A Novel Photoinduced Self-substitution Reaction of Dichloro-1,4-benzoquinones in the Presence of Certain Aliphatic Tertiary Amines

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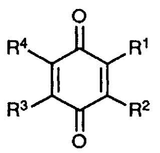
A series of novel compounds has been obtained from the photoinduced self-substitution reactions of 2,5-, 2,6- and 2,3-dichloro-1,4-benzoquinones in the presence of certain hindered *N,N*-dimethylalkylamines, *i.e.* *N,N*-dimethyl-*tert*-butylamine, *N,N*-dimethyl-4-phenylbicyclo[2.2.2]-1-octylamine, *N,N*-dimethyl-1-methylcyclohexylamine, and *N,N*-dimethylcyclohexylamine. The main products were dimer **4a**, trimer **5a** and pentamer **6** from 2,5-dichloro-1,4-benzoquinone, dimers **4b** and **4c** and trimer **5b** from 2,6-dichloro-1,4-benzoquinone, and trimer **5c** from 2,3-dichloro-1,4-benzoquinone respectively. A mechanism involving photoinduced electron transfer from the amine to the dichlorobenzoquinone (Q) as the initial step is proposed for the reaction on the basis of photo-CIDNP and electrochemical experiments.

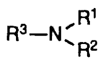
The nucleophilic substitution of quinones and their chloro-derivatives by aliphatic or aromatic amines is of considerable interest and has been extensively studied. The nucleophilic substitution of quinones by primary or secondary amines, in general, produces mono- and/or di-substituted alkylamino- or dialkylamino-quinones.[1] Chloroquinones react with tertiary amines bearing β-hydrogens to form dialkylaminovinylquinones *via* a dehydrogenation reaction.[2] Trimethylamine reacts with chloroquinones to form dimethylaminochloroquinones.[3] However, hindered tertiary amines such as triisopropylamine,[2c] *N*-methylpiperidine[2a] and tributylamine[4] were shown to undergo no such reaction with chloroquinones besides the formation of the corresponding quinone radical anions, but no further work was reported.

Quinones may undergo dimerization under certain conditions. Maruyama *et al.*[5] reported that 2-acyl-1,4-benzoquinone produced the quinone dimer upon irradiation in the presence of rose bengal. The reaction was suggested to involve an electron transfer step between rose bengal and the quinone.

Recently we have reported[6] the first example of a novel self-substitution reaction of 2,5-dichloro-1,4-benzoquinone (**1a**) in its reaction with some hindered aliphatic tertiary amines, *e.g.* *N,N*-dimethyl-*tert*-butylamine (**2a** or *N,N*-dimethyl-4-phenylbicyclo[2.2.2]-1-octylamine (**2b**) in acetonitrile. The trimer **5a** and pentamer **6** of 2,5-dichloro-1,4-benzoquinone (**1a**) were found to be the principal products. This reaction has now been extended to other chlorobenzoquinones, *i.e.* 2,6- and 2,3-dichloro-1,4-benzoquinones (**1b** and **1c**) and other tertiary amines, *i.e.* *N,N*-dimethyl-1-methylcyclohexylamine (**2c**) and *N,N*-dimethylcyclohexylamine (**2d**). Chemically induced dynamic nuclear polarization (CIDNP) and electrochemical study both provided evidence that the reaction is initiated by electron transfer between the chloroquinone and the amine.



1a; $R^1 = R^3 = Cl, R^2 = R^4 = H$
b; $R^1 = R^4 = Cl, R^2 = R^3 = H$
c; $R^1 = R^2 = Cl, R^3 = R^4 = H$



2a; $R^1 = R^2 = CH_3, R^3 =$ *tert*-C_4H_9
b; $R^1 = R^2 = CH_3, R^3 =$ 4-phenylbicyclo[2.2.2]octyl
c; $R^1 = R^2 = CH_3, R^3 =$ 1-methylcyclohexyl
d; $R^1 = R^2 = CH_3, R^3 =$ cyclohexyl
3a; $R^1 = R^2 = H, R^3 =$ *tert*-C_4H_9
b; $R^1 = R^2 = H, R^3 =$ 4-phenylbicyclo[2.2.2]octyl
c; $R^1 = R^2 = H, R^3 =$ 1-methylcyclohexyl
d; $R^1 = R^2 = H, R^3 =$ cyclohexyl

Results and Discussion

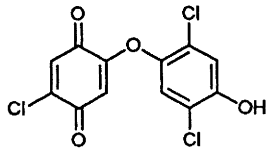
Reactions of Dichloroquinones (**1**) *with Aliphatic Tertiary Amines* (**2**).—When a deoxygenated solution of **1a** in dry acetonitrile with amine (**2a**) added was allowed to stand in sunlight yellow crystals gradually precipitated. The reaction was complete in 24 h. Irradiation with a Hg–Xe lamp for light of wavelength longer than 300 nm (Pyrex filter) accelerated the reaction, bringing about completion within 0.5 h. The main reaction products were isolated by silica gel column chromatography giving the dimer **4a**, trimer **5a** and pentamer **6** of **1a**. Other amines **2b**, **2c** and **2d** could also bring about the self-substitution reaction with different yields. **1b** reacted with amine **2** producing dimers **4b**, **4c** and trimer **5b** under the same conditions. The self-substitution of **1c** in the presence of **2** gave the trimer **5c** as the unique product in good yield. However, when the solution of **1** and **2** was mixed in the dark and allowed to stand at room temperature for 46 h, no reaction was found to take place. The yields of the photoinduced self-substitution of **1** in the presence of **2** are listed in Table 1.

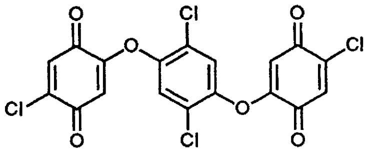
The yields of the self-substitution products listed in Table 1 were determined by TLC based on the quinone consumed except for the **1a**–**2a**, **1a**–**2c**, **1b**–**2a** and **1c**–**2a** systems, wherein the products were isolated by chromatography. The irradiation time was set for about 80% conversion of the quinones. Prolonged irradiation decreased the yields of the main products and increased those of the by-products. No pentamer products were isolated from the reaction of **1b** with **2**. Also, in the **1c**–**2** system, neither the pentamer nor the dimer were obtained. The yields of the self-substitution products of **1** in the presence of **2** were similar whether **1** and **2** were equimolar or in a molar ratio of 2:1. In concentrated solution the rates of the reaction were faster than in dilute solution but the unidentified by-products

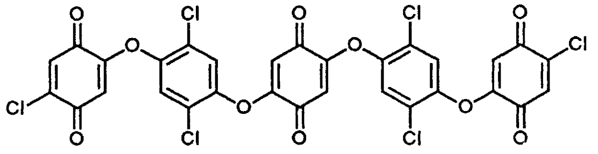
Table 1 Yields of the photoinduced self-substitution of **1** in the presence of **2**

			Yields (%)							
			4			**5**				
Quinone	Amine	Irradiation time/min	**a**	**b**	**c**	**a**	**b**	**c**	**6**	Notes
1a	**2a**	20	2			37			35	*b*
	2b	50	2			20			*a*	*c*
	2c	30	5			37			27	*b*
	2d	30	5			12			*a*	*c*
1b	**2a**	60		4	18		51			*b*
	2b	110		2	<1		20			*c*
	2c	90		4	<1		50			*c*
	2d	90		2	<1		32			*c*
1c	**2a**	30						65		*b*
	2b	50						41		*c*
	2c	30						60		*c*
	2d	30						50		*c*

[a] Undetermined by TLC owing to the poor solubility. [b] Isolated yields based on the quinone consumed. [c] Yields determined by TLC.


4a


5a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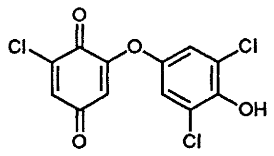
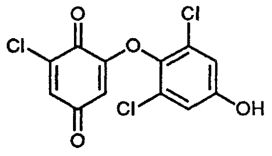

4b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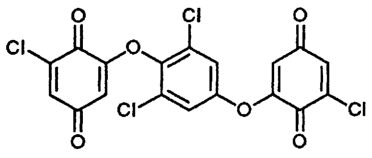
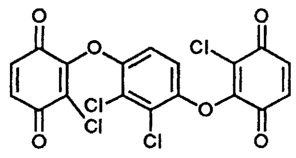

5b


5c

were also increased. Furthermore, under the same conditions the self-substitution rate of **1b** initiated by **2** was much slower than that of **1a** and **1c**. This difference in chemical reactivity between **1b** and **1a** or **1c** may be attributed to the steric effect of the reactive intermediate ($Q^{\bullet -}$) of **1b**.

The molecular structure of amine **2** can also influence the self-substitution rate of the quinone. Comparison of **2a** and **2b** shows that the difference in structure between the amines is the alkyl group. Owing to the fact that the alkyl group of **2a** is smaller than that of **2b**, the former reacted more readily and produced high yields of products, whereas the latter reacted much more slowly and gave only low yields of products. **2d** has α- and β-hydrogens in one group and reacted with **1** to give complicated products. Besides **4** and **5** and unidentified products which remained at the original spot on the TLC, two purple products appeared on the plate which might be nucleophilic substitution products of amine on **1** as reported previously.[2] These purple products were not found in the other systems, *i.e.* **1**–**2a**, **1**–**2b** and **1**–**2c**, however.

In this reaction dichloroquinone **1** gave self-substitution products, while *N*,*N*-dimethylalkylamines **2** gave mainly demethylated products, *i.e.* *N*-methylalkylamines, which were characterized by GC–MS and ^{1}H NMR spectroscopy. Other products, namely, CH_2O and its hydrate, were also detected by ^{1}H NMR spectroscopy. It is interesting to note that self-substitution products were not obtained in the reaction of **1** and **3** under the same conditions and the results indicated that the nucleophilic substitution of the amines on **1** took place. Similar results were also obtained in the reaction of trimethylamine with **1**.

The Mechanism of the Self-substitution of **1** *in the Presence of* **2**.—In order to elucidate the reaction mechanism photo-CIDNP experiments were performed with an 80 MHz NMR spectrometer. Representative NMR spectra of the reaction between **1a** and **2a** are shown in Fig. 1. The polarized signals of self-substitution products were assigned by the addition of the respective products to the reaction mixture. The other polarized signals were assigned on the basis of the ^{1}H NMR chemical shift and GC–MS data. The main features of Fig. 1 are a strong emission at 2.30 ppm, enhanced absorption at 2.78 ppm and around 4.50 ppm, peaks at 7.22, 7.31, 8.33 ppm and, in addition, a broad enhanced absorption at 9.58 ppm. Another feature is the disappearance of the *N*-methyl signal of **2a** at 2.24 ppm. Careful examination of the CIDNP spectra obtained at different time intervals shows that the *N*-methyl peak changed to emission and moved down field gradually to 2.30 then to 2.35 ppm during the course of irradiation (Fig. 2). This may be explained by the formation of the hydrochloride of the amine (*vide infra*) which would cause a downfield shift. Enhanced absorption at 2.78 ppm is assigned to the hydrochloride of demethylated amine ($RNHCH_3{\cdot}HCl$). Enhanced peaks at 9.58 ppm and around 4.50 ppm are assigned to formaldehyde and its hydrate. The broadening of the formaldehyde peak is probably caused by the fast equilibrium of $CH_2O + H_2O \rightleftharpoons$

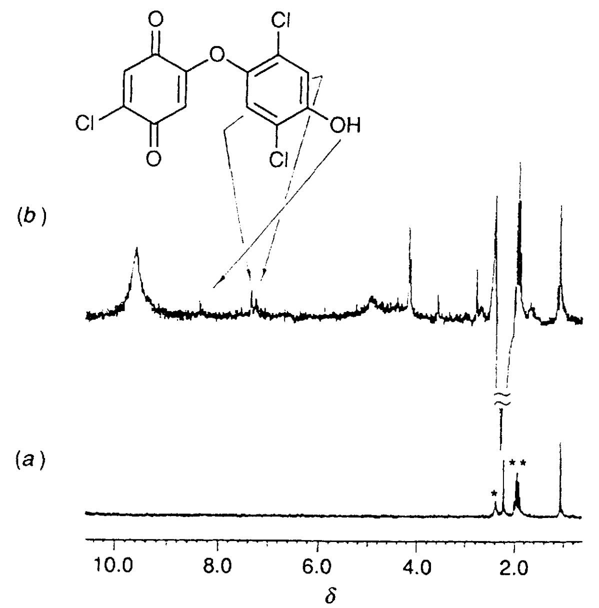


Fig. 1 ^1H NMR spectra of **1a** (0.02 mol dm^{-3}) in the presence of **2a** (0.04 mol dm^{-3}) in [$^2H_3$]acetonitrile. (*a*) Dark, (*b*) light. * H_2O(solvent impurity), ** CHD_2CN(solvent impurity).

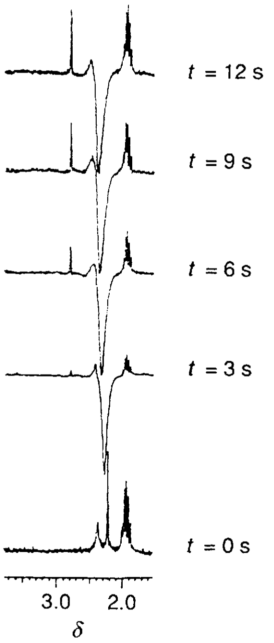
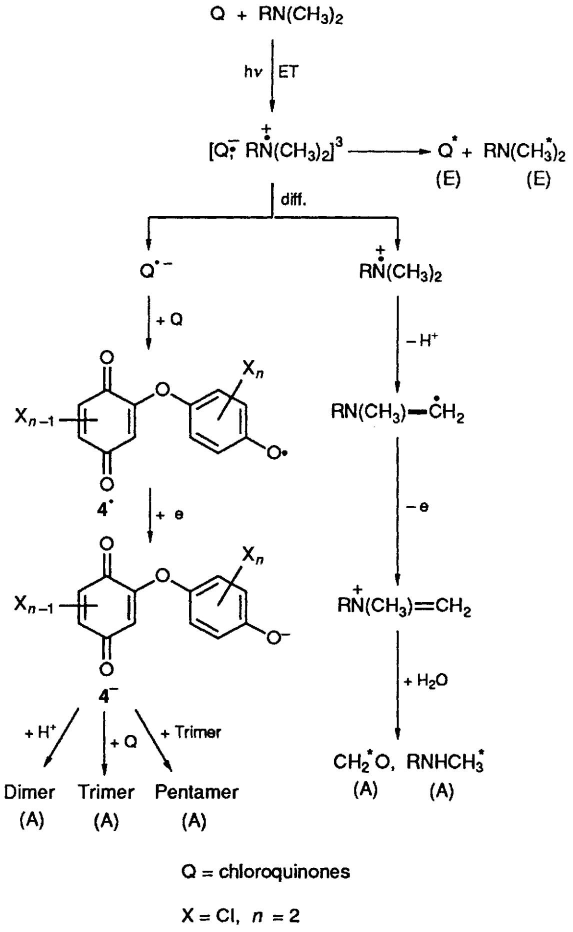


Fig. 2 Part of NMR spectra of the **1a**–**2a** system recorded after different irradiation times

$HOCH_2OH$ as reported previously.[7] Enhanced peaks at 7.22, 7.31 and 8.33 ppm are assigned to the self-substitution products **4a** as shown in Fig. 1.

On the basis of the above results it is suggested that the reaction is initiated by photoinduced electron transfer between **1** and **2** with the triplet radical-ion pair as the reaction precursor (Scheme 1). The polarization phases predicted by Kaptein's rule[8] are indicated in the parentheses which are in agreement with experiment. The intermediacy of the amine radical cation is evidenced by the formation of formaldehyde and the demethylated amine RNHMe which was identified by GC–MS. Both of them are typical fragmentation products of aminium radical cations[9] as shown in Scheme 1.

In this Scheme electron transfer (ET) from amine to quinone constitutes the first ET step. The second ET involves the interaction of $RN(CH_3)\dot{C}H_2$ and $\mathbf{4}^{\bullet}$ to form $\mathbf{4}^{-}$. The CIDNP patterns of the **1b**–**2** and **1c**–**2** systems are the same as that of the **1a**–**2** system. The proton of the hydroxy group of **4** probably comes from the aminium radical cation (Scheme 1) in view of the fact that the polarized phase of the hydroxy proton was the same as that of CH_2O.



Scheme 1 E = emission; A = enhanced absorption

In order to obtain more evidence to support the mechanism, we have also carried out electrolysis of quinone **1** in acetonitrile. The same self-substitution products were obtained as were seen in the amine-initiated photochemical reaction. This offers the most direct evidence for the electron transfer mechanism.

Cyclic voltammetry was employed to determine the redox potentials of dichloroquinone in acetonitrile, and the results are collected in Table 2. The electrolysis potential (EP) was about 30% lower than that of the cathodic peak potential. When the EP was set at the first reduction potential (E_1^{red}, see Table 2) of **1**, yellow solids from **1a** and **1b**, and a red solid from **1c** were obtained after 5 min electrolysis. These products were shown to be the self-substitution products (trimer). Both the R_f values and the absorption wavelength on the TLC, are in agreement with that from the photoreaction between **1** and **2**. On the other hand, when the EP was set at the second reduction potential (E_2^{red}) of **1** no self-substitution products were obtained. The electrochemical results may be rationalized by reaction of the radical anion ($Q^{\bullet -}$ formed at the first reduction peak potential) with the parent dichloroquinone (Q) as the first step leading to trimer **5** (see Scheme 1). The species generated at the second reduction peak potential does not react with the parent dichloroquinone. Since there was no readily available proton source in the medium (other than residual water and the tetrabutylammonium cation), the reaction of the intermediate anion $\mathbf{4}^{-}$ with the parent dichloroquinone to form the trimer **5**

Table 2 Reduction potential[a] and electrolysis potential of quinones **1** at 20 °C

Quinone	$-E_1^{red}$/V *vs.* SCE[b]	$-E_2^{red}$/V *vs.* SCE[b]	Electrolysis potential $-E_{ep}$/V *vs.* SCE	$-E_{\frac{1}{2}}^{red}$/V *vs.* Ag/AgCl[c]
1a	0.22	1.17	0.28	0.18
1b	0.23	0.99	0.30	0.18
1c	0.22	1.13	0.28	—

[a] Reference electrode: SCE, in CH_3CN, sweep rate 0.1 V s^{-1}. [b] Cathodic peak potential. [c] Ref. 16.

was faster than protonation to give the dimer **4**. Obviously, this reaction may be useful in the synthesis of relevant compounds.

In conclusion, the work reported herein illustrates that a series of novel self-substitution products of dichloroquinones could be obtained in the reaction between **1** and certain aliphatic tertiary amine **2** upon irradiation in acetonitrile. A mechanism involving two-step electron transfer from the amine to the quinone is suggested on the evidence of photo-CIDNP and electrolysis studies.

Experimental

Materials.—Quinones **1** were prepared according to the literature,[10,11] purified by chromatography on silica gel (benzene–CH_2Cl_2, 2:1) and then recrystallized from ethanol. Amines **2a**,[12] **2b** and **3b**,[13] **2c** and **3c**[14] and **2d**[15] were synthesized and purified by literature methods. *tert*-Butylamine and cyclohexylamine were commercial products and were purified by distillation before use. The trimethylamine in acetonitrile solution was prepared by passing anhydrous trimethylamine over anhydrous potassium hydroxide (KOH) and through a drying tower filled with KOH into dry acetonitrile. [$^2H_3$]Acetonitrile was obtained from Aldrich. Acetonitrile used in the reaction was purified by standard methods.

General Procedure.—All reactions were carried out in a Pyrex reactor with a SQX 1000 W high pressure Hg–Xe lamp equipped with a Pyrex filter for $\lambda > 300$ nm. Dry acetonitrile was purged with argon before use. The temperature of the reactions was kept at 20 ± 3 °C with cold nitrogen. Photo-CIDNP experiments were performed at 80.131 MHz on a Bruker AC-80 spectrometer equipped with a photo-CIDNP probe which was maintained at 293 K with a Bruker variable temperature control unit. All solutions of the sample in CD_3CN were deaerated by purging with argon and irradiated *in situ* with $\lambda > 300$ nm spectrum of a SQX 1000 W high pressure Hg–Xe lamp.

Melting points were determined on a Kofler hot-stage and were uncorrected. IR spectra were recorded on NICOLET FT-IR spectrophotometer. ^1H and ^{13}C NMR spectra were taken on a Bruker AM 400 NMR spectrometer in [$^2H_6$]-dimethyl sulfoxide and chemical shifts are given in ppm with Me_4Si as an internal standard. *J* Values are in Hz. Mass spectra were determined with a VG-7070E instrument. The reaction products of the amines were identified by gas chromatography–mass spectrometry (GC–MS) with a Hewlett Packard HP 5988A mass spectrometer.

The yields of the products of the reaction between **1** and **2** were determined in a CS-910 Dual-Wavelength TLC Scanner. Because some self-substituted products did not dissolve in acetonitrile, the reaction mixture had to be treated before measurement. After irradiation the reaction mixture was concentrated under vacuum and the residues were then diluted with CH_2Cl_2 until all solids disappeared, except for the **1a**–**2** systems (see Table 1).

The electrochemical experiments in acetonitrile were carried out with a Princeton Applied Research (PAR Model 173) potentiostat equipped with a high-impedance voltage amplifier (PAR Model 178). The working electrode was a platinum plate and the counterelectrode a platinum wire (0.5 mm diameter, 0.5 cm in length). The reference electrode was a saturated calomel electrode. The electrolysis was performed in oxygen-free acetonitrile containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate as supporting electrolyte and 0.05 mol dm^{-3} dichloro-1,4-benzoquinone.

Reaction of **1a** *and* **2a**.—A solution of **1a** (0.80 g, 4.5 mmol) and **2a** (0.23 g, 2.3 mmol) in dry acetonitrile (50 cm^3) was irradiated for 20 min. The precipitated yellow solids were filtered and washed repeatedly with CH_2Cl_2 to give **6** (0.20 g, 0.27 mmol). The filtrate was concentrated under vacuum to give a solid which was subjected to chromatography through silica gel (benzene–CH_2Cl_2–acetone, 20:20:1) to give **4a** (0.012 g, 0.038 mmol), **5a** (0.22 g, 0.48 mmol) and **1a** (0.13 g, 0.74 mmol).

4-(4-*Chloro*-3,6-*dioxocyclohexa*-1,4-*dienyloxy*)-2,5-*dichlorophenol* (**4a**). Dense yellow solid, m.p. 178–180 °C, ν_{max}(KBr)/cm^{-1} 3405, 3067, 1676, 1585, 1477, 1189, 1148, 1081, 1009, 886, 819; δ_H 10.85 (br, 1 H), 7.50 (s, 1 H), 7.39 (s, 1 H), 7.15 (s, 1 H), 5.89 (s, 1 H); δ_C 180.68, 180.32, 159.01, 153.51, 145.77, 142.21, 133.36, 126.14, 125.17, 121.56, 119.43, 112.28; *m*/*z* (relative intensity (EI) 318 (M, 22), 320 (M + 2, 22), 322 (M + 4, 8), 324 (M + 6, <1), 283 (M − Cl, 100), 285 (M + 2 − Cl, 71), 287 (M + 4 − Cl, 14), 255 (M − Cl − CO, 45), 257 (M + 2 − Cl − CO, 30), 141 (8), 113 (7), 88 (15), 69 (39), 53 (94) (Found: C, 45.4; H, 1.7; Cl, 33.4. Calc. for $C_{12}H_5Cl_3O_4$: C, 45.07; H, 1.56; Cl, 33.3%).

1,4-*Bis*(4-*chloro*-3,6-*dioxocyclohexa*-1,4-*dienyloxy*)-2,5-*dichlorobenzene* (**5a**). Yellow solid, m.p. 292–293 °C, (decomp.), ν_{max}(KBr)/cm^{-1} 3084, 1680, 1657, 1625, 1584, 1473, 1179, 1002, 917, 887, 822; δ_H 7.83 (s, 2 H), 7.43 (s, 2 H), 6.48 (s, 2 H); δ_C 179.28, 178.39, 156.50, 146.66, 143.19, 131.97, 124.88, 124.24, 112.44; *m*/*z* (relative intensity) (EI) 458 (M, 18), 460 (M + 2, 26), 462 (M + 4, 15), 464 (M + 6, 6), 466 (M + 8, 1), 423 (M − Cl, 98), 425 (M + 2 − Cl, 100), 427 (M + 4 − Cl, 36), 283 (M − $C_6H_2ClO_2$, 34), 285 (M + 2 − $C_6H_2ClO_2$, 22), 255 (17), 141 (15), 113 (23), 69 (23), 53 (82) **5a** (Found: C, 46.9; H, 1.2; Cl, 31.15. Calc. for $C_{18}H_6Cl_4O_6$: C, 46.96; H, 1.30; Cl, 30.87%).

2,5-*Bis*[4-(4-*chloro*-3,6-*dioxocyclohexa*-1,4-*dienyloxy*)-2,5-*dichlorophenoxy*]*benzoquinone* (**6**). Yellow solid, decomp. temp. 519 °C, ν_{max}(KBr)/cm^{-1} 3069, 1670, 1609, 1473, 1188, 1147, 1088, 1003, 896, 862, 826; δ_H 7.92 (s, 2 H), 7.86 (s, 2 H), 7.45 (s, 2 H), 6.54 (s, 2 H), 6.36 (s, 2 H); δ_C 180.41, 179.43, 178.53, 156.74, 156.61, 146.87, 146.71, 146.56, 143.25, 132.05, 124.96, 124.81, 124.42, 112.47, 110.34 (Found: C, 48.75; H, 1.45; Cl, 28.4. Calc. for $C_{30}H_{10}Cl_6O_{10}$: C, 48.45; H, 1.36; Cl, 28.66%).

Reaction of **1b** *and* **2a**.—A solution of **1b** (0.40 g, 2.3 mmol) and **2a** (0.12 g, 1.2 mmol) in dry acetonitrile (30 cm^3) was irradiated for 60 min. The reaction mixture was concentrated under vacuum. The products were separated by chromatography through silica gel (benzene–CH_2Cl_2–acetone, 20:20:1) to yield **4b** (0.013 g, 0.04 mmol), **4c** (0.059 g, 0.19 mmol) and **5b** (0.19 g, 0.37 mmol) and recovered **1b** (0.07 g, 0.4 mmol).

4-(5-*Chloro*-3,6-*dioxocyclohexa*-1,4-*dienyloxy*)-2,6-*dichlorophenol* (**4b**). Yellow needle crystals, m.p. 166–168 °C, ν_{max}(KBr)/cm^{-1} 3457, 2930, 1694, 1636, 1585, 1472, 1213, 1153, 1121, 962, 898, 853, 801; δ_H 10.35 (br, 1 H), 7.35 (s, 2 H), 7.22 (d, 1 H, *J* 2.32), 5.83 (d, 1 H, *J* 2.32); δ_C 184.73, 173.64, 158.26, 144.87, 140.99, 133.35, 133.32, 122.85, 120.86, 111.96; *m*/*z* (relative intensity) (EI) 318 (M, 81), 320 (M + 2, 82), 322 (M + 4, 27), 324 (M + 6, 2), 283 (M − Cl, 33), 285 (M + 2 − Cl, 20), 255 (M − Cl − CO, 56), 257 (M + 2 − Cl − CO, 35), 141 (27), 113 (31), 69 (23), 53 (100) (Found: C, 45.3; H, 1.8; Cl, 33.15. Calc. for $C_{12}H_5Cl_3O_4$: C, 45.07; H, 1.56; Cl, 33.33%).

4-(5-*Chloro*-3,6-*dioxocyclohexa*-1,4-*dienyloxy*)-3,5-*dichlorophenol* (**4c**). Yellow crystals, m.p. 163–164 °C, ν_{max}(KBr)/cm^{-1} 3465, 2923, 1703, 1646, 1584, 1438, 1211, 1122, 954, 907, 875, 850, 810; δ_H 10.50 (br, 1 H), 7.25 (d, 1 H, *J* 2.32), 6.99 (s, 2 H), 5.86 (d, 1 H, *J* 2.32); δ_C 184.25, 173.09, 156.40, 155.65, 140.94, 136.03, 133.62, 127.13, 116.21, 110.23; *m*/*z* (relative intensity) (EI) 318 (M, 47), 320 (M + 2, 50), 322 (M + 4, 16), 324 (M + 6, 1), 283 (M − Cl, 100), 285 (M + 2 − Cl, 64), 255 (M − Cl − CO, 27), 257 (M + 2 − Cl − CO, 22), 141 (16), 113 (27), 69 (18), 53 (81) (Found: C, 44.8; N, 1.7; Cl, 33.0. Calc. for $C_{12}H_5Cl_3O_4$: C, 45.07; H, 1.56; Cl, 33.33%).

1,4-*Bis*(5-*chloro*-3,6-*dioxocyclohexa*-1,4-*dienyloxy*)-2,6-*dichlorobenzene* (**5b**). Yellow crystals, m.p. 198–200 °C, ν_{max}(KBr)/cm^{-1} 3056, 2924, 1702, 1645, 1589, 1454, 1206, 1122, 969, 917, 878, 817; δ_H 7.67 (s, 2 H), 7.27 (d, 1 H, *J* 2.28), 7.26 (d, 1 H, *J* 2.27), 6.43 (d, 1 H, *J* 2.28), 6.22 (d, 1 H, *J* 2.27); δ_C 185.08, 184.59, 173.56, 172.99, 157.55, 154.94, 151.54, 141.99, 141.05, 140.93, 133.75, 133.47, 128.24, 122.08, 113.67, 111.06; *m*/*z* (relative intensity) (EI) 458 (M, 51), 460 (M + 2, 73), 462 (M + 4, 35), 464 (M + 6, 7), 466 (M + 8, < 1), 423 (M − Cl, 89), 425 (M + 2 − Cl, 87), 427 (M + 4 − Cl, 27), 395 (M − Cl − CO, 26), 397 (M + 2 − Cl − CO, 26), 141 (31), 113 (27), 69 (21), 53 (100) (Found: C, 46.9; H, 1.6; Cl, 30.9. Calc. for $C_{18}H_6Cl_4O_6$: C, 46.96; H, 1.30; Cl, 30.87%).

Reaction of **1c** *and* **2a**.—A solution of **1c** (0.60 g, 3.4 mmol) and **2a** (0.17 g, 1.7 mmol) in dry acetonitrile (40 cm^3) was irradiated for 30 min. The reaction mixture was concentrated under vacuum and the product was purified by chromatography through silical gel (benzene–CH_2Cl_2–acetone, 20:20:1) to give **5c** (0.3 g, 0.68 mmol) as a red solid and **1c** (0.12 g, 0.68 mmol).

1,4-*Bis*(2-*chloro*-3,6-*dioxocyclohexa*-1,4-*dienyloxy*)-2,6-*dichlorobenzene* (**5c**), m.p. 270–271 °C, ν_{max}(KBr)/cm^{-1} 1672, 1631, 1576, 1466, 1231, 1169, 1097, 1001, 927, 876, 817; δ_H 7.21 (s, 2 H), 7.11 (d, 2 H, *J* 10.11), 6.95 (d, 2 H, *J* 10.11); δ_C 179.82, 179.28, 150.06, 148.53, 136.49, 134.87, 130.02, 122.20, 115.82 (Found: C, 47.25; H, 1.25; Cl, 30.9. Calc. for $C_{18}H_6O_6Cl_4$: C, 46.96; H, 1.30; Cl, 30.87%).

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