ to $\mathbf{3}^{\cdot+}$ within the ion radical pairs. The result is a net effect of emission polarization of the methylene protons. Since the spin density in the benzodioxole cation radicals is mainly distributed at the methylene protons, and the aromatic protons share only a small portion of the spin density as reflected by the small hyperfine splitting constants of these protons with the unpaired electron,[21] the polarizations for the aromatic protons are not as strong as that for the methylene protons. The spectra in the aromatic region are also complicated by the presence of other absorptions presumably from unstable intermediates, which make the spectrum in this region not well enough resolved for an accurate peak assignment to be made. Similar emission polarizations for the methylene protons were also observed in the photolyses of CA with each of the benzodioxoles **5–12** in CD_3CN.

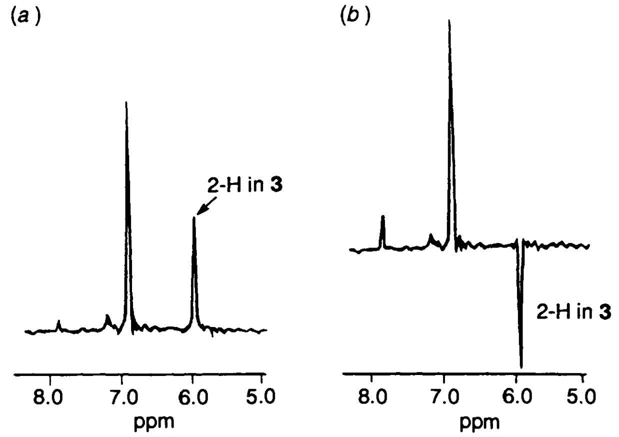


Fig. 1 ^1H NMR of CA (0.02 mol dm^{-3}) and **3** (0.02 mol dm^{-3}) in CD_3CN: (*a*) in the dark; (*b*) during irradiation

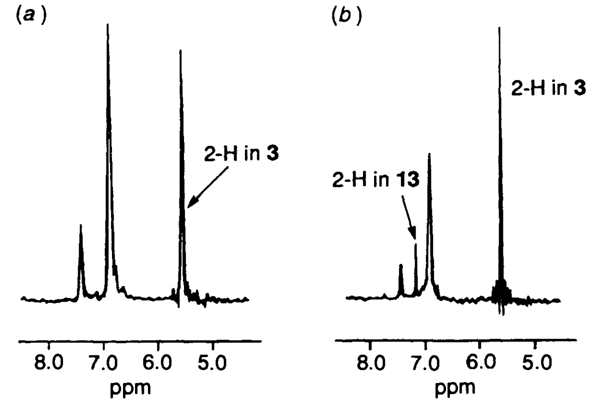


Fig. 2 ^1H NMR of CA (0.02 mol dm^{-3}) and **3** (0.02 mol dm^{-3}) in C_6D_6: (*a*) in the dark; (*b*) during irradiation

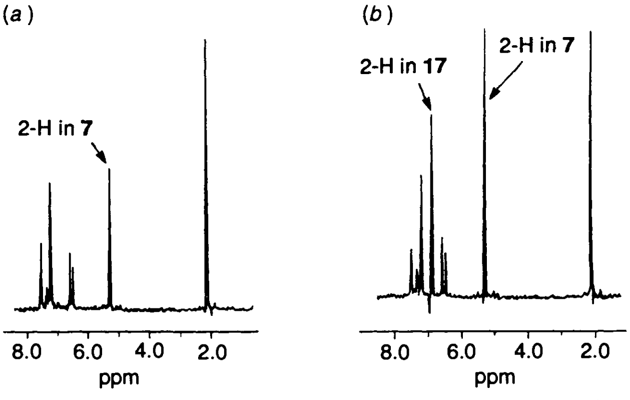


Fig. 3 ^1H NMR of CA (0.02 mol dm^{-3}) and **7** (0.02 mol dm^{-3}) in C_6D_6: (*a*) in the dark; (*b*) during irradiation

Irradiation of a solution of CA with **3** in C_6D_6 leads to a different polarization pattern. The ^1H NMR spectra of (CA–**3**) in C_6D_6 in the dark and during the irradiation are shown in Fig. 2. In contrast with the emission polarization in CD_3CN, the methylene protons show an abnormally enhanced absorption. Irradiation of CA with **5**, **7** and **10** in C_6D_6 similarly resulted in the abnormally enhanced absorption (absorption polarization) of the methylene protons as shown in Figs. 3 and 4 for (CA–**7**) and (CA–**10**), respectively. This polarization pattern shows that neutral radical pairs (RP) (Scheme 2) rather than ion radical pairs are the intermediates in photoinduced reactions of CA with the benzodioxoles in benzene. An electron transfer interaction between $^3CA^*$ and the benzodioxoles in a nonpolar solvent such as benzene resulted in the formation of polar

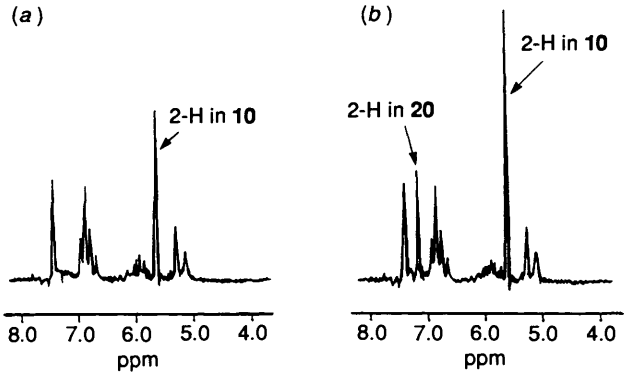


Fig. 4 ^1H NMR of CA (0.02 mol dm^{-3}) and **10** (0.02 mol dm^{-3}) in C_6D_6: (*a*) in the dark; (*b*) during irradiation

exciplexes or contact ion radical pairs (CIP) without further dissociation into solvent separated ion pairs (SSIP). However, radical pair theory for CIDNP demands an inter-radical distance in the pair longer than ~6 Å for the exchange interaction between the radicals to disappear and for the polarization to be created.[22] This requires the formation of ion pairs with the compactness of SSIP or free ions. Since no such highly dissociated ion pairs are formed in benzene, polarization caused by ion radical pair intermediates cannot be observed. On the contrary, neutral radical pairs (RP) formed by hydrogen transfer in the exciplex or proton transfer in the CIP are of triplet multiplicity and can diffuse apart to make the pair loose enough for the nuclear polarization to be developed. In addition, the re-encounter of the randomly diffusing radicals can also make up radical pairs of triplet character, and the same polarization pattern as in the triplet pairs can be created. In these cases, the polarized **3** is regenerated by in-cage reverse hydrogen atom transfer in the neutral triplet radical pairs (μ and ε are both positive); Δg is still negative and, therefore, the negative hyperfine coupling constant of 2-H with the unpaired electron in the neutral radical, which has an opposite sign to that in the cation radical of **3**, leads to the net effect of abnormally enhanced absorption.

Furthermore, we are able to detect the proton nuclear polarization in the product in reactions of CA with **3**, **5**, **7** and **10** in benzene. The main feature of the product polarization is the abnormally enhanced peak of the methine proton (2-H). For example, in Fig. 3, the enhanced peak at δ 7.02 is assigned to 2-H in product **20** by comparison with the ^1H NMR of an authentic sample in the same solvent. This polarization further substantiated the intermediacy of neutral radical pairs (RP) in the formation of the product taking into account the fact that the product is formed by in-cage recombination of the radical pair.

In summary, photoinduced reactions of CA with the benzodioxoles **3**–**12** resulted in the phenoxylation of the benzodioxoles at C_2 to give the triaryl orthoformate products **13**–**22** in high yield. Photo-CIDNP measurements are used to differentiate the reactive intermediates involved in solvents of different polarities and to reveal their mechanistic origins. Solvent separated ion radical pairs of $CA^{\bullet -}$ and benzodioxole$^{\bullet +}$ are formed in acetonitrile, whereas in benzene, neutral CA-semiquinone-1,3-benzodioxol-5-yl radical pairs, derived by hydrogen transfer in the exciplex or proton transfer in the contact ion radical pairs, are the intermediates leading to the product.

Experimental

M.p.s were measured on a microscopic apparatus and are uncorrected. ^1H NMR spectra were recorded on a JEOL PMX-60 SI spectrometer at 60 MHz or a Bruker AC-500 spectrometer at 500 MHz with $SiMe_4$ as internal standard. *J* Values are given in Hz. IR spectra were taken with a Shimadzu IR 408 or a Nicolet 5DX FT-IR spectrometer with KBr pellets. Mass spectra were recorded with a VG ZAB MS spectrometer. UV–VIS spectra were run on a Shimadzu UV-240 spectrophotometer. Cyclic voltammetric measurements were done on a Model 370 Electrochemistry System (EG & G PAR Co).

Acetonitrile (CP grade) was refluxed with phosphorus pentaoxide and distilled, and then refluxed with anhydrous potassium carbonate and redistilled. Benzene (AR grade) was dried with sodium before use. Chloranil (CA) (CP grade) was recrystallized twice from acetone. Compound **10** is commercially available and was distilled before use. Compounds **3**,[24] **4**,[25] **5**,[26] **6**,[27] **7**,[23] **11**[28] and **12**[28] were prepared according to literature procedures. Compounds **8** and **9** were prepared from piperonylic acid by esterification.

Cyclic Voltammetric Measurements on Compounds **3**–**12**.—Oxidation potentials of the benzodioxoles were measured by cyclic voltammetry in dry acetonitrile with tetrabutylammonium perchlorate (0.1 mol dm^{-3}) as supporting electrolyte. Platinum electrodes were used as working electrode and auxiliary electrode, the reference electrode was a saturated calomel electrode (SCE). The scan speed was 50 mv s^{-1}. The solutions were 4 ~ 5 × 10^{-3} mol dm^{-3} in the substrate and were purged with dry nitrogen for 5 min to remove dissolved oxygen before measurements.

Photo-CIDNP Measurements.—Photo-CIDNP measurements were performed on a Bruker AC 80 MHz NMR spectrometer. A solution of CA (0.02 mmol) and the substrate (0.02 mmol) in CD_3CN or C_6D_6 was purged with dry argon for 4 min to remove dissolved oxygen. The ^1H NMR spectrum of the sample solution was then taken before, during and after irradiation. A glass filter which cuts off light with λ < 310 nm was used during the irradiation.

CTC Formation Constants (K_{CT}) *and* ε_{CT} *Measurements.*—UV–VIS spectroscopic measurements were carried out with a matched pair of quartz cells. Solutions of CA (1 × 10^{-3} mol dm^{-3}) with different concentrations of the donor in CCl_4 or $CHCl_3$ were prepared and were purged with dry argon for 5 min to remove dissolved oxygen. The spectrum of each of the solutions was then recorded against a blank containing the same concentration of donor in the same solvent. At least five different donor concentrations were used for each donor. The CTC formation constants (K_{CT}) and the absorption coefficient (ε_{CT}) of the CTC at its absorption maxima were calculated by the Benesi–Hildebrand treatment. The results are recorded in Table 2. The spectroscopic data were also treated with other methods (Scott[18], Scratchard[18]) for all the donors investigated. In each case, they gave K_{CT} and ε_{CT} values in good agreement with that from the Benesi–Hildebrand treatment with errors not exceeding ± 10%.

Preparative Photolysis of CA with the Benzodioxoles.—The reaction scales are shown in Table 1. A solution of CA with the benzodioxole in dry benzene or in acetonitrile (100 cm^3) was purged with dry argon for 20 min and then photolysed with consistent argon purging for the time indicated in Table 1. TLC was used to monitor the reaction. After photolysis, the precipitated solid product was collected by filtration and washed repeatedly with small portions of benzene–diethyl ether (1:1, v/v). The combined washings and the photolysate were concentrated by rotary evaporation and the residue subjected to chromatographic separation on a silica gel column with light petroleum (b.p. 60–90 °C)–ethyl acetate as eluent to give recovered CA (if any) and an additional portion of product. The conversions and the yields are in Table 1.

2-(4-*Hydroxy*-2,3,5,6-*tetrachlorophenoxy*)-1,3-*benzodioxole* **13**. M.p. 169–170 °C; ν_{max}/cm^{-1} 3350, 1482, 1446, 1405, 1235, 1105, 950, 780, 740 and 720; δ[60 MHz; $(CD_3)_2SO$] 7.08–7.20 (4 H, m, ArH), 7.47 (1 H, s, 2-H) and 10.80 (1 H, br, OH); *m/z* 366 (M^+, 0.1%), 332 (0.1), 246 (18.6), 121 (base) and 87 (22.2) (Found: C, 42.5; H 1.65. $C_{13}H_6Cl_4O_4$ requires C, 42.43; H, 1.64).

5-*Bromo*-2-(4-*hydroxy*-2,3,5,6-*tetrachlorophenoxy*)-1,3-*benzodioxole* **14**. M.p. 182–184 °C; ν_{max}/cm^{-1} 3345br, 1475, 1442, 1400, 1358, 1324, 1231, 1102, 960, 783 and 712; δ(60 MHz; $CDCl_3$) 6.13 (1 H br, OH), 6.97 (1 H, d, *J* 9.2, 7-H), 7.13–7.50 (2 H, m, 4-, 6-H) and 7.29 (1 H, s, 2-H); *m/z* 444 (M^+, 0.3%), 246 (23.8), 199 (base), 120 (19.1) and 87 (33.2) (Found: C, 35.1; H, 1.15. $C_{13}H_5BrCl_4O_4$ requires C, 34.94; H, 1.13).

5-*Cyano*-2-(4-*hydroxy*-2,3,5,6-*tetrachlorophenoxy*)-1,3-*benzodioxole* **15**. M.p. 236–238 °C; ν_{max}/cm^{-1} 3400br, 2315, 1618, 1505, 1463, 1412, 1273, 1210, 1105, 993, 811 and 732; δ[500 MHz; $(CD_3)_2SO$] 7.30–7.60 (m, 4 H, ArH and 2-H) and 11.15 (1 H br, OH); *m/z* 391 (M^+, 0.3%), 357 (M^+ − Cl, 0.6), 246 (22.7), 149 (32.0), 146 (base) and 87 (25.1) (Found: C, 43.1; H, 1.3. $C_{14}H_5Cl_4NO_4$ requires C, 42.79; H, 1.28).

2-(4-*Hydroxy*-2,3,5,6-*tetrachlorophenoxy*)-5-*nitro-1,3-benzodioxole* **16**. M.p. 216–217 °C; ν_{max}/cm^{-1} 3400, 1608, 1520, 1484, 1442, 1396, 1346, 1267, 1239, 1185, 1091, 1008, 900, 783, 740 and 713; δ(60 MHz; $CDCl_3$) 6.20 (1 H, br, OH), 7.21 (1 H, d, *J* 8.6), 7.45 (1 H, s, 2-H), 8.00 (1 H, d, *J* 2.1) and 8.18 (1 H, dd, *J* 8.6, 2.1); *m/z* 411 (M^+, 0.2%), 246 (5.9), 166 (base), 120 (55.3) and 87 (9.7) (Found: C, 37.9; H, 1.25. $C_{13}H_5Cl_4NO_6$ requires C, 37.81; H, 1.22).

5-*Acetyl*-2-(4-*hydroxy*-2,3,5,6-*tetrachlorophenoxy*)-1,3-*benzodioxole* **17**. M.p. 201–203 °C; ν_{max}/cm^{-1} 3298br, 1658, 1600, 1542, 1484, 1388, 1350, 1258, 1178, 960, 890, 808, 783 and 706; δ[500 MHz; $(CD_3)_2SO$] 2.56 (3 H, s, CH_3) 7.23–7.78 (3 H, m, ArH), 7.66 (1 H, s, 2-H) and 11.13 (1 H, s, OH); *m/z* 408 (M^+, 0.1%), 393 (0.4), 246 (55.4), 163 (base), 119 (56.8) and 87 (42.7) (Found: C, 44.1; H, 1.95. $C_{15}H_8Cl_4O_5$ requires C 43.94; H 1.97).

Methyl (4-*hydroxy*-2,3,5,6-*tetrachlorophenoxy*)-1,3-*benzodioxole*-5-*carboxylate* **18**. M.p. 206–207 °C; ν_{max}/cm^{-1} 3300br, 1720, 1615, 1492, 1442, 1390, 1342, 1264, 1230, 1186, 1096, 952, 790, 756 and 706; δ[500 MHz; $(CD_3)_2SO$] 3.85 (3 H, s, CH_3), 7.31 (1 H, d, *J* 8.2), 7.62 (1 H, s, 2-H), 7.66 (1 H, d, *J* 1.3), 7.74 (1 H, dd, *J* 8.2, 1.3) and ~11 (1 H, br, OH); *m/z* 424 (M^+, 78.1%), 245 (36.1), 179 (base), 119 (77.8) and 91 (13.7) (Found: C, 42.1; H, 1.9. $C_{15}H_8Cl_4O_6$ requires C, 42.29; H, 1.89).

Ethyl (4-*Hydroxy*-2,3,5,6-*tetrachlorophenoxy*)-1,3-*benzodioxole*-5-*carboxylate* **19**. M.p. 203–204 °C; ν_{max}/cm^{-1} 3380br, 1682, 1602, 1486, 1438, 1386, 1284, 1256, 1152, 1082, 962, 780, 754 and 708; δ[60 MHz; $(CD_3)_2SO$] 1.33 (3 H, t, *J* 7.6, CH_3), 4.33 (2 H, q, *J* 7.6, CH_2), 7.32 (1 H, d, *J* 8.0), 7.66 (1 H, s, 2-H), 7.71 (1 H, d, *J* 2.0) and 7.80 (1 H, dd, *J* 8.0, 2.0); *m/z* 438 (M^+, < 0.1%), 393 (4.7), 246 (49.4), 193 (base), 165 (94.3) and 87 (39.1) (Found: C, 43.8; H, 2.3. $C_{16}H_{10}Cl_4O_6$ requires C, 43.67; H, 2.29).

5-*Allyl*-2-(4-*hydroxy*-2,3,5,6-*tetrachlorophenoxy*)-1,3-*benzodioxole* **20**. M.p. 162–163 °C; ν_{max}/cm^{-1} 3340br, 1632, 1608, 1550, 1490, 1440, 1400, 1328, 1300, 1242, 1100, 952, 894, 790, 760 and 715; δ(500 MHz; $CDCl_3$) 3.37 (2 H, d, *J* 6.3), 5.08 (2 H, d, *J* 11.8, =CH_2), 5.94 (1 H, tt, *J* 11.8, 6.3 CH=), 6.04 (1 H, s, OH), 6.80 (1 H, d, *J* 7.8), 6.84 (1 H, s), 6.92 (1 H, d, *J* 7.8) and 7.15 (1 H, s, 2-H); *m/z* 408 (M^+, 0.4%), 246 (3.2), 210 (0.5) and 161 (base) (Found: C, 47.3; H, 2.5. $C_{16}H_{10}Cl_4O_4$ requires C, 47.09; H, 2.47).

3-[2-(4-*Hydroxy*-2,3,5,6-*tetrachlorophenyl*)-1,3-*benzodioxol*-5-*yl*]-1-*phenylprop*-2-*en*-1-*one* **21**.* M.p. 234–235 °C; ν_{max}/cm^{-1} 3180br, 1659, 1598, 1496, 1444, 1389, 1362, 1248, 1219, 1167, 1091, 984, 769 and 688; δ[500 MHz; $(CD_3)_2SO$] 7.26 (1 H, dd, $J_{7',6'}$ 8.1, $J_{7',4'}$ 2.1, 7′-H), 7.52 (1 H, d, $J_{6',7'}$ 8.1, 6′-H), 7.55–7.60 (2 H, t, *J* 7.3, 3″-5″-H), 7.58 (1 H, s, 4′-H), 7. 67 (1 H, d, *J* 7.3, 4″-H), 7.75 (1 H, d, *J* 15.0, 3-H), 7.92 (1 H, d, *J* 15.0, 2-H), 7.93 (1 H, s, 2′-H), 8.18 (2 H, d, *J* 7.3, 2″-, 6″-H) and 11.19 (br, OH) *m/z* 246 (base), 210 (14.6%), 182 (21.4), 147 (35.3) and 87 (48.7) (Found: C, 52.85; H, 2.4. $C_{22}H_{12}Cl_4O_5$ requires C, 53.05; H, 2.43).

4-[2-(4-*Hydroxy*-2,3,5,6-*tetrachlorophenoxy*)-1,3-*benzodioxol*-5-*yl*]*but*-3-*en*-2-*one* **22**. M.p. 224–225 °C; ν_{max}/cm^{-1} 3065br, 1673, 1638, 1602, 1546, 1497, 1448, 1391, 1244, 1089, 991, 808, 773 and 716; δ[500 MHz; $(CD_3)_2SO$] 2.32 (3 H, s, CH_3), 6.78 (1 H, d, *J* 17.0, CH=), 3.57 (1 H, d, *J* 17.0, CH=), 7.21–7.66 (4 H, m, ArH and 2-H) and 11.19 (1 H, s, OH); *m/z* 434 (M^+, 0.2%), 419 (0.2), 246 (12.7), 189 (base) and 146 (9.9) (Found: C, 46.6; H, 2.3. $C_{17}H_{10}Cl_4O_5$ requires C 46.82; H 2.31).

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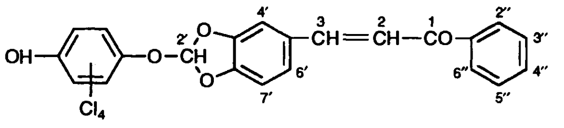
* Numbering system for NMR assignment:



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