Photoinduced Reactions of Chloranil with 1,1-Diarylethenes and Product Photochemistry—Intramolecular [2 + 2] (Ortho-)Cycloadditions of Excited Enedione's C=C Double Bond with Substituted Benzene Ring

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Photoinduced reactions of chloranil (CA) with 1,1-diarylethenes **1** [$(p\text{-X-Ph})_2C{=}CH_2$, X = F, Cl, H, Me] in benzene afforded products **4**−**14**, respectively, with the bicyclo[4.2.0]oct-3-ene-2,5-diones **4**, the 6-diarylethenylcyclohexa-2,5-diene-1,4-diones **5**, and 2,3,5,6-tetrachlorohydroquinone **13** as the major primary products. The cyclobutane products **4** are formed via a triplet diradical intermediate without involvement of single electron transfer (SET) between the two reactants, while **5** is derived from a reaction sequence with initial SET interaction between $^3CA^*$ and the alkene. The 9-arylphenanthrene-1,4-diones **6** and its 10-hydroxy-derivatives **7** are secondary photochemical products derived from **5**. The isomeric cage products **9**−**11** are formed from **4** via intramolecular benzene−alkene [2 + 2] (ortho-)photocycloadditions induced by the triplet excited enedione moiety. The relative amount of the two groups of products (**4** and its secondary products **9**−**11** via non-SET route vs **5** and its secondary products **6**, **7**, **8**, **12**, and **14** via SET route) shows a rather regular change, with the ratio of non-SET route products gradually increasing with the increase in oxidation potential of the alkenes and in the positive free energy change for electron transfer (ΔG_{ET}) between $^3CA^*$ and the alkene, at the expense of the ratio of the products from the SET route. The competition between the SET and non-SET routes was also found to be drastically influenced by solvent polarity, with the SET pathways more favored in polar solvent. Photo-CIDNP investigations suggest the intermediacy of exciplexes or contact ion radical pairs in these reactions in benzene, while in acetonitrile, SET process led to the formation of $CA^{\bullet-}$ and cation radical of the alkene in the form of solvent separated ion radical pairs and free ions.

Introduction

Photoinduced reactions of quinones and haloquinones with alkenes are characterized by the diversity in reaction modes and regioselectivities.[1] The electronic configuration of the quinone reactive excited state; the possibility of single electron transfer (SET) between photoexcited quinone and the alkene in the reactions; special structural features in the alkene moiety, e.g. the presence of allylic hydrogens and steric effect toward cycloadditions; and such reaction conditions as solvent polarity and irradiation wavelength all seem to play important roles in deciding the reaction outcome. While the reactions of the parent benzoquinone with alkenes take place at the carbonyl group and yield spirooxetane products,[1,2] the reactions of the high potential 2,3,5,6-tetrachlorobenzoquinone (chloranil, CA; Chart 1) with alkenes, on the other hand, display varied reaction sites and regioselectivity, depending on the structure of the alkenes and reaction conditions.[3−13] This is partly the result of the exceedingly strong electron acceptor ability of CA,[14] which causes a frequent involvement of single electron transfer (SET) process in its reactions with alkenes. A brief survey of reported results in this field has revealed some common trends in the photoreactions of CA with alkenes concerning the reaction site. For low oxidation potential alkenes able to engage in SET interaction with triplet CA ($^3CA^*$), as signified by a negative value of the free energy change for electron transfer (ΔG_{ET}), which can be estimated by the Weller equation,[17] photoinduced cyclo-

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[14] CA has a half-wave reduction potential of 0.02 V (SCE)[15] and a triplet energy (E_T) of 49 kcal/mol.[16] The reduction potential of the triplet excited state is 2.14 V (SCE).

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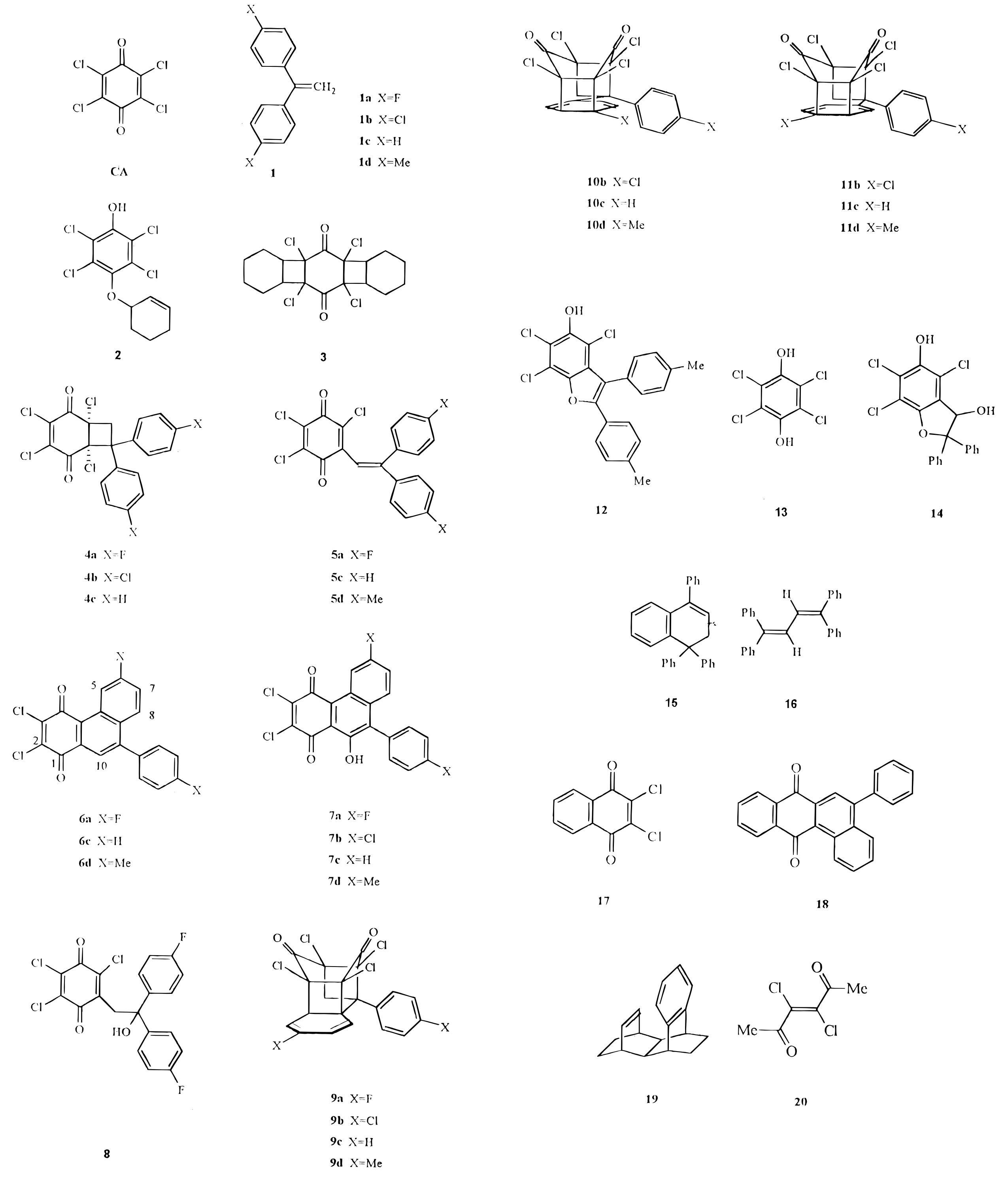
Chart 1



additions take place at the carbonyl group of CA selectively to give spirooxetane as typical products.[6−8,10−12,13b] When the alkenes have a high oxidation potential and a significantly positive ΔG_{ET} value with ^{3}CA*, the reactions proceed without SET process involvement. In these cases, structural features in the alkene that influence the steric hindrance toward cycloadditions play important roles in deciding the reaction site. Therefore, while terminal and cyclic alkenes tend to react with CA's ethene double bond to give cyclobutane products,[3−6,13b] the reaction site is moved to CA's carbonyl group for 1,2-disubstituted (internal) alkenes to yield spirooxetane products.[13a] For alkenes with allylic hydrogens and a negative ΔG_{ET} with ^{3}CA*, formal hydrogen abstraction (via sequential electron transfer from the alkene to ^{3}CA* and proton transfer from the cation radicals of the alkene to $CA^{\bullet-}$ in the radical ion pairs) and subsequent semiquinone−allylic radical pair coupling lead to the formation of phenol type products such as **2**.[9,13b] Since the energetics of the SET process is dependent on solvent polarity,[17] reaction modes could also be influenced by solvent change, which may affect the competition of different reaction pathways. As an example, while the non-SET pathway prevails in photoinduced reactions of CA with cyclohexene in ben-

Table 1. Photoinduced Reactions of CA with Alkenes[a]

alkene	$E_{1/2}^{ox}$ [b] (V, SCE)	solvent	ΔG_{ET} [c] (kcal/mol)	irradiation time (h)	conversion of CA	products and yields (%)[d]
1a	2.04	C_6H_6	7.4	10	95.4%	**4a** (7), **5a** (1.5), **6a** (1.3), **7a** (2.5), **8** (4.5), **9a** (41)
1b	1.96	C_6H_6	5.5	6.5	100%	**4b** (56), **7b** (3), **9b** (7.7), **10b** (3.9), **11b** (1.9)
1c	1.91	C_6H_6	4.4	10	95.9%	**4c** (25), **5c** (6.5), **6c** (3.5), **7c** (10), **9c** (3.1), **10c** (3.7), **11c** (5.5)
1c	1.91	CH_2Cl_2	−2.8	15	51%	**4c** (6), **5c** (41), **6c** (7), **7c** (23), **13** (5), **14** (4), **15**, **16**
1d	1.79	C_6H_6	1.6	40	84.4%	**5d** (19), **6d** (6.7), **7d** (1.7), **12** (18), **13** (9.6), **9d** (0.9), **10d** (2.7), **11d** (12)

[a] See Experimental Section. [b] Measured by cyclic voltametry with platinum as working and auxiliary electrodes and a saturated calomel electrode as a reference. [c] Calculated by eq 1. [d] Yield of isolated product.

zene to give the 2:1 cyclobutane product **3**, the SET pathway predominates when the reaction proceeds in acetonitrile, affording the phenol product **3**. At the same time, if the reaction is conducted in the medium polarity solvent dichloromethane, the two pathways compete with both **2** and **3** as products.[13b]

Therefore, in the photoinduced reactions of CA with alkenes, of particular interest are the cases when the alkenes have such an oxidation potential that their ΔG_{ET} value with $^3CA^*$ is close to zero, because under these circumstances, reaction pathways with and without SET process involvement run competitively, and the results would better reveal the full intricacies in reaction modes and the factors influencing them.

In relation to our continuous interest in exploring the scope and mechanism of photoinduced reactions of CA with alkenes[13] and other electron donors (such as imines[18a] and heterocycles[18b,c]) and with the above-mentioned considerations in mind, we report here the photoinduced reactions of CA with 1,1-diarylethenes **1a**−**d**. These alkenes have oxidation potentials in the range ~2 V (SCE) and their SET interactions with $^3CA^*$ are nearly isothermic in benzene. Furthermore, with the introduction of a substituent in the para-position of the benzene ring, the $E_{1/2}^{ox}$ of the alkenes and the corresponding ΔG_{ET} value between the alkenes and $^3CA^*$ can be progressively adjusted to provide an additional probe to test the effect of the SET process involvement on the reaction mode.

Results

All the alkenes **1a**−**d** are good electron donors (Table 1) and form a ground-state charge-transfer complex (CTC) with CA in solution, as visualized by the occurrence of a reddish color upon the mixing of the alkene with CA in benzene, $CHCl_3$, or CH_2Cl_2. The formation constant (K_{CT}) and extinction coefficient (ϵ_{CT}) of the CTC between CA and the alkenes **1c** and **1d** have been determined with the Benesi−Hildebrand treatment[19,20] by measuring the electronic spectra of a $CHCl_3$ solution of CA at a constant concentration (1.0 mM) with alkenes of increasing concentrations. The results are in Table 2. From these data, the degree of charge-transfer complex excitation involvement in the photolysis can be estimated by considering the concentrations of the CTC and of the uncomplexed CA, as well as the molar extinction coefficient of these two species in the wavelength region used for photolysis. Since light of wavelength longer than 400 nm has been used in the following photolyses, it is estimated that, in the photolysis of CA (50 mM) with **1c** (100 mM), CA absorbs >80% incident light, while in the photoreactions of CA (50 mM) with **1d** (100 mM), CA absorbs ~60% incident light.

Table 2. Formation Constants and Molar Absorption Coefficients of Charge Transfer Complexes between CA and Alkenes

donor	solvent	λ_{CT}	K_{CT}	ϵ_{CT}	γ[a]	S[b]
1c	$CHCl_3$	442	0.67	697	0.9998	0.20−0.53
1d	$CHCl_3$	497	1.18	886	0.9993	0.07−0.27

[a] Linear correlation coefficient in 1/[donor] vs [CA]/A_{CT} plot. [b] Saturation $S = K_{CT}[\text{donor}]/(1 + K[\text{donor}])$. Deranleau, D. *J. Am. Chem. Soc.* **1969**, *91*, 4044.

Irradiation of a benzene solution of CA (0.05 mol L^{-1}) and **1a** (0.10 mol L^{-1}) with light of wavelength longer than 400 nm for 10 h resulted in complete consumption of CA and the formation of products **4a**−**7a**, **8**, and **9a** (Table 1). The structures of these products were determined by spectral and elemental analysis data. The most characteristic spectral feature of these 1:1 cyclobutane products of CA with alkenes is the enedione carbonyl C═O stretching band at 1700 cm^{-1}, which is higher than that in CA (~1680 cm^{-1}) but lower than that in the 2:1 cyclobutane adduct of CA with alkenes as in **3** (at ~1720 cm^{-1}). The cage compound **9a** is derived from the cyclobutane product **4a** by photoinduced intramolecular benzene−alkene [2 + 2] (ortho-)cycloaddition, as is evidenced by a control experiment in which a pure sample of **4a** is irradiated in a benzene solution under same conditions as for the photolysis of CA with **1a** to give the cage product in 94% yield. The C═O stretching absorption in **9a** is at 1750 cm^{-1}, indicative of the absence of any α,β-unsaturation at the carbonyl group. In the ^1H NMR spectrum, the two methylene protons (H-1 and H-2, Figure 1) appear as a pair of doublets at 3.08 and 3.28 ppm, respectively, with a coupling constant of 11.5 Hz. The absorption of H-3 (which was originally an aromatic proton in **4a**) is in the aliphatic region at ~4 ppm with a rather small coupling constant of 4.2 Hz with the olefinic proton H-4 due to the unfavorable dihedral angle between the planes containing the C−H(3) and C−H(4) bonds. This is in sharp contrast with the large coupling constant (9.5 Hz) between the remaining two olefinic protons (H-5 and H-6) in the two coplanar C−H bonds. The 3-vinyl-2,5,6-trichlorobenzoquinone **5a** is a formal substitution product with one of the chlorine atoms in CA replaced by the 2,2-diaryl-1-ethenyl group. The two carbonyl groups in **5a** absorb at 1672 and 1682 cm^{-1}, respectively. A control experiment showed that the phenanthrenedione

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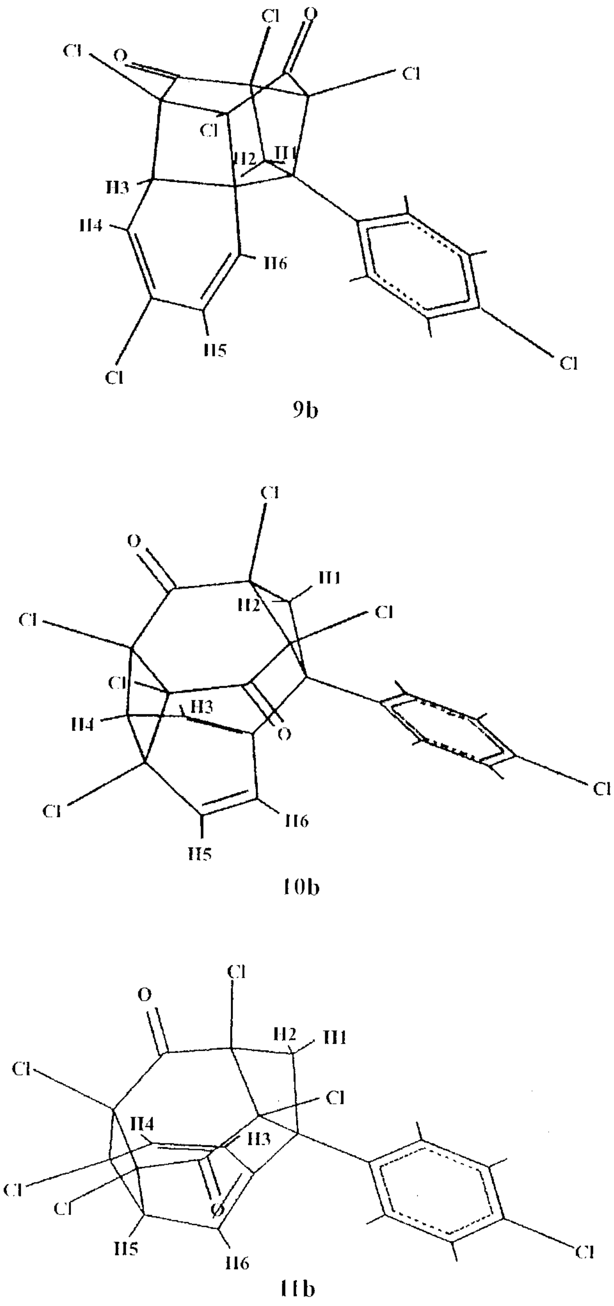

Figure 1. Optimized structures of compounds **9b**, **10b**, and **11b**.

6a is a secondary product derived from **5a** on irradiation by electrocyclic reactions. Product **7a** is formed by the oxidation of **6a** during photolysis by the trace amount of oxygen in the argon stream which was constantly purged though the photolyzate during the irradiation. In product **5a**, the olefinic proton resonates at 6.54 ppm as a singlet, while in **6a**, this singlet is moved to the aromatic region at 8.15 ppm, and in **7a**, this absorption is missing. Another prominent aspect in the NMR spectrum of **6a** and **7a** is that the absorption of H-5 occurs at an unusually low field at δ 9.3–9.4 ppm due to the deshielding effect of the nearby carbonyl. Compound **8** is a hydration product of **5a**. The methylene protons in **8** resonate at δ 3.74 ppm as a singlet in ^{1}H NMR, while in the IR spectrum, the two carbonyl groups absorb at 1683 and 1664 cm^{-1}, respectively.

Photolysis of a benzene solution of CA with **1b** under same conditions as mentioned above afforded products **4b**, **7b** and **9b**–**11b**. Product **4b** constituted the main part of the total products (Table 1). Compounds **9b**–**11b** came as a mixture of three isomers inseparable by conventional preparative chromatography either on silica gel or by thin-layer chromatography. The ratio of the three isomers in the mixture as determined by high resolution ^{1}H NMR measurement is **9b**:**10b**:**11b** = 4.3:2.3:1. A pure analytical sample of **9b** was finally obtained by stepwise crystallization of the mixture with benzene–petroleum ether (60–90 °C) as solvent. The spectral data of **9b** are closely parallel to that of **9a**. The structure of **10b** and **11b** is temporarily assigned mainly by the analysis of their ^{1}H NMR spectral data and by comparing them with that of **9a** and **9b**. Therefore, an inspection of the molecular model of the three isomers showed that, in isomer **9b**, H-6 is in the shielding area of the nearby phenyl ring, and this shielding effect is decreased in isomer **10b** and vanished in isomer **11b** as the distance between the corresponding H-6 and the phenyl ring is becoming larger and larger. As a result, while H-6 in **11b** resonates at 5.77 ppm, typical for olefinic protons in a cyclohexadiene moiety (5.8–5.9 ppm),[21] the absorptions of H-6 in **10b** and **9b** occur at 5.42 and 5.22 ppm, respectively, due to the increasing shielding effect of the phenyl ring. Also, H-1 and H-2 in isomers **10b** and **11b** are slightly deshielded by the flat carbonyl group in the shallow boat conformation of the cyclohexanedione and absorb at lower field (3.10 and 3.27 ppm for **10b** and 3.18 and 3.47 ppm for **11b** respectively) than the H-1 and H-2 in **9b**, where the upward-directed carbonyl group in the rather deeply concave boat conformation of the cyclohexadione has no influence on the absorptions of H-1 and H-2.

Molecular mechanics calculations of the structures of the isomers **9b**, **10b**, and **11b** have been carried out with *minimizer*, using the DREIDING 2.21 force field method, and the optimized structures are depicted in Figure 1. These calculations indicate that all three isomers are highly strained molecules, among which isomer **9b** is the most stable one with a total strain energy of 197 kcal mol^{-1} and the other two are of similar thermodynamic stability with total energy of 213 and 214 kcal mol^{-1}, respectively.

In a control experiment, an isolated pure sample of **4b** was photolyzed in benzene under same conditions as for the photolysis of CA with **1b** to give the mixture of cage products **9b**–**11b** in 95% yield.

The products isolated from the photolysis of CA with **1c** in benzene upon the total conversion of **CA** under the same conditions as mentioned above were **4c**–**7c** and **9c**–**11c**. Compounds **9c**–**11c** also appear as an inseparable mixture of three isomers with the ratio of **9c**:**10c**:**11c** being 1:1.2:1.8. The spectral data of the three isomers closely resemble that of **9b**–**11b** with the exception that in the ^{1}H NMR spectrum, isomer **9c** has four olefinic proton absorptions (5.24–6.06 ppm) and three alkanoic proton absorptions (3.18–3.82 ppm), while isomers **10c** and **11c** have only three olefinic proton absorptions but four alkanoic proton absorptions in similar regions, respectively. This spectral feature further supports the structural assignment for the three isomers **9c**–**11c**. Since the absorptions in the alkanoic region (3–4 ppm)

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(21) Clerk, P.; Simon, S. *Table of Spectral Data for Structure Determination of Organic Compounds*; Spring-Verlag: Berlin, 1983; P H235.

and in the olefinic region (5−6 ppm) in the ^{1}H NMR spectrum of the isomer mixture are seriously overlapped and the absorptions for different isomers are barely discernible to be grouped, we were unable to measure the coupling constants between the aliphatic protons for the two isomers **10c** and **11c**. However, a pure analytical sample of the main isomer **9c** was obtained by stepwise crystallization, and the ^{1}H NMR, IR, and MS data were measured on it.

In this case, independent irradiation of a pure sample of **4c** in benzene also afforded the mixture of the cage products **9c**−**11c** in 87% yield.

In the photoreaction of CA with **1d** under same conditions mentioned above, compounds **5d**−**7d**, **12**, **13**, and **9d**−**11d** were obtained as products (Table 1). The three isomeric cage products were also obtained as a mixture in which the ratio of **9d**:**10d**:**11d** is 1:3:13, as estimated from the high-resolution ^{1}H NMR spectrum of the mixture. Besides **6d** and **7d**, which are akin in their origins to the corresponding products **6a**, **6c**, and **7a**−**c** in the reactions of **1a**−**c**, another product (**12**) was found.

Solvent polarity has a profound effect on the reactions. It is found that photoinduced reactions of CA with **1c** in the more polar dichloromethane took a much longer time to reach similar conversions and resulted in very different product distributions than in benzene. Therefore, photolysis of a dichloromethane solution of CA (0.025 mol L^{-1}) and **1c** (0.050 mol L^{-1}) for 15 h led to a 51% conversion of CA with the 3-vinyl-2,5,6-trichlorobenzoquinone **5c** and its secondary products (**6c**, **7c**, and **14**) constituting the majority (76%) of the total products, while the cyclobutane **4c** accounting for only 6%, together with 4% of tetrachlorohydronquinone **13**. A small amount of the mixture of the dimers of **1c** (**15** and **16** in the ratio of 7:1) were also found in the products (see Table 1 and Experimental Section).

Furthermore, photoinduced reactions of CA with **1c** in acetonitrile gave results entirely contrasting that in benzene, where only the alkene's dimers **15** and **16** and the tetrachlorohydroquinone **13** are formed as products.

Although a complicated mixture of reaction products is formed in these high-conversion photolyses, the reaction products are found to be much simpler at low conversions. In the photoreactions of CA with **1c**, HPLC monitoring of the reaction course showed that, at conversions lower than ~20% in benzene and lower than ~10% in dichloromethane, respectively, **4c** and **5c** are the only products found and none of the secondary products could be detected.

These diverse outcomes of the photoinduced reactions of CA with **1a**−**d** indicated the complexity in reaction mechanisms. As is for all the reactions involving the excited state of CA, the possibility of electron-transfer interaction (SET) between ^{3}CA* and the substrate must be first considered in any discussion of the reaction mechanisms. Therefore, free energy changes for electron transfer (ΔG_{ET}) between ^{3}CA* and the olefins have been estimated by the Weller equation (eq 1), where $E_{1/2}{}^{\mathrm{ox}}$ and

$$\text{in benzene}\quad \Delta G_{\mathrm{ET}} = 23.06\,[E_{1/2}{}^{\mathrm{ox}} - E_{1/2}{}^{\mathrm{red}} - \Delta E^* + 0.38]\quad (\mathrm{kcal/mol})$$

$$\text{in acetonitrile}\quad \Delta G_{\mathrm{ET}} = 23.06\,[E_{1/2}{}^{\mathrm{ox}} - E_{1/2}{}^{\mathrm{red}} - \Delta E^* - 0.06]\quad (\mathrm{kcal/mol})\quad (1)$$

$E_{1/2}{}^{\mathrm{red}}$ are the half-wave oxidation potential of the alkenes and the half-wave reduction potential of the ground state of CA (+0.02 V, SCE), respectively. The ΔE^* is the triplet energy of CA (50 kcal/mol), and the values 0.06 and 0.38 take into consideration the solvation energy of the ion radical pair in MeCN and of the exciplex in benzene, respectively. $E_{1/2}{}^{\mathrm{ox}}$ of the olefins **1a**-**1d** were measured by cyclic voltametry in acetonitrile with a saturated calomel electrode as reference. The ΔG_{ET} values for all the alkenes investigated are listed in Table 1.

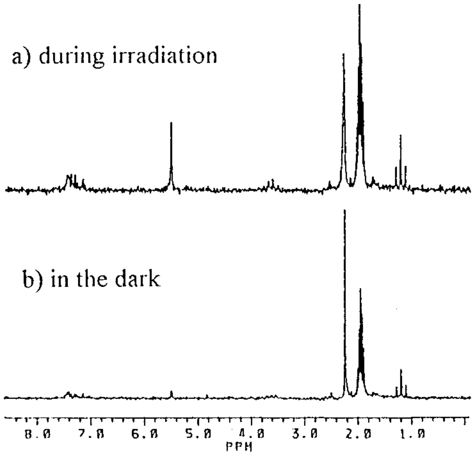

Figure 2. ^{1}H NMR of CA + **1a** in CD$_3$CN.

To get more insight into the reaction mechanisms, photochemically induced dynamic nuclear polarization (photo-CIDNP[22,23]) phenomena during the photoreactions have been investigated. For all the four (CA−**1**) systems investigated, CIDNP phenomena were not observed in deuterated benzene, and no significant difference between the ^{1}H NMR spectra in the dark and during irradiation was found in these cases. On the contrary, irradiation of the four (CA−**1**) systems in deuterated acetonitrile led to the observation of distinct CIDNP phenomena. The nuclear polarization detected came mainly from the regenerated alkenes. In all cases, the methylene protons in **1** show abnormally enhanced absorption (*A*) as shown in Figure 2. For the (CA−**1d**) system (Figure 3), an additional feature is the strong emission peak (*E*) for the protons of the *p*-methyl group. For all the CA−**1** systems investigated, no prominent polarizations were found in the aromatic region.

Discussion

Charge-transfer complex (CTC) formation has been a common phenomenon when CA is mixed with electron rich alkenes[24a] and other electron donors.[24b] In the case of **1a**−**d**, their respective addition to a CA solution in benzene causes significant changes in the long wavelength region of the UV spectrum. As is shown in Table 2, the absorption maxima ($\lambda^{\mathrm{CT}}{}_{\mathrm{max}}$) of the CTC move bathochromically from **1c** to **1d**, while the formation constant of the CTC increases from **1c** to **1d**, in accord with the increasing electron donor ability of the alkenes and a more important contribution of the charge-transfer

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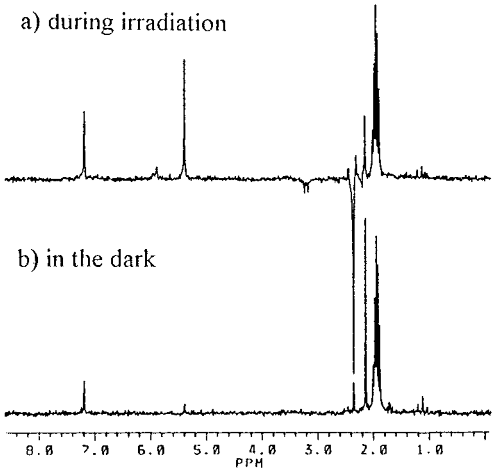
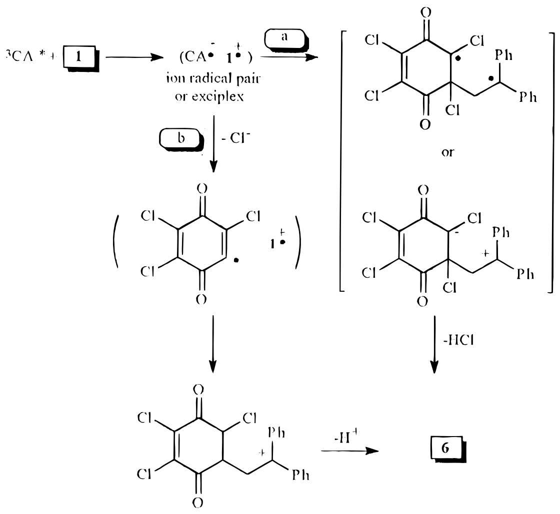


Figure 3. ^{1}H NMR of CA + **1d** in CD_3CN.

component in the complex. In the photolysis of CA with **1a**−**d**, there are therefore two absorbing species—the uncomplexed CA monomer and the CTC in equilibrium with it. Under our reaction conditions, the excitation of uncomplexed CA led to the population of triplet excited state (^{3}CA*) following fast intersystem crossing.[25] From the data in Table 2, it is estimated that, in the photolysis of CA with **1a**−**c** respectively under conditions mentioned above, CA remains the principle absorbing species which absorb >80% of incident light. For **1d**, CA absorbs 60% incident light. As has been shown in many recent investigations,[9,25a,26−29] the excitation of CTC of a donor−acceptor pair in a nonpolar solvent such as benzene leads to the formation of very short-lived singlet contact ion radical pairs which undergo rapid back-electron transfer to regenerate the two ground-state components. The result is a diminished efficiency for the cycloaddition reaction of the two addends. Therefore, excitation of CTC constitutes a rather unproductive and energy wasting route for product formation in the reactions. This could explain in part the much longer irradiation time required to reach similar conversions of the starting CA in the photolysis of CA with **1d** compared with that of **1a**−**c**.

Although the results of these reactions of CA with the alkenes **1** are rather complicated due to the presence of parallel reaction pathways and extensive secondary reactions, the products of all these reactions could be divided into two groups in view of their origins, with **4**, **5**, and **13** as primary products, respectively. The cyclobutane products are formed via a triplet diradical mechanism without SET process involvement. This trend of ^{3}CA* reacting at its C=C double bond with terminal or cyclic alkenes of high oxidation potential with positive ΔG_{ET} values with ^{3}CA* to afford cyclobutanes has been noted in many examples, as in photoinduced reactions of CA with isobutene,[5] several 1,3-dienes,[5] styrene,[3,13b] α-chlorostyrene,[13b] allyl ethyl ether,[13b] cyclohexene,[13b] and cyclooctene.[4] Therefore, products **4** and the isomeric cage products **9**−**11** derived from **4** can be regarded as products from a non-SET route. On the other hand, product **5** is formed via an SET mechanism. This type of product, in which a chlorine atom in the haloquinone is replaced by the alkenyl group, and their secondary cyclization to afford polycyclic products (as **6)** has previously been found in photoinduced reactions of 2,3-dichloronaphthoquinone (**17**) with 1,1-diphenylethenes.[30] The mechanism for the formation of **18**, by analogy with that suggested by Maruyama for the photoreaction of **17** with **1**, is shown in Scheme 1. Electron transfer from **1** to ^{3}CA* led to the formation of highly polar exciplex and/or contact ion radical pairs (CIP), from which reaction sequences (a or b) ensued, resulting in concerted (in route a) or stepwise (in route b) elimination of hydrogen chloride and the formation of **5**. Products **6** are derived from **5** by photochemically allowed intramolecular [$\pi 2_s + \pi 4_a$] electrocyclic addition followed by trans-elimination of hydrogen chloride as was suggested by Maruyama in the rationalization of similar product in the reactions of 2,3-dichloronaphthoquinone **17** with 1,1-diphenylethene.[30] Compound **7**, **8**, **12**, and **14** are also secondary or tertiary products from a common ancestor **5**.

Scheme 1



It is well-known that photoinduced cycloaddition reactions between alkenes and benzenes take place in three different ways: 1,2-(ortho-), 1,3-(meta-) and 1,4-(para-) additions.[31] With the 1,4-(para-)cycloadditions being mainly seen only in photoreactions of benzene with allenes and cyclobutenes, the 1,2-(ortho-) and 1,3-(meta-) additions are by far the most commonly found reaction modes in benzene−alkene photocycloadditions. The preferential reaction mode can be predicted by the ΔI_p (ΔG_{ET}) empirical rule,[32,33] and the factors affecting the regioselectivity and stereoselectivity in these reaction modes

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have been extensively investigated.[32,33] While the meta-cycloadditions are always the predominant reaction pathways for benzenes and alkenes with similar ionization potentials [when the free energy change for electron transfer (ΔG_{ET}) between the photoexcited benzene and the alkene has a significantly large positive value, e.g. >1.7 eV for the reactions of photoexcited benzene with alkenes], a large ionization potential difference (ΔI_p) and the presence of charge-transfer interaction between the two addends (when the ΔG_{ET} has a small positive value, e.g. <1.4 eV for the reactions of photoexcited benzene with alkenes) favor the 1,2-(ortho-)addition pathway. Intramolecular version of the *m*-benzene−alkene photocycloadditions have also been widely investigated and have emerged as a powerful and versatile tool in the syntheses of many natural products for their ability to construct three rings and create up to six stereocenters simultaneously in the adduct.[34] In contrast with this, only a few examples of intramolecular 1,2-(*o*-)benzene−alkene photocycloadditions are known, and reported examples mainly concern *o*- and *p*-butenoxyaceto- and valerophenones,[35] *o*- and *p*-cyano- or methoxycarbonyl-substituted 4-phenoxybut-1-ene[36] systems. In these reactions, it is the triplet excited benzene that adds in the 1,2-fashion to a remote alkene moiety linked to the benzene ring by a flexible chain consisting of three atoms. Photoinduced 1,2-cycloadditions of excited alkene moiety to a ground-state benzene ring, either intermolecular[37] or intramolecular,[38] are scarce.

The following considerations suggest that it is the photoexcited enedione moiety that adds to the ground-state benzene ring in these intramolecular ortho-cycloadditions of **4**. (1) As a model compound of the enedione moiety in **4**, 2-cyclohexene-1,4-dione has a long wavelength absorption band at 368 nm with a log ϵ_{max} of 1.78,[39] while the substituted benzene ring has absorption maxima in the region ~260 nm and is transparent above 300 nm.[40] (2) [2 + 2] (ortho-)cycloaddition of singlet excited benzene ring to a ground-state alkene is symmetry forbidden, while ortho-cycloaddition of a singlet or triplet excited alkene to a ground-state benzene ring is symmetry allowed.[41] Therefore, the transformation of the cyclobutanes **4** to the cage products **9**−**11** not only provided a new example of the rare intramolecular benzene−alkene ortho-photocycloadditions, but to our knowledge, is also the first reported intramolecular benzene−alkene ortho-cycloaddition reaction induced by a triplet excited alkene.

In intermolecular benzene−ethene photocycloadditions, the well-known $\Delta I_p - \Delta G_{ET}$ empirical rules require a significant electron donor−acceptor interaction between the two reactants, as reflected by a relatively large ΔI_p or a slightly positive ΔG_{ET} value (e.g. ~0.5−1.4 kcal/mol for the reactions of benzene with alkenes), for the ortho-cycloaddition to become the major reaction mode. Although this correlation between the ΔI_p (ΔG_{ET}) value and the reaction mode has not been well-tested in intramolecular benzene−alkene photocycloadditions for the lack of enough examples, it has found some support in the intramolecular photocycloadditions of *o*- and *p*-butenoxyaceto- and valerophenones[35] and substituted 4-phenoxybut-1-ene systems,[36] where the benzene ring and the ethene double bond are linked by a flexible chain of three atoms and are not constrained in a fixed geometry. In these systems, the presence of a electron acceptor substituent (acyl, methoxycarboxyl, or cyano group) was found necessary for the triplet excited benzene ring to add to the remote ethene double bond in the ortho-mode exclusively. However, steric factors should play a more important role in intramolecular photocycloadditions than in intermolecular ones. Also, FMO considerations show that the ortho-mode is more favored by frontier orbital overlap than meta- and para-cycloadditions.[42] Therefore, with the two chromophores fixed in a geometry suitable for [2 + 2] cycloadditions in a rigid molecular framework, the ortho-mode could still be the main reaction pathway even in the absence of apparent electron donor−acceptor relationship between the benzene and ethene moieties. This situation is found in the intramolecular ortho-cycloadditions of compound **19**.[43] In the present case of intramolecular cycloadditions from **4**, considerations of the molecular geometry and the electron donor−acceptor relationship between the benzene and enedione fragments show that both factors may have come into play to bring the exclusive [2 + 2] (ortho-) cycloadditions. In **4**, the benzene ring and the enedione C═C double bond are brought close to each other. An inspection of molecular model shows that the benzene ring is situated right above the C═C double bond at a distance convenient for bond formation. However, this molecular geometry is not as rigid as in **19**; as a result, three different regioisomeric cycloadducts could be formed. At the same time, a comparison of the I_p values of the two chromophores reveals that there is an unambiguous electron donor−acceptor relationship between the two. As a structural model of the dichloro-substituted enedione moiety in **4**, the *trans*-3,4-dichloro-3-hexene-2,5-dione **20** has an I_p of 9.77 eV,[44] while as a model of the most electron deficient benzene ring in **4**, the fluorobenzene has an I_p of 9.17 eV.[45] This large ΔI_p also favors the [2 + 2] cycloadditions.

It is interesting to note that, in these intramolecular benzene−alkene ortho-cycloadditions, the reaction site on the benzene ring shows a remarkable dependence on the substituent, and the distribution of the isomeric cage

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products shows a regular change as the substituent on the benzene ring changes. As a rule of thumb, the electron deficient C=C double bond in the dichloro-substituted enedione moiety is inclined to add to that C=C bond in the benzene ring which bears a electron-donating substituent or else has no electron-withdrawing substituent. Therefore, for the reaction of **4a**, compound **9a** is the only product in which the enedione olefinic bond adds to the benzene ring at a C=C bond without the fluorine substituent. In the reactions of **4b**, the product ratio is 3:2.3:1, with the product not involving the chlorine-bearing C=C bond (**9b**) being the major one. For the reaction of **4c** in which the benzene ring are not substituted, the selectivity in reaction site is not obvious, and the three isomers are formed in comparable amounts (**9c**:**10c**:**11c** is 1:1.2:1.8). In contrast, the product distribution in the reaction of **4d** is reversed from that of **4a** and **4b**, and the ratio of **9d**:**10d**:**11d** is 1:3:13. In this case, the enedione olefinic bond adds to the methyl-bearing C=C bond in the benzene ring predominately.

As mentioned above, the products from photoinduced reactions of CA with **1a**−**d** can be divided into two groups according to their origin. The cyclobutane products **4** and the isomeric cage products derived from **4** can be regarded as products via the non-SET route, while products **5** and their secondary products **6**−**8**, **12**, and **14** are derived from the SET route. The results listed in Table 1 show that product distributions in the photoreactions of CA with **1a**−**d** respectively display a rather regular change with the ΔG_{ET} values as the substituent on the benzene ring changes. For **1a** and **1b**, which have the highest $E_{1/2}{}^{ox}$ and comparatively larger positive ΔG_{ET} values of the four alkenes, the non-SET route products predominate. With the decrease in oxidation potential of the alkenes, the SET route products increase at the cost of the non-SET products. For **1d**, the strongest donor of the four, the SET products make up the majority of the total products. This clear tendency that the ratio of SET products rises with the decreasing ΔG_{ET} value strongly supports our discussion on the mechanistic origin of the two groups of products and provided an example to reveal the subtle influence of the SET energetics as reflected by e.g. Weller's ΔG_{ET} value on the reaction outcome.

Since solvent polarity has a significant bearing on the energetics of SET process, the competition of SET vs non-SET reaction pathways are found to be remarkably influenced by solvent change. Therefore, as can be seen in Table 1, in sharp contrast with the reactions of CA with **1c** in benzene where the non-SET products (**4c**, **9c**−**11c**) are formed more preferably than the SET products (**5c**−**7c**), the products from the SET route (**5c**−**7c**, and **14**) constitute the overwhelming majority of the total products in the reaction of CA with **1c** in the more polar CH_2Cl_2, where the ΔG_{ET} value between $^3CA^*$ and **1c** is −2.8 kcal mol^{-1}, as is estimated by eq 2.[17] At the same

$$\Delta G_{ET} = 23.06[E_{1/2}{}^{ox} - E_{1/2}{}^{red} - E_T + 2.6/\epsilon - 0.13] \quad (\text{kcal/mol}^{-1}) \quad (2)$$

time, a small amount of dimers of **1c** (**15** and **16** in a ratio of 7:1) has also been obtained in the reactions in CH_2Cl_2, which are derived in a reaction sequence initiated by attack of the escaped cation radical $\mathbf{1c}^{\bullet+}$ toward neutral **1c**. Similar formation of dimers **15** and **16** from **1c** have been found in SET reactions of **1c** in MeCN with 9,10-dicyanoanthracene (DCA), etc., as an acceptor sensitizer.[46]

It is further noted that the products in photoinduced reactions of CA with **1c** in MeCN are totally different then that in benzene. In MeCN, the ΔG_{ET} between $^3CA^*$ and **1c** turns to be more negative (−6 kcal mol^{-1}). Therefore, the non-SET reaction pathways are suppressed and the corresponding products **4** and **9**−**11** are fully eliminated. Furthermore, solvent polarity also affect the form of the intermediate generated in SET process. Therefore, not only the non-SET products (**4**, **9**−**11**) are no longer formed as the ΔG_{ET} becomes more negative, but the products **5**−**8** which are formed via exciplex or CIP intermediates in benzene and in dichloromethne have also been eliminated as a result of the further dissociation of the solvent separated ion radical pairs formed in MeCN, and the only products formed are the alkene dimers derived from attack of the escaped cation radical to a neutral molecule of **1c**.

To get more information concerning the reaction mechanisms, photo-CIDNP experiments have been conducted for these CA−**1** systems.

As mentioned above, photo-CIDNP phenomena were not observed in deuterated benzene solution for all the (CA−**1**) systems investigated. Electron-transfer quenching of the $^3CA^*$ by an electron donor in a nonpolar solvent such as benzene resulted in the formation of triplet contact ion radical pairs which can be viewed as excited complexes with a large charge-transfer component contribution.[20] Since in the radical pair theory of the CIDNP phenomena,[22] the evolution of nuclear polarizations in the in-cage geminate and out-of-cage trapping products require a large distance (9 Å) between the cation and anion radicals, which corresponds to a compactness of solvent separated ion pairs (SSIP) or free ions, the absence of nuclear polarizations in the regenerated alkenes and in the product **5** formed via the SET route further substantiated that products **5** were formed in exciplex or CIP intermediate in benzene. In contrast with the situation in benzene, strong nuclear polarizations have been detected for all the (CA−**1**) systems in deuterated acetonitrile, and the polarization patterns are compatible with an SET mechanism, in which the polarized starting alkenes are regenerated by in cage back electron transfer between $CA^{\bullet-}$ and $\mathbf{1}^{\bullet+}$ in singlet ion radical pairs (single exit). The other parameters that decide the polarization direction by Kaptain's rule[47] for net effect (eq 3) are as follows. The ion radical pairs

$$\Gamma_{net} = \mu\epsilon\Delta g a \quad (3)$$

generated in SET process are of triplet multiplicity because they have a triplet precursor $^3CA^*$. The alkene cation radicals should have a smaller g value than $CA^{\bullet-}$ (the g value of $CA^{\bullet-}$ is 2.0046[48]), the Δg value is therefore negative. The methylene protons in $\mathbf{1}^{\bullet+}$ have a negative hyperfine coupling constant with the unpaired electron.[49] These lead to an abnormally enhanced absorption (A) for

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the methylene protons in the regenerated **1**, as is actually observed in Figure 2. Since in the cation radical of **1** spin density mainly concentrates at the methylene carbon atom and the carbon atoms in the phenyl group share only a small fraction of spin density,[49] no significant polarization was observed for the ring protons. In the case of **1d**, the protons of the *p*-methyl group on the benzene ring have a positive hyperfine coupling constant with the unpaired spin, while all the other parameters in eq 3 are unchanged, as mentioned above for the methylene protons. This resulted in an emission peak (*E*), which is also in accord with the experimental result. Therefore, these photo-CIDNP phenomena in acetonitrile suggested the formation of SSIP or free ions in this solvent by SET between ^{3}CA* and **1**.

In summary, in photoinduced reactions of the high potential quinone chloranil (CA) with substituted 1,1-diarylethylenes **1a**−**d**, reaction pathways with and without electron transfer (SET) from the alkenes to ^{3}CA* run competitively as a result of the nearly isothermic nature of the SET process. This competition is subtly influenced by the change of substituent in the benzene ring of the alkene, which causes a progressive change of the alkene oxidation potential and a corresponding change in SET energetics. Therefore, the relative amount of the non-SET products vs the SET products increases with an increasingly positive free energy change (ΔG_{ET}) with ^{3}CA*, whereas that of the non-SET products displays an inverse trend. Photo-CIDNP investigations provided further evidence for the intermediacy of polar exciplex or contact ion radical pairs (CIP) in benzene and solvent separated ion radical pairs (SSIP) or free ions in acetonitrile in the reactions. The formation of the isomeric cage products **9**−**11** from the cyclobutane products **4** provided the first example of intramolecular [2 + 2] ortho-cycloaddition of the ethene C═C bond of a triplet excited enedione moiety to the benzene ring. These diversified reaction outcomes caused by parallel reaction pathways and various secondary reactions of the products showed that the long standing pursuit of new photochemical reactions between haloquinones and alkenes is still far from being exhausted and remains an area from which both synthetic application and mechanistic explorations can be rewardingly exploited.

Experimental Section

General. Melting points are uncorrected. The chemical shifts are reported in δ (ppm) relative to tetramethylsilane as internal standard. *J* values are given in hertz. Infrared spectra were taken in KBr pellets. Acetonitrile (AR grade) was first refluxed with phosphorus pentoxide and distilled and then refluxed with anhydrous potassium carbonate and redistilled. Benzene (AR grade) was dried with sodium and distilled before use. Chloranil (CA) (CP grade) was recrystallized twice from acetone. Methanol (AR grade) was refluxed with magnesium and distilled. 1,1-Diarylethylenes were prepared by literature procedures. Other reagents were CP or AR grade and were used as received without further purification

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 mM) with different concentrations of the donor in $HCCl_3$ 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.

Cyclic Voltammetric Measurements on 1,1-Diarylethylenes. Oxidation potential of the alkenes were measured by cyclic voltammetry in dry acetonitrile with tetrabutylammonium perchlorate (0.1 M) as supporting electrolyte. Platinum electrodes were used as working electrode and auxiliary electrode, and the reference electrode was a saturated calomel electrode (SCE). The scan speed was 100 mV s^{-1}. The solutions were 0.1−1 mM in the substrate and were purged with dry nitrogen for 10 min before measurements to remove dissolved oxygen.

Photo-CIDNP Measurements. Photo-CIDNP measurements were performed on a Bruker AC 80 MHz NMR spectrometer. A solution of CA (4 mM) and the substrate (8 mM) in C_6D_6 or CD_3CN was purged with dry argon for 5 min to remove dissolved oxygen. The ^{1}HNMR spectrum of the example solution was then taken before, during, and after irradiation. A glass filter which cuts off light with $\lambda < 310$ nm was used during the irradiation.

Molecular Mechanics Calculations. Computational results were obtained using software programs Cerious^2 3.5 from Molecular Simulations Inc.; the structures of compounds **9b**−**11b** were drawn with a 3D-sketcher of visualizer and optimized with *minimizer*, using DREIDING 2.21 force field. The graphic displays were printed out from the Cerius^2 molecular modeling system. All the calculations were done on SGI Origin 200 server.

General Procedure of Preparative Photolysis of CA with the 1,1-Diarylethylenes. The light source was a 500 W medium-pressure mercury lamp in a cooling water jacket which was further surrounded by a 1 cm thick layer of solution filter (20% aqueous sodium nitrite) to cut off light of wavelength shorter than 400 nm. The solution of the respective 1,1-diarylethylene and CA was placed in glass tubes (20 mL each) around the light source and was photolyzed for the time indicated in Table 1. A stream of dry argon was purged through the solution 0.5 h prior to and throughout the irradiation. The reaction course was monitored by TLC and HPLC. At the end of reaction, the solvents were removed in vacuo, and the photoproducts were separated by column chromatography on silica gel column with petroleum ether (bp 60−90 °C)−ethyl acetate as eluents. For the isomeric cage products (**9**−**11**) obtained as a mixture in the reactions of CA with **1b**−**d**, the relative ratio of the three isomers was determined by 500 MHz ^{1}H NMR measurements. Some of the pure isomers (**9a**−**c** and **11d**) could be isolated from the isomeric mixture by stepwise crystallization from chloroform (or benzene)−petroleum ether (60−90 °C).

Irradiation of CA with 1a. A solution of CA (984 mg, 4 mmol) and 1,1-bis(4,4-fluorophenyl)ethylene (1728 mg, 8 mmol) in benzene (80 mL) was photolyzed for 10 h to lead to a 95.4% conversion of CA. Work up as mentioned above afforded **4a** (120 mg, 7%), **5a** (25 mg, 1.5%), **6a** (20 mg, 1.3%), **7a** (40 mg, 2.5%), **8** (80 mg, 4.5%), and **9a** (720 mg, 41%).

1,3,4,6-Tetrachloro-7,7-bis(4-fluorophenyl)bicyclo[4,2,0]-oct-3-ene-2,5-dione (4a). Recrystallization from petroleum ether (bp 60−90 °C)−chloroform gave slightly yellow crystals: mp 159−160 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ 3.49 (d, *J* = 12.0 Hz, 1H), 4.29 (d, *J* = 12.0 Hz, 1H), 6.69−7.53 (m, 8H); IR (KBr) 1700, 1600, 844 cm^{-1}; MS (EI) *m*/*z* 426 (M$^+$ − Cl, 62), 390 (100). Anal. Calcd for $C_{20}H_{10}Cl_4F_2O_2$: C, 51.98; H, 2.18. Found: C, 51.82; H, 2.21.

2,3,5-Trichloro-6-(2,2-bis(4-fluorophenyl)ethen-1-yl)cyclohexa-2,5-diene-1,4-dione (5a). Recrystallization from petroleum ether (bp 60−90 °C)−ethyl acetate gave red needles: mp 196 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.54 (s, 1H), 7.00−7.40 (m, 8H); IR (KBr) 1682, 1672, 1598, 822 cm^{-1}; MS (EI) *m*/*z* 424 (M$^+$, 0.66), 87 (100). Anal. Calcd for $C_{20}H_9Cl_3F_2O_2$: C, 56.40; H, 2.12. Found: C, 56.48; H, 2.09.

2,3-Dichloro-6-fluoro-9-(4-fluorophenyl)phenanthrene-1,4-dione (6a). Recrystallization from petroleum ether (bp 60−90 °C)−chloroform gave red needles: mp 218−220 °C; ^{1}H NMR (60 MHz, CD_3COCD_3) δ 7.50 (br, 5H), 7.90−8.10 (m, 1H), 8.15 (s, 1H), 9.40 (m, 1H); IR (KBr) 1675, 1600, 1575, 835 cm^{-1};

MS (EI) *m*/*z* 388 (M^+, 100). Anal. Calcd for $C_{20}H_8Cl_2F_2O_2$: C, 61.70; H, 2.06. Found: C, 61.42; H, 2.20.

2,3-Dichloro-6-fluoro-9-(4-fluorophenyl)-10-hydroxyphenanthrene-1,4-dione (7a). Recrystallization from petroleum ether (bp 60−90 °C)−chloroform gave red needles: mp 211−212 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.13 (s, OH), 7.23−7.33 (m, 4H), 7.47 (t, J = 6.7 Hz, 1H), 8.40 (dd, J = 6.7 Hz, 10.7 Hz, 1H), 9.30 (d, J = 10.7 Hz, 1H); IR (KBr) 3400, 1678, 1597, 850 cm^{-1}; MS (EI) *m*/*z* 404 (M^+, 100). Anal. Calcd for $C_{20}H_8Cl_2F_2O_3$: C, 59.26; H, 1.98. Found: C, 59.50; H, 1.95.

2,3,5-Trichloro-6-(2-hydroxy-2,2-bis(4-fluorophenyl)ethyl)cyclohexa-2,5-diene-1,4-dione (8). Recrystallization from petroleum ether (bp 60−90 °C)−ethyl acetate gave yellow needles: mp 182−183 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.77 (s, 2H), 7.00 (t, J = 8.5 Hz, 4H), 7.34 (dd, J = 6.2, 8.5 Hz, 4 H); IR (KBr) 3550, 1683, 1664, 1600, 1578, 824 cm^{-1}; MS (EI) *m*/*z* 424 ($M^+ - H_2O$, 0.37), 123 (100). Anal. Calcd for $C_{20}H_{11}Cl_3F_2O_3$: C, 54.11; H, 2.48. Found: C, 54.01; H, 2.57.

11-Fluoro-4-(4-fluorophenyl)-1,3,6,8-tetrachloropentacyclo[6,6,0,0,^{3,6}0,^{4,5}0,^{4,14}0^{9,14}]tetradeca-10,12-diene-2,7-dione (9a). Recrystallization from benzene gave a white solid: mp 181−184 °C; ^{1}H NMR (500 MHz, CD_3COCD_3) δ 3.08 (d, J = 11.5 Hz, 1H), 3.28 (d, J = 11.5 Hz, 1H), 4.08 (dd, J = 4.2, 6.5 Hz, 1H), 5.19 (d, J = 6.5 Hz, 1H), 5.74 (dd, J = 4.2, 9.5 Hz, 1H), 5.97 (t, J = 9.5 Hz, 1H), 7.18−7.22 (m, 2H), 7.42 (br, 2H); IR (KBr) 1750, 1673, 1604, 1514, 1409, 1163, 1110, 840, 817, 771, 710, 675 cm^{-1}; MS (EI) *m*/*z* 425 ($M^+ - Cl$, 7.4), 83 (100); HRMS (*m*/*z*) calcd for $C_{20}H_9Cl_3F_2O_2$ ($M^+ - HCl$) 423.9637, found 423.9620 (mmu 1.6).

Irradiation of CA with 1b. A solution of CA (1476 mg, 6 mmol) and 1,1-bis(4-chlorophenyl)ethylene (2988 mg, 12 mmol) in benzene (120 mL) was photolyzed for 6.5 h to lead to the total conversion of CA and afforded **4b** (1650 mg, 56%), **7b** (80 mg, 3%), and a mixture of the isomeric cage products **9b**, **10b**, and **11b** (400 mg, 14%) in a ratio of 4:2:1 as estimated from the 500 MHz ^{1}H NMR spectrum of the mixture.

1,3,4,6-Tetrachloro-7,7-bis(4-chlorophenyl)bicyclo[4,2,0]oct-3-ene-2,5-dione (4b). Recrystallization from petroleum ether (bp 60−90 °C)−chloroform gave a slightly yellow crystal: mp 163−164 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ 3.46 (d, J = 12.0 Hz, 1H), 4.26 (d, J = 12.0 Hz, 1H), 7.10−7.60 (m, 8H); IR (KBr) 1717, 1702, 1590, 837 cm^{-1}; MS (FAB) *m*/*z* 457 ($M^+ - Cl$, 5.2), 178 (100). Anal. Calcd for $C_{20}H_{10}Cl_6O_2$: C, 48.89; H, 1.89. Found: C, 48.53; H, 2.04.

2,3-Dichloro-6-chloro-9-(4-chlorophenyl)-10-hydroxyphenanthrene-1,4-dione (7b). Recrystallization from petroleum ether (bp 60−90 °C)−chloroform gave red needles: mp 192 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.11 (s, OH), 7.21(d, J = 8.3, 2H), 7.45 (m, 1H), 7.58 (d, J = 8.3 Hz, 1H), 7.64 (dd, J = 8.5, 1.6 Hz, 1H), 8.31 (d, J = 8.5 Hz, 1H), 9.62 (d, J = 1.6 Hz, 1H); IR (KBr) 3460, 1675, 1650, 1600, 865 cm^{-1}; MS (EI) *m*/*z* 436 (M^+, 42), 406 (100). Anal. Calcd for $C_{20}H_8Cl_4O_3$: C, 54.79; H, 1.83. Found: C, 54.87; H, 1.95.

4-(4-Chrolophenyl)-1,3,6,8,11-pentachloropentacyclo[6,6,0,0,^{3,6}0,^{4,5}0,^{4,14}0^{9,14}]tetradeca-10,12-diene-2,7-dione (9b). This isomer **9b** could be isolated from the mixture of **9b**, **10b**, and **11b** by stepwise crystallization from benzene−petroleum ether (60−90 °C) to give colorless crystals: mp 192−194 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.96 (d, J = 11.2 Hz, 1H), 3.11 (d, J = 11.2 Hz, 1H), 3.92 (d, J = 3.4 Hz, 1H), 5.22 (d, J = 10.2 Hz, 1H), 5.80 (d, J = 3.4 Hz, 1H), 5.94 (d, J = 10.2 Hz, 1H), 7.09 (br, 2H), 7.40 (d, J = 8.9 Hz, 2H); IR (KBr) 1755, 1596, 826 cm^{-1}; MS (FAB) *m*/*z* 457 ($M^+ - Cl$, 0.3), 91 (100). HRMS (*m*/*z*) calcd for $C_{20}H_9Cl_5O_2$ ($M^+ - HCl$) 455.9047, found 455.9042 (mmu 0.4).

4-(4-Chrolophenyl)-1,3,6,8,14-pentachloropentacyclo[6,6,0,0,^{3,6}0,^{4,5}0,^{4,11}0^{9,14}]tetradeca-10,12-diene-2,7-dione (10b): ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.10 (d, J = 11.6 Hz, 1H), 3.27 (d, J = 11.6 Hz, 1H), 3.58 (d, J = 3.3 Hz, 1H), 5.42 (d, J = 10.2 Hz, 1H), 5.74 (d, J = 3.3 Hz, 1H), 5.96 (d, J = 10.2 Hz, 1H), 6.88 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H).

4-(4-Chrolophenyl)-1,3,6,8,9-pentachloropentacyclo[6,6,0,0,^{3,6}0,^{4,5}0,^{4,12}0^{9,14}]tetradeca-10,12-diene-2,7-dione (11b): ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.18 (d, J = 11.7 Hz, 1H), 3.47 (d, J = 11.7 Hz, 1H), 3.82 (d, J = 3.3 Hz, 1H), 5.34 (d, J = 9.9 Hz, 1H), 5.77 (d, J = 3.3 Hz, 1H), 6.01 (d, J = 9.9 Hz, 1H), 6.95 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 8.3 Hz, 2H).

Irradiation of CA with 1c. In benzene. A solution of CA (1230 mg, 5.0 mmol) and 1,1-diphenyl ethylene (1800 mg, 10 mmol) in benzene (100 mL) was photolyzed for 10 h to lead to a 95.9% conversion of CA. Workup as before afforded **4c** (500 mg, 25%), **5c** (120 mg, 6.5%), **6c** (60 mg, 3.5%), **7c** (180 mg, 10%) and a mixture of the isomeric cage products **9c**, **10c**, and **11c** (250 mg, 12%) in a ratio of 1:1.2:1.8 as estimated from the 500 MHz ^{1}H NMR spectrum of the mixture.

In dichloromethane. A solution of CA (738 mg, 3.0 mmol) and 1,1-diphenylethylene (1080 mg, 6.0 mmol) in dichloromethane (120 mL) was photolyzed for 15 h to lead to a 51% conversion of CA. Workup as before afforded **4c** (40 mg, 6%), **5c** (260 mg, 41%), **6c** (40 mg, 7%), **7c** (130 mg, 23%), **13** (20 mg, 5%), **14** (25 mg, 4%), and a mixture of products **15** and **16** (25 mg) in a ratio of 7:1 as estimated from the 300 MHz ^{1}H NMR spectrum of the mixture.

1,3,4,6-Tetrachloro-7,7-diphenylbicyclo[4,2,0]oct-3-ene-2,5-dione (4c). Recrystallization from petroleum ether (bp 60−90 °C)−chloroform gave slightly yellow crystals: mp 143−145 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ 3.46 (d, J = 12.0 Hz, 1H), 4.28 (d, J = 12.0 Hz, 1H), 6.90−7.60 (m, 10H); IR (KBr) 1701, 1596, 750, 710 cm^{-1}; MS (EI) *m*/*z* 424 (M^+, 0.9), 390 (100). Anal. Calcd for $C_{20}H_{12}Cl_4O_2$: C, 56.37; H, 2.84. Found: C, 55.96; H, 2.70.

2,3,5-Trichloro-6-(2,2-diphenylethen-1-yl)cyclohexa-2,5-diene-1,4-dione (5c). Recrystallization from petroleum ether (bp 60−90 °C)−chloroform gave red needles: mp 171 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.60 (s, 1H), 7.00−7.40 (m, 10H); IR (KBr) 1672, 1600, 742, 705 cm^{-1}; MS (EI) *m*/*z* 388 (M^+, 66), 255 (100). Anal. Calcd for $C_{20}H_{11}Cl_3O_2$: C, 61.62; H, 2.82. Found: C, 61.74; H, 2.79.

2,3-Dichloro-9-phenylphenanthrene-1,4-dione (6c). Recrystallization from ethyl acetate gave red needles: mp 170−171 °C; ^{1}H NMR (60 MHz, CD_3COCD_3) δ 7.50 (br, 5H), 7.30−8.20 (m, 3H), 8.17 (s, 1H), 9.58 (d, J = 9.7 Hz, 1H); IR (KBr) 1672, 1593, 764, 702 cm^{-1}; MS (EI) *m*/*z* 352 (M^+, 100), 317 (23), 289 (28), 226 (69). Anal. Calcd for $C_{20}H_{10}Cl_2O_2$: C, 68.01; H, 2.85. Found: C, 67.72; H, 2.66.

2,3-Dichloro-9-phenyl-10-hydroxyphenanthrene-1,4-dione (7c). Recrystallization from petroleum ether (bp 60−90 °C)−chloroform gave a red solid: mp 243 °C; ^{1}H NMR (500 MHz, CD_3Cl_3) δ 6.16 (s, OH), 7.26 (s, 3H), 7.56 (d, J = 7.0 Hz, 1H), 7.60 (t, J = 7.0 Hz, 2H), 7.68 (t, J = 7.0 Hz, 1H), 7.79 (t, J = 7.8 Hz, 1H), 9.35 (d, J = 7.8 Hz, 1H); IR (KBr) 3480, 1680, 1650, 1600, 760, 710 cm^{-1}; MS (EI) *m*/*z* 368 (M^+, 100). Anal. Calcd for $C_{20}H_{10}Cl_2O_3$: C, 65.22; H, 2.72. Found: C, 65.16; H, 2.72.

4-Phenyl-1,3,6,8-tetrachloropentacyclo[6,6,0,0,^{3,6}0,^{4,5}0,^{4,14}0^{9,14}]tetradeca-10,12-diene-2,7-dione (9c). This isomer **9c** could be isolated from the mixture of **9c**−**11c** by stepwise crystallization from chloroform−ethyl ether to give colorless crystals: mp 196−198 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.18 (d, J = 11.5 Hz, 1H), 3.49 (d, J = 11.5 Hz, 1H), 3.82 (br, 1H), 5.24 (d, J = 9.6 Hz, 1H), 5.72 (d, J = 9.6 Hz, 1H), 5.89 (d, J = 6.8 Hz, 1H), 6.06 (dd, J = 6.8, 9.6 Hz, 1H), 7.02 (d, J = 7.4, 2H), 7.36−7.43 (m, 3H); IR (KBr) 1750, 760, 710 cm^{-1}; MS (FAB) *m*/*z* 425 ($M^+ + 1$, 17), 91 (100). HRMS (*m*/*z*) calcd for $C_{20}H_{11}Cl_3O_2$ ($M^+ - HCl$): 387.9826 found: 387.9800 (mmu: 2.5).

4-Phenyl-1,3,6,8-tetrachloropentacyclo[6,6,0,0,^{3,6}0,^{4,5}0,^{4,11}0^{9,14}]tetradeca-10,12-diene-2,7-dione (10c): ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.12 (d, J = 11.4 Hz, 1H), 3.30 (d, J = 11.4 Hz, 1H), 3.76 (br, 1H), 3.60 (br, 1H), 5.35 (d, J = 9.7 Hz, 1H), 5.68−5.83 (m, 1H), 5.98−6.04 (m, 1H), 6.95 (d, J = 7.5, 2H), 7.31−7.44 (m, 3H).

4-Phenyl-1,3,6,8-tetrachloropentacyclo[6,6,0,0,^{3,6}0,^{4,5}0,^{4,12}0^{9,14}]tetradeca-10,12-diene-2,7-dione (11c): ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.98 (d, J = 11.5 Hz, 1H), 3.14 (d, J = 11.5 Hz, 1H), 3.93 (br, 1H), 3.65 (br, 1H), 5.14 (d, J = 9.7 Hz, 1H), 5.68−5.83 (m, 1H), 5.98−6.04 (m, 1H), 7.15 (br, 2H), 7.31−7.44 (m, 3H).

2,3-Dihydro-2,2-diphenyl-4,6,7-trichlorobenzofuran-3,5-diol (14). Recrystallization from chloroform gave colorless needles: mp 146−147 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.89 (s, 1H), 7.33−7.43 (m, 6H), 7.55−7.64 (m, 4H); IR (KBr) 3350, 1600, 890, 760, 705 cm^{-1}; MS (EI) *m*/*z* 406 (M^+, 100), 239 (45), 167 (100). Anal. Calcd for $C_{20}H_{13}Cl_3O_3$: C, 58.90; H, 3.19. Found: C, 59.02; H, 3.16.

Irradiation of CA with 1d. A solution of CA (1476 mg, 6 mmol) and 1,1-bis(4-methylphenyl)ethylene (2496 mg, 12 mmol) in benzene (120 mL) was photolyzed for 40 h to lead to a 84.4% conversion of CA and afforded **5d** (400 mg, 19%), **6d** (130 mg, 6.7%), **7d** (35 mg, 1.7%), **12** (415 mg, 18%), **13** (230 mg, 9.6%), and a mixture of **9d**, **10d**, and **11d** (350 mg, 15%) in a ratio of 1:3:13 as estimated from the ^{1}H NMR spectrum of the mixture.

2,3,5-Trichloro-6-(2,2-bis(4-methylphenyl)ethen-1-yl)-cyclohexa-2,5-diene-1,4-dione (5d). Recrystallization from petroleum ether (bp 60−90 °C)−chloroform gave red needles: mp 167−169 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.95 (s, CH_3), 2.00 (s, CH_3), 6.49 (s, 1H), 6.90−7.40 (m, 8H); IR (KBr) 1681, 1671, 1611, 1593, 825 cm^{-1}; MS (EI) *m*/*z* 416 (M^+, 11), 57 (100). Anal. Calcd for $C_{22}H_{15}Cl_3O_2$: C, 63.23; H, 3.59. Found: C, 63.26; H, 3.62

2,3-Dichloro-6-methyl-9-(4-methylphenyl)phenanthrene-1,4-dione (6d). Recrystallization from benzene gave red needles: mp 264−266 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ 2.49 (s, CH_3), 2.62 (s, CH_3), 7.20−8.10 (m, 6H), 8.13 (s, 1H), 9.42 (m, 1H); IR (KBr) 1672, 1615, 1594, 851 cm^{-1}; MS (EI) *m*/*z* 380 (M^+, 100). Anal. Calcd for $C_{22}H_{14}Cl_2O_2$: C, 69.31; H, 3.70. Found: C, 69.44; H, 3.92.

2,3-Dichloro-6-methyl-9-(4-methylphenyl)-10-hydroxyphenanthrene-1,4-dione (7d). Recrystallization from petroleum ether (bp 60−90 °C)−ethyl acetate gave red needles: mp 264 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.49 (s, CH_3), 2.61 (s, CH_3), 6.14 (s, OH), 7.14 (d, *J* = 6.8, 2H), 7.39 (d, *J* = 6.8, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 9.31 (s, 1H); IR (KBr) 3495, 1680, 1658, 1608, 1560, 830 cm^{-1}; MS (EI) *m*/*z* 396 (M^+, 100), 381 (69). Anal. Calcd for $C_{22}H_{14}Cl_2O_3$: C, 66.50; H, 3.53. Found: C, 66.30; H, 3.56.

11-Methyl-4-(4-methylphenyl)-1,3,6,8-tetrachloropentacyclo[6,6,0,0,^{3,6}0,^{4,5}0,^{4,14}0^{9,14}]tetradeca-10,12-diene-2,7-dione (9d): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.67 (s, CH_3), 2.63 (s, CH_3), 2.93 (d, *J* = 11.2 Hz, 1H), 3.10 (d, *J* = 11.2 Hz, 1H), 3.87 (br, 1H), 5.41 (br, 1H), 5.12 (d, *J* = 9.7 Hz, 1H), 5.84 (d, *J* = 9.7 Hz, 1H), 7.15−7.18 (m, 2H), 7.04 (br, 2H).

14-Methyl-4-(4-methylphenyl)-1,3,6,8-tetrachloropentacyclo[6,6,0,0,^{3,6}0,^{4,5}0,^{4,11}0^{9,14}]tetradeca-10,12-diene-2,7-dione (10d): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.69 (s, CH_3), 2.33 (s, CH_3), 3.09 (d, *J* = 11.2 Hz, 1H), 3.26 (d, *J* = 11.2 Hz, 1H), 3.72 (br, 1H), 5.32 (d, *J* = 9.7 Hz, 1H), 5.33 (br, 1H), 5.86 (d, *J* = 9.7 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H).

9-Methyl-4-(4-methylphenyl)-1,3,6,8-tetrachloropentacyclo[6,6,0,0,^{3,6}0,^{4,5}0,^{4,12}0^{9,14}]tetradeca-10,12-diene-2,7-dione (11d). This isomer **11d** could be isolated from the mixture of **9d**−**11d** by stepwise crystallization from chloroform−ether to give a white solid: mp 208−210 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.71 (s, CH_3), 2.36 (s, CH_3), 3.13 (d, *J* = 11.2 Hz, 1H), 3.44 (d, *J* = 11.2 Hz, 1H), 3.76 (br, 1H), 5.36 (br, 1H), 5.22 (d, *J* = 9.8 Hz, 1H), 5.90 (d, *J* = 9.8 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H); IR (KBr) 1749, 1612, 820 cm^{-1}; MS (EI) *m*/*z* 452 (M^+, 1.2), 418 (100). HRMS (*m*/*z*) calcd for $C_{22}H_{15}Cl_3O_2$ (M^+ − HCl) 416.0139, found 416.0080 (mmu 5.8).

2,3-Bis(4-methylphenyl)-4,6,7-trichlorobenzofuran-5-ol (12). Recrystallization from petroleum ether (bp 60−90 °C)−benzene gave colorless needles: mp 245−247 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.31 (s, CH_3), 2.45 (s, CH_3), 5.76 (s, OH), 7.08 (d, *J* = 8.1, 2H), 7.25 (d, *J* = 8.1, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.7, 145.0, 144.4, 139.1, 138.1, 130.8, 129.6, 129.3, 129.2, 128.5, 126.7, 117.1, 116.7, 114.8, 109.9, 21.5, 21.4; IR (KBr) 3500, 1610, 820 cm^{-1}; MS (EI) *m*/*z* 416 (M^+, 100). Anal. Calcd for $C_{22}H_{15}Cl_3O_2$: C, 63.23; H, 3.59. Found: C, 63.46; H, 3.64.

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Supporting Information Available: Results of molecular mechanics calculations on compounds **9b**, **10b** and **11b** (total strain energy and energy decomposition) and copies of ^{1}H NMR for compounds **9a**−**c** and the mixture of compounds **15** and **16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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