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# Photochemical Reactions of Chloranil with Cyclooctene, 1,5-Cyclooctadiene, and Cyclohexene Revisited

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*Dedicated to Professor Siegfried Hünig on the occasion of his 90th birthday*

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Depending on the reaction conditions, excited chloranil ($^3$**CA**) and *cis*-cyclooctene (*cis*-**CO**) furnished three types of products, which all contain carbocyclic four-membered rings. The illumination of a solution in benzene by light bulbs gave rise to the all-*cis* 1:1 cycloadduct (**11a**) in 76% yield. On its part, this compound reacted with *cis*-**CO** under the action of better sources for UV light with the formation of three isomeric 1:2 cycloadducts. Two of them underwent a photochemical dechlorination leading to a cyclobutene derivative. Albeit rather sluggishly, $^3$**CA** and *trans*-cyclooctene (*trans*-**CO**) brought about an unsymmetrical 1:1 and a 1:2 cycloadduct. By contrast, excited **11a** reacted smoothly with *trans*-**CO** and afforded a 72% yield of the unsymmetrical 1:2 cycloadduct that resulted from $^3$**CA** and *cis*-**CO** in addition to two symmetrical 1:2 cycloadducts. Also, excited **11a** and cyclohexene (**CH**) furnished a bis(cyclobutane) derivative, a significant portion of which was subject to a dechlorination to give a cyclobutene derivative. *cis*,*cis*-1,5-Cyclooctadiene (**COD**) and **CH** were transformed by $^3$**CA** to 1:1 and 1:2 cycloadducts, analogous to *cis*- and *trans*-**CO**. In addition to this, $^3$**CA** suffered photoreduction in the presence of **COD** and **CH**. The [2+2] cycloaddition onto a carbonyl group of $^3$**CA** with formation of a spirooxetane occurred to a small extent only with **COD**, but not at all with *cis*- and *trans*-**CO** and **CH**.

## Introduction

Among the light-induced cycloadditions of quinones with alkenes[1,2] those of chloranil (**CA**) are of particular importance because of the great variety of possible processes. The rapid intersystem crossing ensures that all conversions of excited **CA**, leading to a chemical change of **CA**, start from its triplet state ($^3$**CA**).[3] Depending on the properties of the substrate, $^3$**CA** behaves as a diradical or an electron acceptor. Based on their experimental results and the application of the Weller equation,[4] Xu et al.[5] concluded that $^3$**CA** takes an electron from alkenes with an oxidation potential of $< 2$ V and reacts as a diradical with alkenes having one of $> 2$ V (vs. SCE).

The result of an electron transfer from an alkene to $^3$**CA** is a triplet radical-ion pair, which may collapse to give a cycloadduct onto a carbonyl group of **CA**. As intermediates in this process, diradicals as well as zwitterions can be considered, in which an oxygen atom and a carbonyl carbon atom of **CA**, respectively, have formed a bond to the alkene. Typical cycloadducts are spirooxetanes as in the case of 1,1-dimethylindene,[6] indene,[5] diphenylvinylene carbonate, and a number of stilbenes.[7] If the subunit of the intermediate originating from the alkene has the possibility to undergo a rearrangement, spirotetrahydrofurans can emerge in addition to spirooxetanes as with benzvalene[8] and norbornadiene.[9] With homobenzvalene only products resulting from a rearrangement arise, namely two spirotetrahydrofurans and a spirotetrahydropyran.[9] If the alkene has allylic hydrogen atoms, the radical-ion pair may react to give tetrachlorohydroquinone (**TCH**) or the respective monocycloalkenyl ether of it, as in the cases of 1,3,5-cycloheptatriene,[10] 1,3-cyclohexadiene,[11] cyclohexene, indene, allyl ethyl ether,[5] 2,3-dihydrofuran, and 3,4-dihydro-2*H*-pyran.[12]

The attack of $^3$**CA** as a diradical at an alkene leads to [2+2] cycloadducts of a dichloroethene moiety of **CA**, that is, cyclobutanes. Examples of such alkenes are 2-methylpropene, 1,3-butadiene, 2,3-dimethyl-1,3-butadiene,[13] allyl ethyl ether, methyl methacrylate, vinyl acetate, styrene, α-chlorostyrene, α,*p*-dichlorostyrene,[5] and 1,1-diarylethenes.[14] Cyclobutanes are also formed with cyclopentene (**CP**), norbornene, and bicyclo[2.1.1]hex-2-ene, but significant portions of these cycloalkenes undergo a cycloaddition with $^3$**CA** that eventually gives rise to tetrachlorobenzofuranone derivatives.[15] Apparently, a deep-seated rearrangement of the subunit stemming from **CA** proceeds in these reactions. Scheme 1 summarises the compounds obtained

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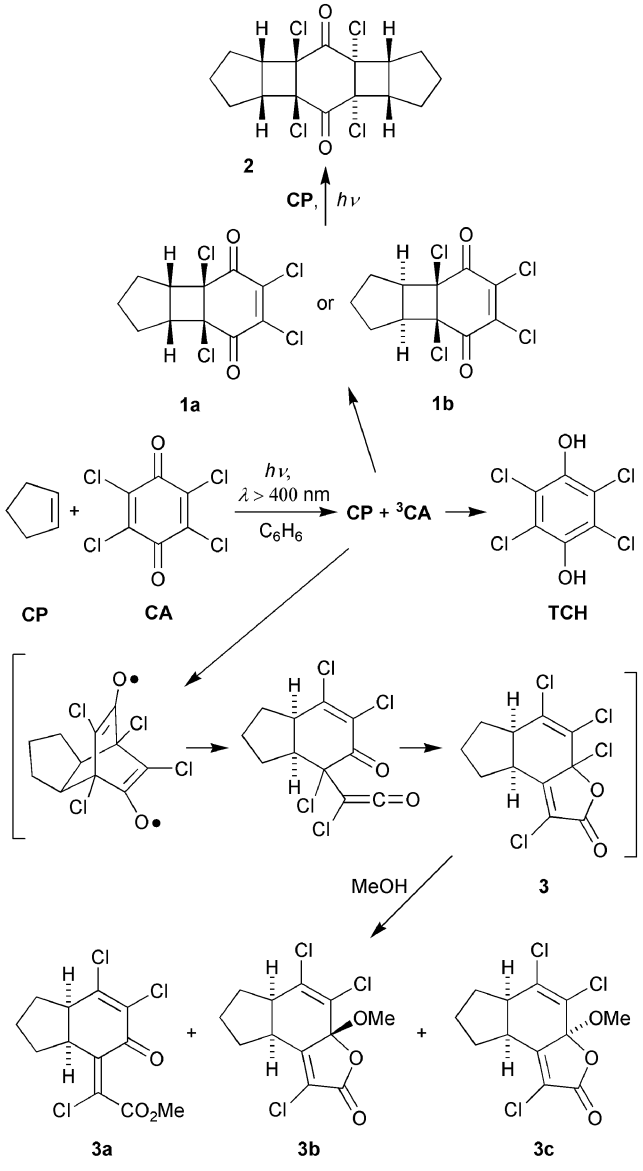
from **CP**, with which $^3$**CA** undergoes three parallel reactions: the photoreduction to give **TCH** (8% yield), a [2+2] cycloaddition, resulting in cyclobutane **1a** or **1b** (9%) and eventually also in **2** (8%), and a [4+2] cycloaddition. The latter leads to a diradical (Scheme 1), a C–C bond of which breaks with formation of an α-chloro-β-oxo ketene. This compound rearranges to give the tetrachlorobenzofuranone **3**, which was not isolated but exposed to methanol. The methyl ester **3a** (15%) and the methyl pseudoesters **3b**,**c** (13%) were then obtained.[15] By using norbornene as a substrate, the pseudoacyl chloride analogous to **3** was isolated in 67% yield.[15]




Scheme 1. Compounds formed in the photochemical reaction of chloranil (**CA**) with cyclopentene (**CP**) in the ratio of 1:2 and the pathway to products **3a**–**c** according to ref.[15]

Alkenes with an oxidation potential close to the value of 2 V (vs. SCE) may give products that result from an electron transfer to $^3$**CA** and from the addition of $^3$**CA** as a diradical to the substrate. The product ratio depends on the solvent polarity in such cases.[5,7,14,15]

When dividing the alkenes into two kinds of different behaviour towards $^3$**CA**, that is, electron transfer to $^3$**CA** and addition of $^3$**CA** as a diradical, the oxidation potential of 2 V (vs. SCE) is not a strict borderline. There are exceptions to this rule, for example (*E*)-β-bromostyrene and α,β-unsaturated carbonyl compounds, which have oxidation potentials of 2.3 and about 2.4 V, respectively, and yet exclusively produce spirooxetanes.[5,7] Steric hindrance of the addition of these alkenes onto a dichloroethene moiety of $^3$**CA** in favour of that onto a carbonyl group has been invoked to explain the outcome.[5,7]

The present work describes the addition of **CP** onto $^3$**CA** under conditions different from those in the previous experiment[15] and deals with the reactions of *cis*- and *trans*-cyclooctene (*cis*- and *trans*-**CO**), *cis*,*cis*-1,5-cyclooctadiene (**COD**), and cyclohexene (**CH**). Those of *cis*-**CO**, **COD** and **CH** have already been investigated; the structures of the products claimed are collected in Figure 1.

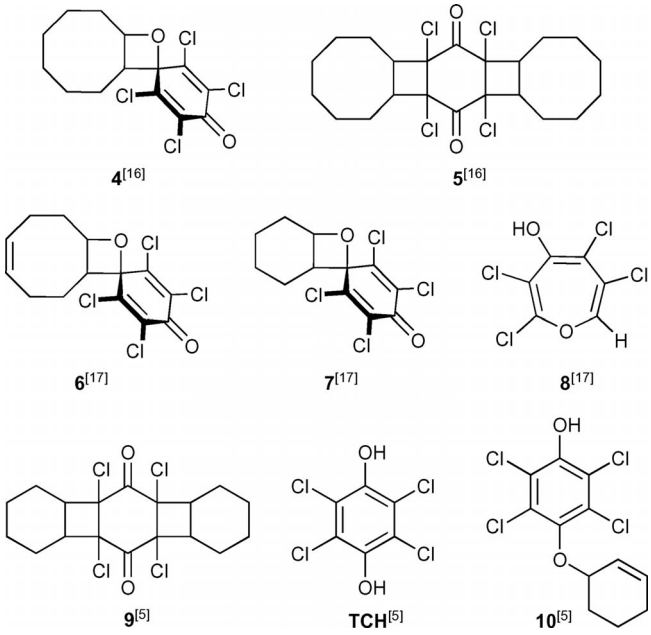



Figure 1. Structures of the products described in the literature[5,16,17] to be formed from excited chloranil ($^3$**CA**) with *cis*-cyclooctene (*cis*-**CO**), *cis*,*cis*-1,5-cyclooctadiene (**COD**), and cyclohexene (**CH**).

Bryce-Smith and Gilbert[16] reported the formation of the spirooxetane **4** and the 1:2 cycloadduct **5**, having two cyclobutane subunits, on irradiation of **CA** in benzene in the presence of *cis*-**CO**. They also noted that "1,5-cyclooctadiene shows closely parallel behaviour to that of cyclooctene". Kim et al.[17] described the production of the spirooxetanes **6** and **7** with **COD** and **CH**, respectively, both dissolved in dichloromethane together with **CA**. Further, they claimed the conversion of **CA** into the oxepin **8** during the photoreaction of **CA** with **CH** as well as with 1,3-cyclohexadiene and 1,3,5-cycloheptatriene. Without reference to the Korean work,[17] Xu et al.[5] published their results on

the irradiation of **CA** in the presence of **CH**, for which they utilised a filter solution that prevented the entrance of light of $\lambda < 400$ nm into the reaction vessel. They obtained the 1:2 cycloadduct **9** and **TCH** from the photolysis in benzene solution, whereas the reaction in acetonitrile brought about only **TCH** and the monocyclohexenyl ether **10** of **TCH**. When dichloromethane served as solvent, all of the compounds **9**, **10**, and **TCH** were found.

As to the oxepin **8**, we believe that the authors[17] are in error, since neither Xu et al.[5] gave any indication nor did we find a clue for **8** (see below). Rather, **TCH** was mistaken for **8**, as the melting point of 240 °C is very close to that of **TCH** (m.p. 236–237 °C[18]), and the two signals in the $^1$H NMR spectrum ($\delta$ = 8.90 and 3.75 ppm), assigned to OH and CH of **8**, most probably originate from OH of **TCH** and residual water of [$D_6$]acetone used as solvent. The final proof is provided by the other published spectroscopic data (MS, IR, UV),[17] which virtually exactly match our data of **TCH**. Only in the IR spectrum did we find important bands at 1411 and 1307 cm$^{-1}$ in addition to those mentioned by Kim et al.[17]

The first motivation for the present study was to find out whether or not **CH** and *cis*-**CO** give rise to tetrachlorobenzofuranone derivatives analogous to **3** (Scheme 1). In the case of **CP**, **3a**–**c**, the consecutive products of **3** with methanol, constituted about 50% of the amount of the products isolated, and a spirooxetane was not observed. Norbornene furnished the tetrachlorobenzofuranone derivative as major product by far and a small amount of a cyclobutane analogous to **1**, when the substrates were irradiated in benzene. The utilisation of a 1:1 mixture of benzene/methanol as solvent led to a dramatic setback of the yields, but also to the formation of a small amount of the spirooxetane. Dissolved in benzene, bicyclo[2.1.1]hex-2-ene gave a cyclobutane and a tetrachlorobenzofuranone derivative in addition to the spirooxetane, which was the main product. In the series of these three cycloalkenes, the tendency for spirooxetane formation increases with decreasing oxidation potential: **CP**, 2.03 V; norbornene, 1.95 V; bicyclo[2.1.1]hex-2-ene, 1.88 V (all vs. SCE).[15]

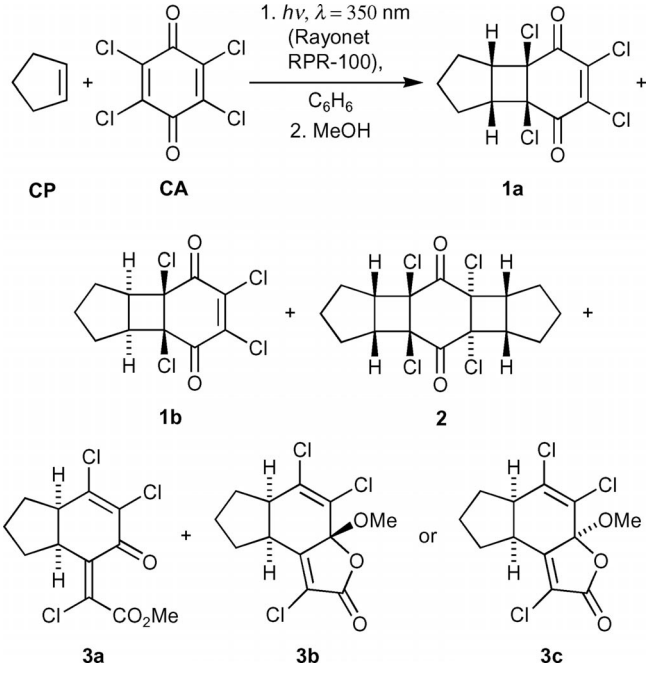
The oxidation potentials of **CH** and *cis*-**CO** are 2.14 and 2.01 V (vs. SCE),[19] respectively, and are thus significantly higher and only marginally lower than that of **CP**. Hence, the electron transfer from these cycloalkenes onto $^3$**CA** should occur more difficult than and similarly difficult as from **CP**, where merely **TCH**, isolated in a yield of 8%, can be rated as an indication of an intermediate radical-ion pair. If it is accepted that the formation of spirooxetanes also proceeds via radical-ion pairs, the production of **7** and **4** (Figure 1) from **CH** and *cis*-**CO**, respectively, is hard to conceive on the basis of the oxidation potentials of the latter. Thus, the examination of whether or not **CH** and *cis*-**CO** bring about spirooxetanes with $^3$**CA** in benzene was the second motivation for our investigation.

Finally, there was the question for 1:1 cycloadducts of **CH** and *cis*-**CO** onto **CA** containing a cyclobutane moiety, which do have to be considered as intermediate compounds en route to the 1:2 cycloadducts **9** and **5**, respectively. After all, the corresponding 1:1 cycloadduct **1** was observed in addition to the 1:2 cycloadduct **2** in the case of **CP** (Scheme 1). However, Xu et al.[5] did not mention a respective compound derived from **CH**, and Bryce-Smith and Gilbert[16] explicitely excluded such a compound derived from *cis*-**CO**.

## Results and Discussion

### 1. Reaction of Chloranil (CA) with Cyclopentene (CP) under Conditions Different from Those of the Previous Experiment

Illustrated in Scheme 1, the products of the first experiment had ensued from **CP** and **CA** in a ratio of 2:1 in benzene, irradiated by a Hanovia medium-pressure mercury lamp (450 W) through a glass filter that was believed to prevent the passage of light of $\lambda < 400$ nm. Now, we employed a Rayonet photochemical reactor RPR-100, radiating at $\lambda$ = 350 nm, and used **CP** and **CA** in a ratio of 1.00:1.22. This changed the product spectrum (Scheme 2) somewhat, as not only one of the 1:1 cycloadducts **1** was obtained, but both of them resulted (**1a** and **1b**). However, it still remains open whether configuration **1a** or **1b** has to be assigned to the previously described compound and which configuration to the newly observed one. As expected from the substoichiometric quantity of **CP**, just a very small amount of the 1:2 cycloadduct **2** was formed. That only one of the methyl pseudoesters **3b** and **3c** was observed and no **TCH** may be an artefact of the chromatographic workup.



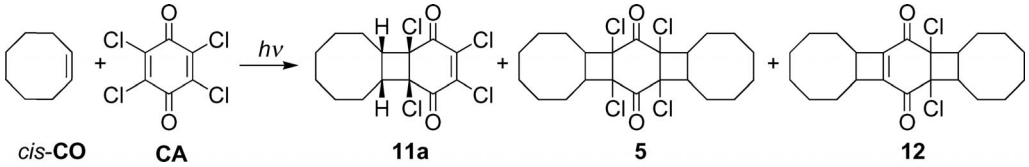

Scheme 2. Products of the photochemical reaction of chloranil (**CA**) with cyclopentene (**CP**) in a ratio of 1.22:1.00.

### 2. 1:1 Cycloadduct of *cis*-Cyclooctene (*cis*-CO) onto Chloranil (CA)

The first experiment (Entry 1 of Table 1) was conducted as the reactions of **CP**, norbornene, and bicyclo[2.1.1]hex-

Table 1. Conditions and products of a series of photochemical reactions of **CA** with *cis*-**CO**.




*cis*-**CO** **CA** **11a** **5** **12**

| Entry | *cis*-**CO** [mmol] | **CA** [mmol] | Solvent | Light source | Duration of illumination [h] | Yield of **11a** [%] | Yield of **5** [%] | Yield of **12** [%] |
|---|---|---|---|---|---|---|---|---|
| 1 | 8.14 | 4.07 | $C_6H_6$ | Hanovia 450 W, glass filter, $\lambda > 400$ nm | 5 | 13 | 32 | [a] |
| 2 | 8.14 | 8.13 | $C_6H_6$ | Rayonet RPR-100, $\lambda = 350$ nm | 2.5 | 39 | [b] | [a] |
| 3 | 16.2 | 8.13 | $C_6H_6$ | Rayonet RPR-100, $\lambda = 350$ nm | 3 | 2 | 14 | 18 |
| 4 | 81.2 | 40.7 | $C_6H_6$ | light bulbs, total power 500 W | 60 | 76 | [b] | [a] |
| 5 | 32.6 | 3.25 | $CH_3CN$ | light bulbs, total power 1000 W | 3.5 | [c] | [c] | [a] |
| 6 | 72.6 | 16.3 | $CH_2Cl_2$ | light bulbs, total power 1000 W | 36 | [d] | 46 | [a] |
| 7 | 461 | 16.3 | $C_6H_6$ | medium-pressure Hg lamp, 150 W, Pyrex immersion well | 13.5 | [d] | 33[e] | [a] |

[a] No **12** observed. [b] No **5** observed. [c] The products **5c** and **11a** were formed in a ratio of 1.0:1.3. [d] No **11a** observed. [e] Yield of pure **5c**. The combined amount of **5a**, **5b**, and **5c** in the crude product corresponds to a yield of 79%.

2-ene with $^3$**CA**.[15] Hence, the crude product of the irradiation was treated with methanol, but no compounds containing a methoxy group were discovered. The chromatographic workup provided three fractions, the first two of which consisted of three 1:2 cycloadducts of the constitution **5** (see Section 3). Owing to the chemical shifts and the number of the signals, the $^{13}$C NMR spectrum of the third fraction immediately disclosed constitution and symmetry of the 1:1 cycloadduct **11a**, which was obtained as a slightly contaminated colourless oil.

Whereas *cis*-**CO** and **CA** were used in a ratio of 2:1 in the above experiment, we chose a ratio of 1:1 of the substrates, again dissolved in benzene, for the second experiment (Entry 2 of Table 1), which was carried out in a Rayonet photochemical reactor, radiating at $\lambda = 350$ nm. The 1:1 cycloadduct of the first experiment was formed as the only product of a significant amount and purified by chromatography to give crystals in 39% yield. A single-crystal X-ray diffraction analysis corroborated the constitution and established the all-*cis* configuration as illustrated by formula **11a**.[20] After a 2:1 mixture of *cis*-**CO**/**CA** in benzene had been irradiated in the Rayonet reactor (Entry 3 of Table 1), only a small quantity of **11a** was observed as well as some **5** and, being the main result, two new compounds, which were identified to be the consecutive products **12** of **5** (see Section 3). The best yield of **11a** (76%) was achieved by illumination of a 2:1 mixture of *cis*-**CO**/**CA** just with light bulbs (Entry 4 of Table 1).

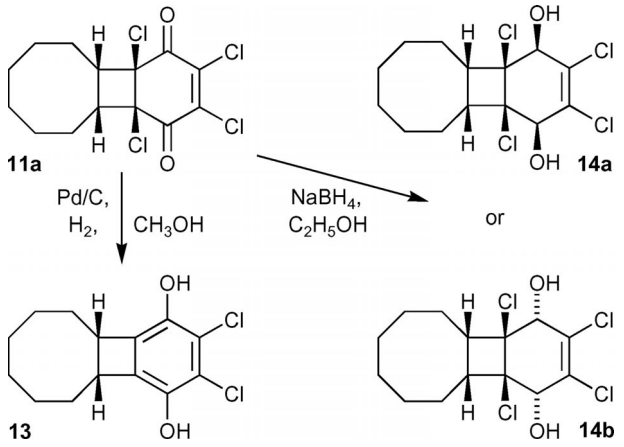
The change of the solvent from benzene to acetonitrile and dichloromethane (Entries 5 and 6 of Table 1) furnished different results on irradiation with light bulbs, as **5** emerged in addition to **11a** and exclusively, respectively. Since the latter solvents are more transparent for UV light than benzene, it has to be concluded that **11a** is very effectively excited by the weak UV radiation generated by light bulbs and is highly prone to cycloaddition in that state.

Finally, we employed conditions that approached those described by Bryce-Smith and Gilbert[16] as close as possible to us (Entry 7 of Table 1). Instead of a Hanovia S-500 medium-pressure mercury lamp, we utilised a 150 W lamp of the same kind. The amounts of **CA**, *cis*-**CO**, and benzene given yield a suspension of **CA**, which is why we stirred the mixture. The irradiation was then performed at 10 °C for 13.5 h, whereas it had been conducted at 30 °C over 64 h on the fivefold scale previously. We exclusively observed three products **5** and isolated **5c** (see Section 3) in 33% yield. On the basis of the melting point, this compound had been obtained in 42% yield earlier.[16] There was no indication for both **11a** and the spirooxetane **4**. The isolation of the latter in 51% yield had been claimed in 1964.[16] The fact that we did not find a 1:1 cycloadduct could have had its cause in the different lamp employed and the complete conversion of **CA** in our case as compared to only 30% previously.[16]

As to the spirooxetane **4**, we suspect that Bryce-Smith and Gilbert[16] mistook **11a** for **4**. In 1964, $^{13}$C NMR spectroscopy was not available, and the authors had to rely on less direct evidence. However, even this evidence is at variance with the properties of **11a**. Strong IR absorptions at 1675 and 965 cm$^{-1}$ were reported as well as a UV band at 262 nm ($\log\varepsilon = 3.81$).[16] Compound **11a** shows strong IR absorptions at 1715 and 1697 cm$^{-1}$, whereas the one closest to the value of 965 is at 945 cm$^{-1}$, but only of medium intensity. The maximum of the UV spectrum lies at 282 nm with $\log\varepsilon = 4.08$. In addition, the catalytic hydrogenation of the alleged **4** was carried out and believed to result in a

monohydric phenol with a melting point of 190 °C.[16] We hydrogenated **11a** and obtained the hydroquinone derivative **13** (Scheme 3), the structure of which was easily deduced from its $^{13}C$ NMR spectrum and which has a melting point of 208 °C. Barltrop und Hesp[13] had arrived at similar hydroquinones on hydrogenation of the 1:1 cycloadducts of 1,3-butadiene and 2,3-dimethyl-1,3-butadiene.




Scheme 3. Hydrogenation of **11a** and its reduction with sodium borohydride.

Interestingly, the reduction of **11a** with sodium borohydride did not lead to **13** but to a product that contained 2 equiv. of hydrogen chloride more than **13**, and for which we propose structure **14a** or **14b** (Scheme 3). This result may be taken as indication against the hydrogenation of the carbonyl groups en route to **13**, as it would give rise to an isomer **14** as well. Rather, the hydrogenolysis of the C–Cl bonds[21] at the four-membered ring could have occurred, with the resultant product tautomerising to **13**.

### 3. Cycloadducts of *cis*- (*cis*-CO) and *trans*-Cyclooctene (*trans*-CO) as well as Cyclohexene (CH) onto the 1:1 Cycloadduct 11a

In order to confirm the assumption that the route to the 1:2 cycloadducts **5** of *cis*-**CO** onto **CA** proceeds via the 1:1 cycloadduct **11a**, we monitored the course of the reaction by HPLC. The ratio of the substrates, the solvent and the irradiation conditions were close to those of Entry 3 of Table 1; only the scale was reduced to one quarter. Recorded before the lamps of the reactor were turned on, the first chromatogram showed already a small signal of **11a** in addition to that of **CA**. Apparently, the daylight had started the photocycloaddition. After 30 min of irradiation, the concentration of **CA** had substantially decreased and that of **11a** was at its maximum. No further compounds in significant quantities were discernible at that time. After 1 h, **CA** had been consumed completely, the concentration of **11a** had decreased somewhat, and two new products were present, which were characterised to be **5** and **12** on the basis of the retention times by injection of authentic samples. On further irradiation, the decrease of the concentration of **11a** continued, and that of **5** diminished as well, whereas that of **12** increased. Constructed from data of the irradiation over 2.5 h, the turnover diagram is in line with the conversions of **CA** into **11a**, of **11a** into **5**, and of **5** into **12**. In these processes, the second and third step require direct excitation of the respective substrate by light, as **CA** is not present anymore and could thus not act as a sensitiser after 1 h.

In view of the longest-wavelenght absorption of **11a** ($\lambda$ = 282 nm), it is surprising that **11a** was excited and underwent cycloaddition with *cis*-**CO** even under irradiation with light of $\lambda > 400$ nm (Entry 1 of Table 1). The UV spectrum of **11a** supports an $\varepsilon$ value of 10 $L\,mol^{-1}\,cm^{-1}$ or less at 400 nm as compared to 12023 $L\,mol^{-1}\,cm^{-1}$ at 282 nm. Therefore, either the excitation of **11a** must have been very efficient or the glass filter utilised in the experiment did not completely inhibit the passage of light with $\lambda < 400$ nm. We tend to believe the latter, since the illumination of a benzene solution of the substrates with light bulbs brought about **11a** exclusively (Entry 4 of Table 1). Under these conditions, the excitation of **11a** by 400-nm light would have been possible but apparently did not occur. However, if solvents more transparent for UV light than benzene were taken, the formation of **5** proceeded smoothly (Entries 5 and 6 of Table 1), even promoted by the weak UV irradiation of the light bulbs. The exclusive production of **11a** on irradiation in the Rayonet reactor ($\lambda$ = 350 nm, Entry 2 of Table 1) was due to the ratio **CA**/*cis*-**CO** = 1:1. Obviously, *cis*-**CO** was very efficiently used up by $^3$**CA**, and the excitation of **11a** was much less successful than that of **CA** under these conditions, which is why after the consumption of **CA** no *cis*-**CO** was left for the reaction with **11a**.

Previously, the question of isomerism possible for the constitution **5** remained unaddressed.[16] In addition to some **11a**, our first experiment (Entry 1 of Table 1) furnished a mixture of three diastereomers **5**. One of them had already been isolated by Bryce-Smith and Gilbert[16] and was now again prepared as a pure compound in the experiments of Entries 1, 6, and 7 (Table 1). Owing to only six signals in the $^{13}C$ NMR spectrum, three of them stemming from the methylene groups, the molecule must have two symmetry elements. Since the shape of half the molecule is determined by the $C_s$ symmetry of its precursor, i.e. **11a**, the molecular point group must be either $C_{2h}$ or $C_{2v}$ and, hence, the structure **5c** or **5c′** (Figure 2). En route to **5c′**, *cis*-**CO** would have to approach the excited **11a** from the *endo* side, which is sterically strongly hindered by the cyclooctane subunit, and thus we prefer **5c** over **5c′**, although there is no reliable experimental evidence for this assumption. This uncertainty also pertains to the configuration of the other isomers **5** (Figure 2) as well as **9** (Scheme 8), **12** (Scheme 5), **15** and **16** (Scheme 6), and **18** (Scheme 7).

The identity of the two further diastereomers of **5** was clarified by an independent experiment, in which **11a** was illuminated in the presence of *trans*-cyclooctene (*trans*-**CO**) to give an unsymmetrical diastereomer **5** in 72% yield (Scheme 4). This compound turned out to be one of the diastereomers of **5** observed in the experiments of Entries 1 and 3 (Table 1) by comparison of the $^{13}C$ NMR spectra.

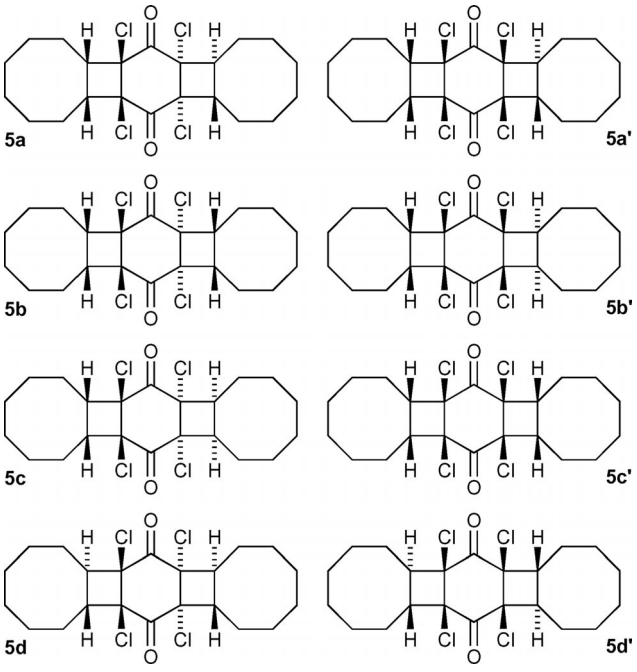
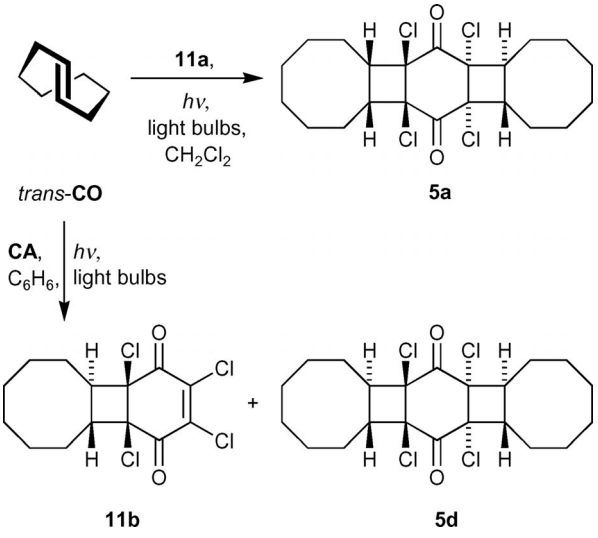



Figure 2. Possible configurations of 1:2 cycloadducts of excited chloranil ($^3$**CA**) onto *cis*- (*cis*-**CO**) and *trans*-cyclooctene (*trans*-**CO**). It is discussed in the text why we favour **5a**–**d** over **5a′**–**d′**.

From the expected 22 signals, 21 were resolved, and the double intensity of the line at $\delta$ = 24.7 ppm indicated the coincidence of two signals. By taking into account the $C_s$ symmetry of **11a**, again two possibilities are in accord with the data, namely the structures **5a** and **5a′** of Figure 2. Again we favour the result of the *exo* addition of the olefin (*trans*-**CO**) onto the excited **11a**, i.e. **5a**, since the *endo* addition, from which **5a′** would emerge, should severely suffer from steric encumbrance by the cyclooctane subunit of **11a**.




Scheme 4. Products of the photochemical reactions of chloranil (**CA**) and the 1:1 cycloadduct **11a** of **CA** onto *cis*-cyclooctene (*cis*-**CO**) with *trans*-cyclooctene (*trans*-**CO**).

Observed in the experiments of Entries 1 and 3 (Table 1) and having the constitution **5**, the third diastereomer could not be isolated. Its configuration was deduced from the $^{13}$C NMR spectrum of the three-component mixture by subtraction of the signals of **5a** or **5a′** and **5c** or **5c′**. Eight lines were the result, in particular one of carbonyl, two of CCl and two of CH groups. This supported a structure with a symmetry plane, if the symmetry plane of the precursor (**11a**) is accounted for. The missing of three signals originating from methylene groups was readily explained by superposition of absorptions of **5a** or **5a′** and **5c** or **5c′**, which cause 15 signals in the narrow region from $\delta$ = 23.4 to 29.4 ppm. Based on the steric hindrance of the *endo* addition of *cis*-**CO** onto excited **11a**, already advanced with regard to the formation of **5a** or **5a′** and **5c** or **5c′**, we prefer structure **5b** over the alternative **5b′** (Figure 2). By the way, the configuration of **5b** corresponds to that of **2**, the only 1:2 cycloadduct of **CP** onto **CA** (Scheme 1) known so far.[15]

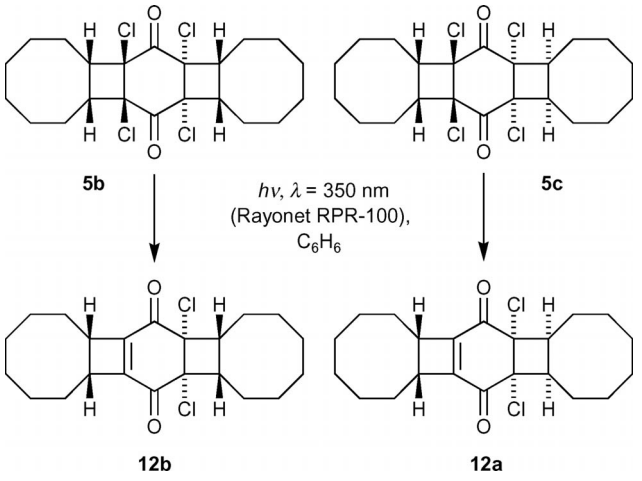
A fourth diastereomer with the constitution **5** was obtained when a mixture of **CA** and *trans*-**CO** in benzene was irradiated. Its $^{13}$C NMR spectrum contained 11 signals, and hence the $C_i$ and $C_s$ symmetric structures **5d** and **5d′** (Figure 2), respectively, are possible. We prefer **5d**, since en route to this compound the excited precursor **11b** (Scheme 4) would have bound *trans*-**CO** at the *exo* side, whereas **5d′** would have resulted from an *endo* addition, which should be impeded by steric overcrowding.

It is interesting to note that the reactions of $^3$**CA** with *cis*- and *trans*-**CO** did not lead to a common product. Somewhat differently, the additions of excited **11a** onto *cis*- and *trans*-**CO** both yielded **5c** or **5c′**, which was the sole product emerging from *trans*-**CO**, but only one of three isomers in the case of *cis*-**CO**.

On irradiation of a 2:1 mixture of *cis*-**CO**/**CA** in benzene in the Rayonet reactor ($\lambda$ = 350 nm), two diastereomers with the constitution **12** were formed as major products (Entry 3 of Table 1). When a 1:1 mixture of **11a**/*cis*-**CO** was treated in the same way, only the isomers **12** were obtained. Their origin from the 1:2 cycloadducts **5** was obvious from the monitoring of the reaction course by HPLC (see above). This dechlorination was corroborated by the irradiation of a pure sample of **5c** or **5c′**, dissolved in $C_6D_6$ in an NMR tube. Although a number of byproducts were generated, the conversion of **5c** or **5c′** into only one of the diastereomers **12** was proved beyond doubt. Provided the structure **5c** is correct, the configuration of the dechlorination product must be **12a** (Scheme 5). Akin to **12a**, its diastereomer is also characterised by a plane of symmetry, which is why it cannot be a consecutive product of **5a** or **5a′**, but had to arise from **5b** or **5b′**. We assign structure **12b** or the corresponding alternative configuration to it (Scheme 5).

The formation of the cyclohexenediones **12** occurred only on irradiation in the Rayonet reactor ($\lambda$ = 350 nm), but did not with the other light sources. Probably, in the case of the latter, the intensity of the UV light necessary to excite the saturated ketones **5** is too low. The dechlorination of **5** should start with the breaking of a C–Cl bond, which is a β cleavage within an excited ketone. Such reactions are well known for α-functionalised ketones, among them α-

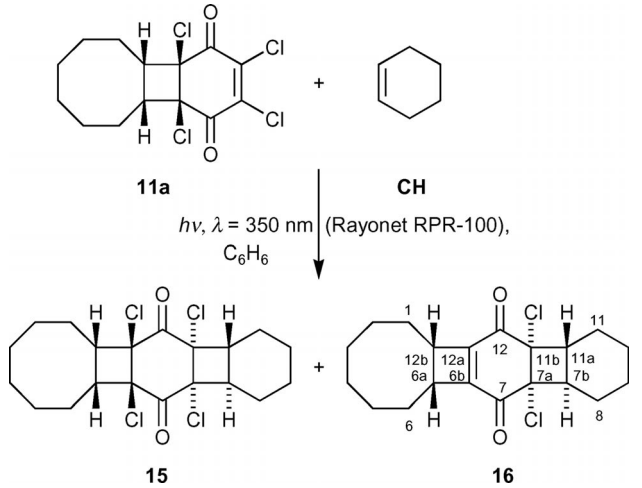
  




Scheme 5. Photodechlorination of the 1:2 cycloadducts **5b** and **5c**.

halo ketones.[22,23] In addition, photochemical β eliminations of two chlorine or two fluorine atoms with formation of a C–C double bond were discovered some time ago.[24,25]

Using **11a** as an easily available and excitable substrate, we not only performed the addition of *cis*- and *trans*-**CO** but also that of cyclohexene (**CH**). Because of the Rayonet reactor ($\lambda$ = 350 nm) being the light source, the [2+2] cycloadduct and its dechlorination product were obtained in yields of 33 and 45%, respectively. We assign them the structures **15** and **16** (Scheme 6). As 20 signals in the $^{13}C$ NMR spectrum indicate, the [2+2] cycloadduct does not possess any symmetry. On the basis of the $C_s$ symmetry of **11a**, **CH** was attached antarafacial. Thus, the newly formed bicyclo[4.2.0]octane system has a *trans* ring junction (see Section 5 for the strain energy difference of *cis*- and *trans*-bicyclo[4.2.0]octane). We propose structure **15**, because the assemblage of the central unit with two cyclobutane moieties located *trans* at the cyclohexanedione subunit should suffer from much less steric congestion than the alternative with mutually *cis*-orientated cyclobutanes.

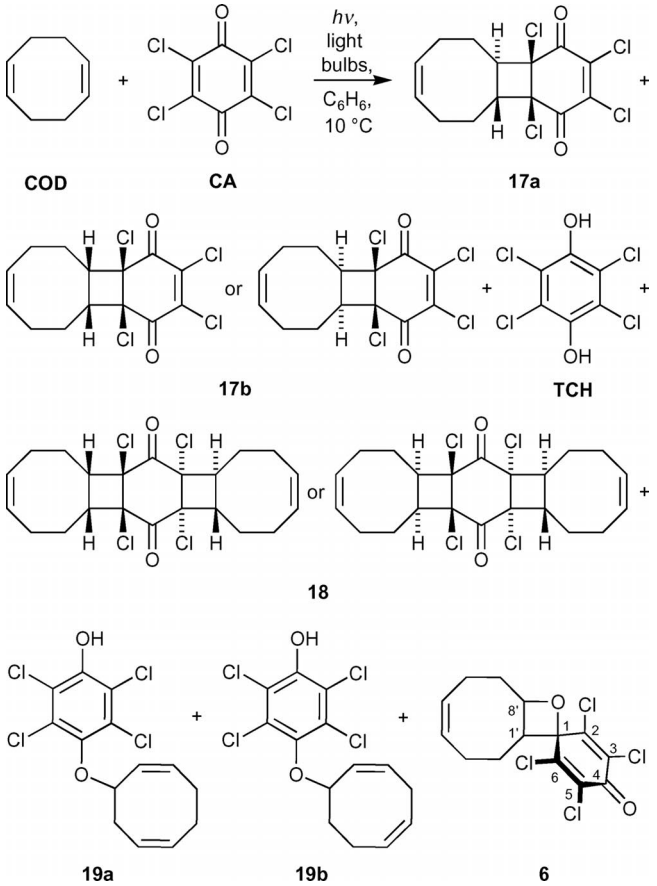



Scheme 6. Products of the photochemical reaction of **11a** with cyclohexene (**CH**).

With respect to the dechlorination of **15**, there are two possibilities, one at the side of the cyclohexane and the other at the side of the cyclooctane moiety. Giving rise to **16**, the latter mode was proved by NMR experiments. At first, the signals of cyclobutene protons were identified by means of an HMBC spectrum due to their coupling with the olefinic carbon atoms. And secondly, it was shown by an H,H-COSY spectrum that the CH groups of the cyclobutene subunit are parts of an eight-membered rather than a six-membered ring.

### 4. Reaction of Chloranil (CA) with *cis*,*cis*-1,5-Cyclooctadiene (COD) and an Attempt To Use 1,3,5,7-Cyclooctatetraene (COT) as Substrate

For the reaction with *cis*,*cis*-1,5-cyclooctadiene (**COD**), **CA** was dissolved in benzene and excited with light bulbs. Thus, the conditions were similar to those of the cycloaddition onto *cis*-**CO** as given in Entry 4 of Table 1. A large excess of **COD** was used (ratio of **COD**/**CA** = 20:1) in the first experiment, which gave rise to an oxetane **6** (7% yield), a 1:2 cycloadduct **18** (22% yield), the monocyclooctadienyl ethers **19** (24% yield) of tetrachlorohydroquinone (**TCH**) and **TCH** (6% yield) (Scheme 7). Signals of a 1:1 cycloadduct **17** could not be discerned in the NMR spectra of the




Scheme 7. Products of the photochemical reactions of chloranil (**CA**) with *cis*,*cis*-1,5-cyclooctadiene (**COD**).

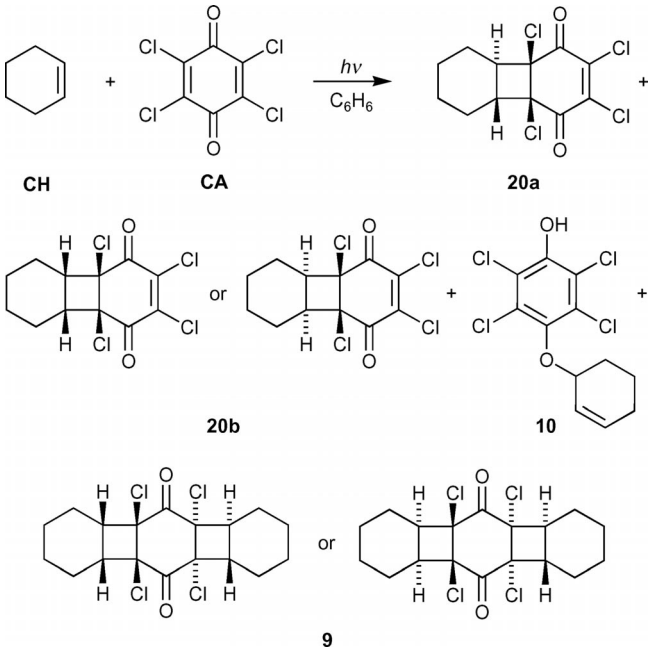
crude product. In order to obtain information whether or not **17** is an intermediate en route to **18**, we performed the second experiment with a ratio of **COD/CA** = 1:1. Indeed, two diastereomers with the constitution **17** (Scheme 7) were obtained in addition to the two isomers **19** and a small amount of **6**. The spectra of the crude product provided no evidence for **18**. Although **6** and **19** could be removed from the mixture by chromatography, we failed to separate the diastereomers **17** and even to prepare an analytically pure sample of their mixture. However, as judged on the basis of their $^{13}C$ NMR chemical shifts, the configurations of the diastereomers **17** (Scheme 7) are likely to be analogous to those of **11a** and **11b**.

Beyond the fact that **18** is unsymmetric, we have no evidence as to its precise configuration. However, we prefer the *trans* orientation of the two cyclobutane entities at the six-membered ring (Scheme 7) according to the reasoning advanced for the case of the compounds **5** (Figure 2). Also, we made no attempt to establish the junction of the four- and the eight-membered ring of **6** to be *cis* or *trans*. Further, the routine NMR spectroscopic data do not allow the assignment of the structure **19a** or **19b** to the major one of the two isomers.

In view of the fair yield of **18**, we were encouraged to attempt the cycloaddition of 1,3,5,7-cyclooctatetraene (**COT**) onto **CA**, all the more so as this substrate has no allylic hydrogen atoms and hence cannot furnish products like **19**. Unfortunately, we did not observe any reaction at all. The reason for this may be the colour of **COT**, which does have the absorption maximum at 280 nm, but the band extends into the visible region, which is why **COT** is yellow.[26] Thus, it may prevent the excitation of **CA** by completely consuming the relevant light.

## 5. Reaction of Chloranil (CA) with Cyclohexene (CH)

Three products were isolated after a benzene solution of a 2:1 mixture of **CH/CA** had been irradiated with a Hanovia medium-pressure mercury lamp, which was surrounded by a glass filter supposed to inhibit the passage of light of $\lambda < 400$ nm. According to the melting point and the elemental analyses, two of the products were identified as the 1:2 cycloadduct **9** (30% yield) and the monocyclohexenyl ether **10** (20% yield) of **TCH**, which had been obtained by Xu et al.[5] previously. These authors did not address the configuration of **9**. Based on the $^{13}C$ NMR spectrum, we ascribe **9** an unsymmetrical structure. The ranges of the $^{13}C$ NMR chemical shifts of the $CH_2$, the CH, and the CCl groups of **9** are well in accord with the presence of a *cis*- and a *trans*-bicyclo[4.2.0]octane system, since the values of the respective parent hydrocarbons exhibit substantial differences.[27] As estimated by quantum chemical calculations, the strain energy of *trans*-bicyclo[4.2.0]octane exceeds that of the *cis* isomer by only 4.6 kcal mol$^{-1}$.[28] Certainly, this quantity is not large enough to restrict the system to the *cis* annulation. As in the case of 1:2 cycloadducts **5**, we assume that the cyclobutane entities should be orientated *trans* at the cyclohexanedione core for steric reasons (see Figure 2). Even then, two configurations have to be taken into account for **9**, which are illustrated in Scheme 8.




Scheme 8. Products of the photochemical reactions of choranil (**CA**) with cyclohexene (**CH**).

Isolated in 10% yield, the third product was characterised to be the 1:1 cycloadduct **20a** by the $^{13}C$ NMR spectrum due to its similarity to the spectra of **11a** and **11b**. The number of lines indicates an unsymmetrical structure, which should be caused by the *trans* junction of the four-membered and the saturated six-membered ring. Another origin for the missing symmetry could be the *trans* junction of the cyclobutane and the cyclohexenedione subunit. However, this possibility seems unlikely because of the rigidity of the unsaturated six-membered ring, which would result in a significantly higher strain energy than that accepted by the *trans* annulation of the cyclohexane subunit.

In a second experiment, a 1:1 mixture of **CH/CA**, dissolved in benzene, was irradiated in a Rayonet photochemical reactor with light of $\lambda = 350$ nm. Two of the three products formed were the same as in the first experiment, namely **10** and **20a**. In addition, a symmetrical diastereomer of **20a** was obtained, for which the two structures **20b** are possible (Scheme 8). The 1:2 cycloadduct **9** was not observed. Apparently, all **CH** was consumed by excited **CA**, and hence it was no longer available for the addition onto the excited enediones **20**.

In none of the two experiments, was any evidence found for the spirooxetane **7**. Thus, we believe that the report of Kim et al.[17] is in error with regard to **7**. On treatment of the crude product of the first experiment with methanol, no compounds carrying a methoxy group were generated. This finding excludes a photochemical process that would give rise to a tetrachlorobenzofuranone derivative analogous to compound **3** in the reaction of **CP** (Scheme 1).

### 6. Comparison of the Cycloalkenes as to Their Reactivity towards Excited Chloranil ($^3$CA) and the Stereochemical Course of Their Cycloadditions

In contrast to that of cyclopentene (**CP**), the reactions of cyclohexene (**CH**) and *cis*-cyclooctene (*cis*-**CO**) with excited **CA** do not produce tetrachlorobenzofuranone derivatives. Such a transformation seems to require the angle strain of **CP** and its derivatives. No spirooxetanes emerged from **CH** and *cis*-**CO**. In this respect, these cycloalkenes behaved like **CP**, which is in accord with the rule of Xu et al.[5] that an electron transfer from the alkene onto $^3$**CA** initiates spirooxetane formation, but occurs only with alkenes having an oxidation potential of $< 2$ V vs. SCE. On the basis of the values of 2.01 (*cis*-**CO**),[19] 2.03 (**CP**),[29] and 2.14 V (**CH**),[19] the previous reports about the production of the spirooxetanes **4**[16] and **7**[17] from *cis*-**CO** and **CH**, respectively, seemed unlikely and have indeed to be revised. However, the outcome of the photochemical reaction of **CA** with *cis*,*cis*-1,5-cyclooctadiene (**COD**) shows that the oxidation potential is not a reliable criterion for or against spirooxetane formation. The value of 2.07 V vs. SCE[19] is larger than those of *cis*-**CO** and **CP**, and yet the spirooxetane **6** was isolated in 7% yield in addition to the cyclobutane derivatives **17** and **18**, tetrachlorohydroquinone (**TCH**), and its monocyclooctadienyl ethers **19**. Thus, the claim of Kim et al.[17] was correct with regard to the observation of **6**.

In the case of *trans*-cyclooctene (*trans*-**CO**), the oxidation potential is not a good lead either, since the value of about 1.75 V vs. SCE, estimated from the first vertical ionisation potential (8.69 V[30])[31] would support the expectation of an electron transfer onto $^3$**CA** and thus the generation of a spirooxetane, which we did not observe. Surprisingly, the reaction of *trans*-**CO** did not proceed as smoothly as that of *cis*-**CO**, which is testified by our failure to isolate pure **11b**. It seems that the strain energy of *trans*-**CO** does not promote the addition onto $^3$**CA**, although it exceeds that of *cis*-**CO** by 9.3 kcal mol$^{-1}$.[32]

The only cycloalkene to produce a 1:1 cycloadduct with $^3$**CA** in good yield, namely **11a**, was *cis*-**CO**. The consecutive reaction of **11a** with *cis*-**CO** could easily be avoided by the choice of light bulbs for the irradiation and benzene as solvent. With **CP**, **CH**, and **COD**, $^3$**CA** gave rise to two 1:1 cycloadducts each, the yields of which were diminished, however, by the photoreduction of **CA**, furnishing **TCH** or its monocycloalkenyl ethers. These products resulted from the abstraction of an allylic hydrogen atom by $^3$**CA** and a second abstraction by the radical generated from $^3$**CA** or by the collapse of this radical with the allyl radical that originated from the cycloalkene. Presumably, an allylic C–H bond prefers this reaction type the better the closer parallel it is orientated relative to the p orbitals that establish the π bond, since then the transition state can optimally take advantage from the resonance of the incipient allyl radical. The halfchair conformation of **CH** may best meet this prerequisite, whereas *cis*- and *trans*-**CO** cannot fulfil it all.

Particularly interesting is the stereochemical course of the cycloadditions onto $^3$**CA**, which proceed in two steps, since a spin inversion has to take place. Thus, diradicals are necessary intermediates. The unsymmetrical products **17a** and **20a**, which arose with **COD** and **CH**, respectively, in addition to the symmetrical ones **17b** and **20b**, show that the intermediate diradicals exist in two conformations, one of which undergoes the ring closure to cause a *cis* and the other the *trans* annulation. Only one diradical conformation each seems to be effective with *cis*- and *trans*-**CO**, namely that which closely approaches the shape of the starting cycloalkene and hence ensures a suprafacial cycloaddition.

The mechanism of the reactions that the 1:1 cycloadducts of **CA** are subject to with another molecule of cycloalkene should be very similar to the pathway leading to them. Nevertheless, the stereochemical course of some of these processes deviates from that giving rise to the 1:1 cycloadducts. Thus, **11a** was formed from $^3$**CA** and *cis*-**CO** as the sole isomer and reacted with *cis*-**CO** to give the three 1:2 cycloadducts **5a**–**c** or **5a′**–**c′**, two of which (**5b**,**c** or **5b′**,**c′**) exhibit a *cis* and the third (**5a** or **5a′**) a *trans* configuration. In contrast, the additions of *trans*-**CO** and **CH** onto **11a** proceeded highly stereoselectively and yielded **5a** or **5a′** and **15** indicating a suprafacial and an antarafacial cycloaddition, respectively. The suprafacial course was exclusively observed also on addition of *trans*-**CO** onto **11b**, albeit the low yield of **5d** or **5d′** limits the significance of this result.

Since the addition of **COD** and **CH** onto $^3$**CA** gave rise to two 1:1 cycloadducts each (**17a**,**b** and **20a**,**b**, respectively), it is surprising that only one 1:2 cycloadduct each (**18** and **9**, respectively) was obtained. A tentative explanation is that the cycloalkenes added suprafacially onto the *trans* isomers **17a** and **20a** and antarafacially onto the *cis* isomers **17b** and **20b**. Beyond the finding that *trans*-**CO** reacted exclusively suprafacially, further trends cannot be discerned, which is why predictions are difficult as to the stereochemical course of new reactions of the present types.

## Conclusions

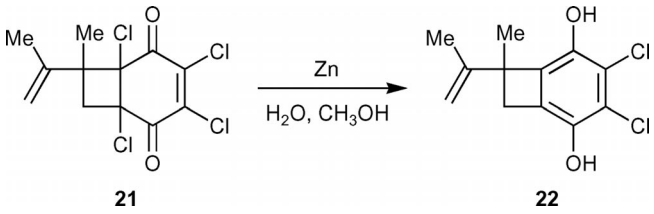
The merit of this work consists in the elucidation of courses and products of the photochemical reactions of **CA** with several cycloalkenes. The best condition for the preparation of 1:1 cycloadducts of the cyclobutane type is the irradiation of the substrates in a ratio of 1:1 in benzene as solvent. Particularly beneficial is the employment of light bulbs for the illumination, since they require no special equipment, emit only little UV radiation and thus restrict to a minimum the excitation of the 1:1 cycloadducts, which gives rise to 1:2 cycloadducts if the cycloalkene is present in excess. The good yield of **11a**, obtained from **CA** and *cis*-**CO**, shows that benzene as solvent is able to completely suppress the excitation of **11a**. However, except for *cis*- and *trans*-**CO**, the photoreduction of **CA** occurs even under these conditions with formation of **TCH** and/or its monocycloalk-2-en-1-yl ether, if the cycloalkene possesses allylic hydrogen atoms.

Owing to its good accessibility and its photoreactivity, **11a** is well suited for the preparation of bis(cyclobutanes)

such as **5a** or **5a′** and **15**. Presumably, numerous alkenes, in addition to *trans*-**CO** and **CH**, readily react with excited **11a** and give rise to 1:2 cycloadducts of **CA**. On the other hand, a series of 1:1 cycloadducts was synthesised from noncyclic alkenes and $^3$**CA** previously.[5,13] Akin to **11a**, these compounds should be able to undergo a photochemical [2+2] cycloaddition with various alkenes with formation of 1:2 cycloadducts of **CA**. Such reactions are easily performed, and thus the resulting bis(cyclobutanes) could gain synthetic importance, because the elimination of the four chlorine atoms should be possible. The products would be quinones having two cyclobutene subunits annulated. The first half of such a transformation is documented by the photoeliminations **5b** → **12b**, **5c** → **12a**, and **15** → **16**.

Barltrop and Hesp[13] reduced the adduct **21** of $^3$**CA** onto 2,3-dimethyl-1,3-butadiene with zinc in methanol/water and isolated mainly the hydroquinone **22** (Scheme 9). If these conditions can be successfully applied to 1:2 cycloadducts of **CA** such as **5**, **15**, and analogous compounds, which should be accessible as proposed above, a route existed for the preparation of hydroquinones containing no chlorine atoms and having two cyclobutene subunits annulated. The synthesis of the target quinones mentioned above would then just be a matter of an oxidation of the hydroquinones.




**21** **22**

Scheme 9. Dechlorination of the 1:1 photocycloadduct **21** according to Barltrop and Hesp.[13]

## Experimental Section

**General Details:** NMR: Bruker AC 200, AC 250, Avance 400, and DMX 600 spectrometers; chemical shifts are given in ppm relative to $Me_4Si$ ($\delta$ = 0.00 ppm) by using signals of the solvent ($CDCl_3$) as internal reference ($\delta$ = 7.26 and 77.0 ppm; $^1$H NMR signal of $CHCl_3$ and $^{13}$C NMR signal of $CDCl_3$, respectively). The assignments of the $^{13}$C NMR signals are based on DEPT and C,H COSY spectra. IR: Perkin–Elmer 1420 ratio-recording infrared spectrophotometer, Perkin–Elmer 1605 FT-IR. UV: Hitachi U-3200. MS: Varian MAT CH 7, Finnigan MAT 8200, and MAT 90. Melting points: Kofler hot stage apparatus from C. Reichert, Optische Werke AG, Vienna, Austria. Elemental analyses: Carlo Erba Strumentatione Elemental Analyser Mod. 1106 and LECO Elemental Analyser CHNS 932. Frequently used solvents: LP = light petroleum ether (b.p. 40–65 °C), EA = ethyl acetate.

**General Conditions for the Photochemical Reactions:** Thoroughly dried solvents were used. A stream of nitrogen was passed through the solution of the substrates for 15 min prior to irradiation. The progress of the reaction, i.e. the consumption of chloranil (**CA**), was monitored by TLC ($SiO_2$; LP/EA, 15:1) or by drop analysis with a saturated solution of hexamethylbenzene in benzene, which gives rise to a red charge-transfer complex with **CA**.

**Irradiation of Chloranil (CA) in the Presence of Cyclopentene (CP):** At variance with this reaction carried out previously,[15] now the ratio of **CA**/**CP** was 1.22:1.00, and the light source was a Rayonet photochemical reactor RPR-100 ($\lambda$ = 350 nm). A solution of **CA** (1.00 g, 4.07 mmol) and **CP** (227 mg, 3.33 mmol) in benzene (250 mL) was irradiated at 20 °C for 2.5 h. The solvent was then quickly evaporated in vacuo. Anhydrous methanol (150 mL) was immediately added to the remaining buff oil, and the mixture was refluxed for 16 h. After evaporation of the methanol in vacuo, the residue was subjected to flash chromatography ($SiO_2$; LP/EA, 25:1) at –30 °C. Three fractions were collected, all of which were somewhat contaminated by **CA** and other impurities. The first fraction (227 mg, 21%) mainly contained the previously isolated 3b,5,6,7a-tetrachloro-2,3,3a,3b,7a,7b-hexahydro-1*H*-cyclopenta[3,4]cyclobuta[1,2]benzene-4,7-dione[15] (**1a** or **1b**) and a small quantity of the 1:2 cycloadduct **2**[15] (ratio of **1a** or **1b**/**2** = 15:1). The second fraction (193 mg, 18%) mainly consisted of the previously isolated **1a** or **1b** and its isomer **1b** or **1a** in a ratio of 1.0:1.5. The third fraction (309 mg, 30%) was mainly a 1.0:4.4 mixture of the methyl pseudoester **3b** or **3c** that was obtained as the minor isomer previously and the methyl ester **3a**.[15] Newly observed **(3bα,7aα)-3b,5,6,7a-tetrachloro-2,3,3a,3b,7a,7b-hexahydro-1*H*-cyclopenta[3,4]-cyclobuta[1,2]benzene-4,7-dione (1b or 1a):** $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 0.90 (m, 1 H), 1.40–2.30 (m, 5 H), 3.21 (m, 2 H) ppm. $^{13}$C NMR (63 MHz, $CDCl_3$): $\delta$ = 26.6 (C-2), 29.7 (C-1, C-3), 46.3 (C-3a, C-7b), 71.7 (C-3b, C-7a), 145.0 (C-5, C-6), 182.4 (C-4, C-7) ppm.

**Irradiation of Chloranil (CA) in the Presence of *cis*-Cyclooctene (*cis*-CO):** Entry 1 of Table 1. A solution of **CA** (1.00 g, 4.07 mmol) and *cis*-**CO** (897 mg, 8.14 mmol) in benzene (150 mL) was irradiated at 10 °C by a medium-pressure mercury lamp (Hanovia, 450 W) by utilising a Pyrex immersion well containing a glass filter, which surrounded the lamp and was supposed to prevent the passage of light of $\lambda$ < 400 nm, for 5 h. The solvent was then evaporated in vacuo. Anhydrous methanol (150 mL) was added to the residue and the mixture refluxed for 16 h. After evaporation of the methanol in vacuo, the residue was subjected to flash chromatography ($SiO_2$; pentane/EA, 35:1) with three fractions collected. The first one was a yellow oil (430 mg, 23%), consisting of a 4:2:1 mixture of the three 1:2 cycloadducts (6aα,6bβ,7aα,7bα,13aα,13bα,14aβ,14bβ)- (**5a**) or (6aα,6bα,7aα,7bα,13aα,13bα,14aα,14bβ)- (**5a′**), (6aα,6bβ,7aα,7bα,13aα,13bα,14aβ,14bα)- (**5b**) or (6aα,6bβ,7aβ,7bβ,13aβ,13bβ,14aβ,14bα)- (**5b′**), and (6aα,6bα,7aβ,7bβ,13aβ,13bβ,14aα,14bα)- (**5c**) or (6aα,6bα,7aα,7bα,13aα,13bα,14aα,14bα)-6b,7a,13b,14a-tetrachloroeicosahydrobenzo-[1′′,2′′:3,4;4′′,5′′:3′,4′]dicyclobuta[1,2:1′,2′]dicyclooctene-7,14-dione (**5c′**). The second fraction was also a yellow oil (170 mg, 9%) and turned out to be pure **5c** or **5c′**, which crystallised on treatment with EA. According to the m.p., this compound had been obtained previously.[16] The third fraction (colourless oil, 190 mg, 13%) was shown to be almost pure (4aα,4bα,10aα,10bα)-2,3,4a,10b-tetrachloro-4a,4b,5,6,7,8,9,10,10a,10b-decahydrobenzo[3,4]cyclobuta-[1,2]cyclooctene-1,4-dione (**11a**).

**Compound 5b or 5b′:** $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.10–2.00 (m, 24 H, $CH_2$), 2.96–3.22 (m, 4 H, CH) ppm. $^{13}$C NMR (63 MHz, $CDCl_3$): $\delta$ = 23.4, 24.7, 25.2 ($CH_2$, 3 further signals of $CH_2$ groups are superimposed by signals of **5a** or **5a′** and **5c** or **5c′**), 47.8, 52.7 (CH), 70.6, 78.8 (CCl), 194.2 (CO) ppm. The MS of the 4:2:1 mixture of **5a** or **5a′**, **5b** or **5b′**, and **5c** or **5c′** is very similar to that of pure **5c** or **5c′** (see below).

**Compound 5c or 5c′:** M.p. 234–237 °C (ref.[16] 235 °C). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.19–1.76 (m, 24 H, $CH_2$), 3.13 (m, 4 H,

CH) ppm. $^{13}$C NMR (63 MHz, $CDCl_3$): $\delta$ = 24.0, 25.0, 29.1 ($CH_2$), 53.5 (CH), 73.6 (CCl), 194.3 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2920 (s, br.), 2855 (m), 1716 (s) (ref.[16] 1720), 1463 (m), 1445 (m), 1159 (m), 1139 (m), 1056 (s), 879 (m), 843 (m), 787 (m), 672 (m) cm$^{-1}$. MS (EI, 70 eV): *m*/*z* (%) = 466 (0.1) $[M]^+$, 435, 433, 431, 429 (0.7, 6, 16, 16) $[M - Cl]^+$, 395 (14), 394 (15), 393 (18), 110 (87), 109 (60), 95 (34), 91 (14), 82 (100), 81 (51), 79 (14), 77 (11), 69 (12), 68 (23), 67 (77), 55 (32), 54 (25), 41 (40). $C_{22}H_{28}Cl_4O_2$ (466.3): calcd. C 56.67, H 6.05; found C 56.44, H 6.13.

For the data of compounds **11a** and **5a** or **5a′**, see the next experiment and another one further below.

Entry 2 of Table 1: A solution of **CA** (2.00 g, 8.13 mmol) and *cis*-**CO** (897 mg, 8.14 mmol) in benzene (250 mL) was irradiated at 20 °C in a Rayonet photochemical reactor RPR-100 ($\lambda$ = 350 nm) for 2.5 h. After evaporation of the benzene in vacuo, the remaining buff oil was purified by flash chromatography ($SiO_2$; LP/EA, 35:1). The resulting light yellow crystals of **11a** (1.43 g) were washed with pentane and recrystallised from EA to give colourless crystals (1.13 g, 39%), m.p. 108–109 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.20–1.50 (m, 8 H, $CH_2$), 1.60–1.85 (m, 4 H, $CH_2$), 3.21 (m, 2 H, CH) ppm. $^{13}$C NMR (63 MHz, $CDCl_3$): $\delta$ = 23.9, 24.7, 28.9 ($CH_2$), 52.5 (CH), 71.4 (saturated CCl), 146.4 (olefinic CCl), 180.7 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2940 (s), 2915 (s), 2911 (s, br.), 2870 (m), 2850 (m), 1715 (s), 1697 (s), 1561 (s), 1461 (m), 1266 (m), 1198 (s), 1173 (m), 1121 (m), 1066 (m), 1022 (m), 945 (m), 772 (m), 702 (s) cm$^{-1}$. UV ($CH_2Cl_2$): $\lambda_{max}$ = 282 ($\log\varepsilon$ = 4.08) nm. MS (EI, 70 eV): *m*/*z* (%) = 325, 323, 321, 319 (2, 21, 63, 64) $[M - Cl]^+$, 227 (21), 225 (21), 110 (25), 109 (54), 108 (20), 95 (29), 93 (20), 82 (63), 81 (46), 69 (20), 68 (23), 67 (100), 55 (43), 54 (34), 41 (56). $C_{14}H_{14}Cl_4O_2$ (356.1): calcd. C 47.22, H 3.96; found C 47.12, H 3.90.

Entry 3 of Table 1: A solution of **CA** (2.00 g, 8.13 mmol) and *cis*-**CO** (1.79 g, 16.2 mmol) in benzene (300 mL) was irradiated at 10 °C in a Rayonet photochemical reactor RPR-100 ($\lambda$ = 350 nm) for 3 h. The resulting brown solution was filtered through silica gel (5 g) and then concentrated in vacuo. The residue was subjected to flash chromatography ($SiO_2$; LP/EA, 20:1) with four fractions collected, which were characterised by their $^{13}$C NMR spectra. First fraction (456 mg, 12%): a mixture of the 1:2 cycloadducts **5a** or **5a′**, **5b** or **5b′** (minor component), and **5c** or **5c′** (major component). Second fraction (155 mg, 4%): a 1:1 mixture of **5c** or **5c′** and the 1:1 cycloadduct **11a**. Third fraction (260 mg, 8%, of yellow crystals after crystallisation from LP/EA): (6aα,7aβ,7bβ,13aβ,13bβ,14bα)- or (6aα,7aα,7bα,13aα,13bα,14bα)-7a,13b-dichloro-1,2,3,4,5,6,6a,7a,7b,8,9,10,11,12,13,13a,13b,14b-octadecahydrobenzo[1′′,2′′:3,4;4′′,5′′:3′,4′]dicyclobuta[1,2:1′,2′]-dicyclooctene-7,14-dione (**12a**). Forth fraction (306 mg, 10%, of yellow crystals after crystallisation from LP/EA): (6aα,7aβ,7bα,13aα,13bβ,14bα)- or (6aα,7aα,7bβ,13aβ,13bα,14bα)-7a,13b-dichloro-1,2,3,4,5,6,6a,7a,7b,8,9,10,11,12,13,13a,13b,14b-octadecahydrobenzo[1′′,2′′:3,4;4′′,5′′:3′,4′]dicyclobuta[1,2:1′,2′]dicyclooctene-7,14-dione (**12b**).

**Compound 12a:** M.p. 136–140 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.00–2.10 (m, 22 H, $CH_2$), 2.12 (apparent br. d, line distance 14 Hz, 2 H, $CH_2$), 3.08 (m, 2 H, CH), 3.28 (apparent d, line distance 11 Hz, 2 H, CH) ppm. $^{13}$C NMR (63 MHz, $CDCl_3$): $\delta$ = 24.2, 24.6, 24.8, 25.7, 29.0, 29.8 ($CH_2$), 47.3, 52.4 (CH), 75.0 (CCl), 157.4 (C=C), 185.0 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2943 (m), 2919 (s), 2850 (m), 1695 (s), 1680 (s), 1627 (m), 1466 (m), 1442 (m), 1290 (w), 1100 (w), 810 (w), 694 (w) cm$^{-1}$. MS (CI, $NH_3$, 150 eV): *m*/*z* (%) = 433, 431, 429 (10, 55, 85) $[M + N_2H_7]^+$, 416, 414, 412 (17, 76, 100) $[M + NH_4]^+$, 359 (13), 342 (15). $C_{22}H_{28}Cl_2O_2$ (395.4): calcd. C 66.83, H 7.14; found C 66.58, H 7.15.

**Compound 12b:** M.p. 136–140 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.15–2.08 (m, 22 H, $CH_2$), 2.13 (apparent br. d, line distance 14 Hz, 2 H, $CH_2$), 2.66 (m, 2 H, CH), 3.29 (apparent d, line distance 11 Hz, 2 H, CH) ppm. $^{13}$C NMR (63 MHz, $CDCl_3$): $\delta$ = 24.6, 24.7, 25.2, 25.8, 28.8, 29.8 ($CH_2$), 46.5, 47.5 (CH), 76.9 (CCl), 157.2 (C=C), 186.4 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2924 (s), 2852 (m), 1686 (s), 1464 (w), 1447 (w), 1321 (w), 1290 (w) cm$^{-1}$. MS (CI, $NH_3$, 150 eV): *m*/*z* (%) = 433, 431, 429 (10, 68, 100) $[M + N_2H_7]^+$, 416, 414, 412 (10, 48, 72) $[M + NH_4]^+$, 359 (18), 342 (13). $C_{22}H_{28}Cl_2O_2$ (395.4): calcd. C 66.83, H 7.14; found C 66.73, H 7.09.

Entry 4 of Table 1: A stirred suspension of **CA** (10.0 g, 40.7 mmol) in a mixture of benzene (200 mL) and *cis*-**CO** (8.95 g, 81.2 mmol) was illuminated at 10 °C by several light bulbs (Osram, total power 500 W) for 60 h. Then the mixture was concentrated in vacuo and the solid residue recrystallised from LP/EA to give pure **11a** (11.0 g, 76%) as light yellow crystals.

Entry 5 of Table 1: A solution of **CA** (800 mg, 3.25 mmol) and *cis*-**CO** (3.59 g, 32.6 mmol) in acetonitrile (20 mL) was illuminated at 10 °C by several light bulbs (Osram, total power 1000 W) for 3.5 h. Then the mixture was concentrated in vacuo and the residue analysed by $^1$H NMR spectroscopy. In addition to **5c** or **5c′** and **11a** in a ratio of 1.0:1.3, further products were not present in a significant quantity.

Entry 6 of Table 1: A stirred suspension of **CA** (4.00 g, 16.3 mmol) in a mixture of dichloromethane (100 mL) and *cis*-**CO** (8.00 g, 72.6 mmol) was illuminated at 10 °C by several light bulbs (Osram, total power 1000 W) for 36 h. About 90% of the volatiles were then evaporated in vacuo, and the oily residue was dissolved in a small amount of LP. Storage of this solution at –35 °C afforded pure **5c** or **5c′** (3.47 g, 46%) as colourless crystals.

Entry 7 of Table 1: A stirred suspension of **CA** (4.00 g, 16.3 mmol) in a mixture of benzene (30 mL) and *cis*-**CO** (60 mL, 461 mmol) was irradiated at 10 °C by a medium-pressure mercury lamp (Hanau, 150 W) by utilising a Pyrex immersion well for 13.5 h. The volatiles were then evaporated in vacuo, and the residue was analysed by $^{13}$C NMR spectroscopy. In addition to the signals of *cis*-**CO** and the 1:2 cycloadducts **5a** or **5a′**, **5b** or **5b′**, and **5c** or **5c′** (ratio of 2:5:5) those of unidentified components were present, but the search for absorptions of the spirooxetane **4** was of no avail, and even for **11a** no evidence was found. The crude product was extracted with hot LP until it had turned into a colourless solid, which was identified to be **5c** or **5c′** (1.69 g, 22%). The combined extracts were concentrated to dryness in vacuo, and the solid residue was recrystallised from LP/EA to furnish a second crop of **5c** or **5c′** (846 mg, 11%). A yield of 42% was reported previously.[16]

**Hydrogenation of the 1:1 Cycloadduct 11a:** In a solution of **11a** (2.10 g, 5.90 mmol) in methanol (100 mL), Pd/C (100 mg) was suspended, and the mixture was stirred at room temperature in a hydrogenation apparatus under hydrogen (5 bar) for 5 d. The catalyst was then removed by filtration through Celite, and the solvent was evaporated in vacuo. The residue was recrystallised from glacial acetic acid to give pure (4bα,10aα)-2,3-dichloro-4b,5,6,7,8,9,10,10a-octahydro-1,4-dihydroxybenzo[3,4]cyclobuta[1,2]cyclooctene (**13**; 1.47 g, 87%) as colourless needles, m.p. 208 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.35–1.80 (m, 10 H), 2.15 (apparent br. d, line distance 12 Hz, 2 H), 3.43 (apparent d, line distance 10 Hz, 2 H, CH), 5.12 (s, 2 H, OH) ppm. $^{13}$C NMR (63 MHz, $CDCl_3$): $\delta$ = 25.9, 26.0, 30.1 ($CH_2$), 46.3 (CH), 116.9 (CCl), 131.4 (C-4a, C-10b), 141.3 (COH) ppm. IR (KBr): $\tilde{\nu}$ = 3300 (s, br.), 2920 (s), 2850 (m), 1420 (s), 1340 (m), 1320 (m), 1260 (w), 1240 (w), 1220 (w), 1180 (w), 875 (m), 835 (w), 805 (w) cm$^{-1}$. MS (EI, 70 eV): *m*/*z* (%) = 290, 288, 286 (10, 63, 100) $[M]^+$, 245 (25), 243 (30), 232 (26), 231

(44), 230 (38), 229 (46), 217 (21), 207 (23), 206 (22), 205 (23), 204 (26), 195 (26), 194 (20), 193 (30), 181 (22). $C_{14}H_{16}Cl_2O_2$ (287.2): calcd. C 58.55, H 5.62; found C 58.25, H 5.70.

**Reduction of the 1:1 Cycloadduct 11a with $NaBH_4$:** A stirred solution of **11a** (2.00 g, 5.62 mmol) in ethanol (15 mL) was treated with small portions of $NaBH_4$ (total amount 500 mg, 13.2 mmol) at room temperature. Stirring was then continued for 1 h, after which period the mixture was refluxed for 15 min, cooled to room temperature and acidified with 2 M hydrochloric acid. Some insoluble material was removed by filtration, and the filtrate was extracted with diethyl ether (5 × 20 mL). The combined extracts were dried with $MgSO_4$ and concentrated to dryness in vacuo. By recrystallisation from glacial acetic acid, the residue furnished colourles crystals of (1α,4α,4aα,4bα,10aα,10bα)- (**14a**) or (1α,4α,4aβ,4bβ,10aβ,10bβ)-2,3,4a,10b-tetrachloro-1,4,4a,4b,5,6,7,8,9,10,10a,10b-dodecahydro-1,4-dihydroxybenzo[3,4]cyclobuta[1,2]cyclooctene (**14b**) (1.72 g, 85%), which turned out to be hygroscopic, m.p. 243–246 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.03–1.46 (m, 6 H), 1.53–1.69 (m, 4 H), 2.16 (br. dt, $J$ = 14.1, 3.9 Hz, 2 H), 2.82 (br. d, $J$ = 2.5 Hz, 2 H, OH), 3.01 (AA′ part of an AA′XX′ spectrum, 2 H, 4b-H, 10a-H), 4.44 (d, $J$ = 2.5 Hz, 2 H, 1-H, 4-H) ppm; the assignment of the signal at $\delta$ = 2.82 ppm to the OH groups was achieved by treatment of the sample with $D_2O$, which made the br. d disappear and the d at $\delta$ = 4.44 ppm collapse to a sharp s. $^{13}$C NMR (63 MHz, $CDCl_3$): $\delta$ = 21.1, 25.6, 30.1 ($CH_2$), 50.5 (C-4b, C-10a), 73.5 (C-1, C-4), 75.6 (C-4a, C-10b), 128.5 (C-2, C-3) ppm. IR (KBr): $\tilde{\nu}$ = 3447 (s, br.), 3378 (s, br.), 2952 (m), 2922 (m), 2848 (m), 1618 (w), 1468 (m), 1444 (m), 1418 (m), 1387 (m), 1348 (m), 1277 (w), 1144 (s), 1128 (m), 1114 (m), 1032 (m), 1007 (m), 943 (m), 825 (m), 652 (m) cm$^{-1}$. MS (CI, isobutane, 120–150 eV): $m/z$ (%) = 347, 345, 343, 341 (6, 25, 54, 42) $[M - OH]^+$, 311, 309, 307, 305 (4, 28, 93, 100) $[M - OH - HCl]^+$, 289 (10), 287 (13), 271 (18), 269 (13), 253 (11), 225 (19), 223 (19), 213 (16), 211 (46), 209 (48), 127 (11), 110 (16), 109 (43). $C_{14}H_{18}Cl_4O_2 \cdot 2H_2O$ (396.1): calcd. C 42.45, H 5.60; found C 42.63, H 4.76.

**Monitoring of the Photochemical Reaction Between CA and *cis*-CO by HPLC:** A solution of **CA** (500 mg, 2.03 mmol) and *cis*-**CO** (450 mg, 4.08 mmol) in benzene (100 mL) was irradiated at 10 °C in a Rayonet photochemical reactor RPR-100 ($\lambda$ = 350 nm). Before the reactor was turned on and then every 30 min up to 2.5 h, a sample of the mixture was withdrawn and immediately analysed by HPLC. Instrument: Bruker LC 21. Column: Phenomenex Prodigy reversed-phase ODS-3 (20 × 4.6 mm, 5 μm). Solvent: acetonitrile/water (90:1). Detector: Bruker UVD 160, operating at 280 nm. Determined by injection of authentic samples, the retention times were 2.30 (**CA**), 6.06 (**11a**), 14.7 (**12a**, **12b**), and 18.5 min (**5c** or **5c′**).

**Irradiation of 11a in the Presence of *trans*-Cyclooctene (*trans*-CO). Formation of 5a or 5a′:** Pure *trans*-**CO** was prepared according to ref.[33] A solution of **11a** (700 mg, 1.97 mmol) and *trans*-**CO** (217 mg, 1.97 mmol) in dichloromethane (30 mL) was illuminated at 10 °C by several light bulbs (Osram, total power 1000 W) for 48 h. The mixture was then concentrated in vacuo. A $^{13}$C NMR spectrum of the crude product indicated the presence of almost pure **5a** or **5a′**, which gave light yellow crystals (660 mg, 72%) on treatment with LP/EA, m.p. 164–166 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.05–2.05 (m, 24 H, $CH_2$), 2.80–2.98 (m, 2 H, CH), 3.00–3.22 (m, 2 H, CH) ppm. $^{13}$C NMR (63 MHz, $CDCl_3$): $\delta$ = 23.4, 23.7, 24.7 (double intensity), 25.8, 26.5, 27.0, 27.5, 28.6, 29.14, 29.17, 29.4 ($CH_2$), 48.1, 52.88, 52.94, 55.5 (CH), 70.3, 72.1, 74.1, 81.5 (CCl), 191.0, 193.9 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2926 (s), 2858 (m), 1723 (s), 1459 (m), 1446 (m), 1158 (w), 1070 (m), 874 (w), 674 (m) cm$^{-1}$. MS (EI, 70 eV): $m/z$ (%) = 435, 433, 431, 429 (0.4, 5, 16, 18) $[M - Cl]^+$, 396 (16), 395 (19), 394 (24), 393 (20), 321 (11), 320 (11), 299 (14), 110 (34), 109 (96), 95 (40), 93 (12), 91 (22), 82 (47), 81 (44), 79 (23), 77 (17), 70 (16), 69 (15), 68 (15), 67 (100), 61 (11), 55 (38), 54 (19), 45 (15), 43 (91), 42 (21), 41 (59), 39 (13). $C_{22}H_{28}Cl_4O_2$ (466.3): calcd. C 56.67, H 6.05; found C 56.39, H 5.97.

**Irradiation of CA in the Presence of *trans*-CO. Formation of (4aα,4bα,10aβ,10bα)-2,3,4a,10b-Tetrachloro-4a,4b,5,6,7,8,9,10,10a,10b-decahydrobenzo[3,4]cyclobuta[1,2]cyclooctene-1,4-dione (11b) and (6aα,6bβ,7aα,7bα,13aβ,13bα,14aβ,14bβ)- or (6aα,6bβ,7aβ,7bβ,13aα,13bβ,14aβ,14bβ)-6b,7a,13b,14a-Tetrachloroeicosahydrobenzo[1″,2″:3,4;4″,5″:3′,4′]dicyclobuta[1,2:1′,2′]dicyclooctene-7,14-dione (5d or 5d′):** A solution of **CA** (2.00 g, 8.13 mmol) and *trans*-**CO** (1.20 g, 10.8 mmol) in benzene (220 mL) was illuminated at 10 °C by several light bulbs (Osram, total power 1000 W) for 4.5 h. After concentration of the mixture in vacuo, a $^{13}$C NMR spectrum of the residue indicated the presence of **11b** as major component. Dissolution of the residue in the minimum amount of acetone and storage of the solution at –35 °C gave rise to light yellow crystals of **5d** or **5d′** (138 mg, 4% and 5% with reference to **CA** and *trans*-**CO**, respectively). After concentration of the mother liquor in vacuo, the residue was subjected to flash chromatography, but the crystallisation of **11b** could not be achieved, which is why it is characterised by NMR spectra only.

**Compound 11b:** Oil (impure). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.00–2.25 (m, 11 H), 2.37 (m, 1 H), 2.82–3.04 (m, 2 H) ppm. $^{13}$C NMR (63 MHz, $CDCl_3$): $\delta$ = 26.2, 27.2 (double intensity), 27.8, 29.6, 29.7 ($CH_2$), 50.6, 53.9 (CH), 68.4, 77.2 (saturated CCl), 144.9, 145.6 (olefinic CCl), 180.0, 181.1 (CO) ppm.

**Compound 5d or 5d′:** M.p. 178–181 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.05–1.40 (m, 10 H), 1.60–1.90 (m, 12 H), 2.15 (m, 2 H), 2.46 (m, 2 H), 2.84 (m, 2 H) ppm. $^{13}$C NMR (63 MHz, $CDCl_3$): $\delta$ = 25.8, 27.0, 27.1, 27.5, 28.7, 29.2 ($CH_2$), 50.5, 55.1 (CH), 68.7, 80.3 (CCl), 191.7 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2933 (s), 2850 (m), 1727 (s), 1450 (m), 1436 (m), 1177 (m), 1115 (m), 1077 (m), 1005 (m), 764 (m), 605 (m) cm$^{-1}$. MS (EI, 70 eV): $m/z$ (%) = 466 (0.3) $[M]^+$, 435, 433, 431, 429 (0.6, 4, 11, 12) $[M - Cl]^+$, 396 (18), 395 (17), 394 (27), 393 (15), 358 (14), 356 (11), 322 (10), 320 (11), 299 (16), 110 (19), 109 (100), 95 (43), 91 (14), 82 (24), 81 (27), 79 (14), 77 (11), 68 (11), 67 (83), 55 (39), 54 (11), 41 (34). $C_{22}H_{28}Cl_4O_2$ (466.3): calcd. C 56.67, H 6.05; found C 56.68, H 5.89.

**Irradiation of 11a in the Presence of *cis*-CO. Formation of the Dechlorination Products 12a and 12b:** A solution of **11a** (1.47 g, 4.13 mmol) and *cis*-**CO** (456 mg, 4.14 mmol) in benzene (250 mL) was irradiated at 10 °C in a Rayonet photochemical reactor RPR-100 ($\lambda$ = 350 nm) for 2 h. The resulting brown solution was filtered through silica gel (5 g). Then the solvent was evaporated in vacuo, and the residue was subjected to flash chromatography ($SiO_2$; LP/EA, 20:1), which furnished two yellow solids. The first fraction consisted of **12a** (131 mg, 8%) and the second of **12b** (186 mg, 11%).

**Photolysis of 5c or 5c′. Formation of 12a or the Corresponding Alternative Isomer:** A solution of **5c** or **5c′** (38 mg, 0.081 mmol) in $C_6D_6$ (0.7 mL) was irradiated at room temperature in a Rayonet photochemical reactor RPR-100 ($\lambda$ = 350 nm) for 75 min. Thereafter, the $^{13}$C NMR spectrum documented a ratio of **5c** or **5c′**/**12a** or the corresponding alternative isomer = 1:2. The $^1$H NMR spectrum was charcterised by a substantial line broadening. The sample showed a smell of hydrogen chloride, and a wet test paper indicated the presence of an acid. Continued irradiation did not change the ratio of **5c** or **5c′**/**12a** or the corresponding alternative

isomer, but the $^1$H NMR spectrum displayed a progressive decomposition of the sample.

**Irradiation of 11a in the Presence of Cyclohexene (CH). Formation of (6aα,6bα,7aβ,7bβ,11aα,11bβ,12aα,12bα)- or (6aα,6bα,7aα,7bβ,11aα,11bα,12aα,12bα)-6b,7a,11b,12a-Tetrachlorooctadecahydrocycloocta[3,4]cyclobuta[1,2-*b*]biphenylene-7,12-dione (15) and (6aα,7aβ,7bβ,11aα,11bβ,12bα)- or (6aα,7aα,7bβ,11aα,11bα,12bα)-7a,11b-Dichloro-1,2,3,4,5,6,6a,7a,7b,8,9,10,11,11a,11b,12b-hexadecahydrocycloocta[3,4]cyclobuta[1,2-*b*]biphenylene-7,12-dione (16):** A solution of **11a** (2.00 g, 5.61 mmol) and **CH** (923 mg, 11.2 mmol) in benzene (220 mL) was irradiated at 10 °C in a Rayonet photochemical reactor RPR-100 ($\lambda$ = 350 nm) for 4 h. The mixture was then concentrated in vacuo, and the residue was subjected to flash chromatography [$SiO_2$; LP/EA (20:1) 1 L, then (10:1) 0.5 L, finally (5:1) 0.5 L]. In the order of elution, **15** (814 mg, 33%) and **16** (503 mg, 24%) were obtained. Recrystallisation from LP/EA furnished a colourless and a yellow solid, respectively.

**Compound 15:** M.p. 269–271 °C. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 1.15–2.00 (m, 20 H), 2.48 (ddd, $J$ = 13.6, 9.6, 3.6 Hz, 1 H, 7b-H or 11a-H), 2.70 (ddd, $J$ = 13.6, 11.0, 3.3 Hz, 1 H, 11a-H or 7b-H), 3.05–3.21 (m, 2 H, 6a-H, 12b-H) ppm. $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 22.9, 24.5, 24.7, 24.8, 24.9, 25.1, 27.4 (double intensity), 29.0, 29.2 ($CH_2$), 48.6, 52.5, 53.2, 55.2 (CH), 69.6, 74.2, 75.1, 82.2 (CCl), 190.5, 194.8 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2935 (s), 2866 (m), 1734 (s), 1724 (s), 1461 (m), 1448 (m), 1167 (m), 1133 (m), 1109 (m), 914 (m), 767 (m), 684 (m), 609 (m) cm$^{-1}$. MS (EI, 70 eV): *m*/*z* (%) 442, 440, 438, 436 (0.2, 0.4, 0.7, 0.4) $[M]^+$, 407, 405, 403, 401 (1, 7, 21, 22) $[M - Cl]^+$, 368 (20), 367 (34), 366 (25), 365 (46), 109 (50), 95 (23), 91 (32), 82 (50), 81 (70), 79 (26), 77 (32), 67 (100), 55 (29), 41 (47). $C_{20}H_{24}Cl_4O_2$ (438.2): calcd. C 54.82, H 5.52; found C 54.61, H 5.60.

**Compound 16:** M.p. 270–272 °C. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 1.21–1.37 (m, 3 H), 1.40–1.48 (m, 6 H), 1.55–1.68 (m, 3 H), 1.69–1.76 (m, 3 H), 1.78–1.86 (m, 2 H), 1.97 (ddd, $J$ = 13.1, 10.8, 3.6 Hz, 1 H, 7b-H or 11a-H), 2.05 (m, 1 H), 2.11 (dm, $J$ = 15 Hz, 1 H, 1-H or 6-H), 2.18 (dm, $J$ = 15 Hz, 1 H, 6-H or 1-H), 2.57 (ddd, $J$ = 13.1, 11.4, 3.2 Hz, 1 H, 11a-H or 7b-H), 3.25 (ddd, $J$ = 12.0, 4.3, 1.9 Hz, 1 H, 6a-H or 12b-H), 3.31 (ddd, $J$ = 12.1, 4.3, 2.0 Hz, 1 H, 12b-H or 6a-H) ppm. $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ = 24.5, 24.8 (C-1, C-6), 25.1, 25.4 (C-9, C-10), 25.79, 25.82 (C-3, C-4), 27.3, 27.8 (C-8, C-11), 29.8, 29.9 (C-2, C-5), 47.2, 47.3 (C-6a, C-12b), 51.5, 51.8 (C-7b, C-11a), 72.4, 82.2 (C-7a, C-11b), 156.5, 157.3 (C-6b, C-12a), 184.3, 185.3 (C-7, C-12) ppm; the assignments are based on HMBC, C,H-COSY, and H,H-COSY spectra. IR (KBr): $\tilde{\nu}$ = 2919 (s), 2850 (m), 1697 (s), 1686 (s), 1462 (m), 1321 (m), 1098 (w), 993 (m), 808 (w), 688 (w), 590 (m) cm$^{-1}$. MS (CI, $NH_3$, 150 eV): *m*/*z* (%) = 405, 403, 401 (11, 65, 100) $[M + N_2H_7]^+$, 388, 386, 384 (7, 39, 56) $[M + NH_4]^+$. $C_{20}H_{24}Cl_2O_2$ (367.3): calcd. C 65.40, H 6.59; found C 65.17, H 6.42.

**Irradiation of CA in the Presence of *cis*,*cis*-1,5-Cyclooctadiene (COD)**

**Isolation of 2,3,5,6-Tetrachlorospiro[cyclohexa-2,5-diene-1,10′-[9]oxabicyclo[6.2.0]dec[4]en]-4-one (6), 6b,7a,13b,14a-Tetrachloro-1,2,5,6,6a,6b,7a,7b,8,9,12,13,13a,13b,14a,14b-hexadecahydrobenzo-[1′′,2′′:3,4;4′′,5′′:3′,4′]dicyclobuta[1,2:1′,2′]dicyclooctene-7,14-dione (18), 2,3,5,6-Tetrachloro-4-(cycloocta-2′,6′-dien-1′-yloxy)phenol (19a), 2,3,5,6-Tetrachloro-4-(cycloocta-2′,5′-dien-1′-yloxy)phenol (19b), and TCH:** A stirred suspension of **CA** (2.00 g, 8.13 mmol) in a mixture of **COD** (20 mL, 163 mmol) and benzene (10 mL) was illuminated at 10 °C by several light bulbs (Osram, total power 1000 W) for 30 h. Then the volatiles were removed in vacuo, and the residue was subjected to flash chromatography [$SiO_2$; LP/EA (20:1) 2 L, then (10:1) 1 L] to give four fractions, which were colourless solids. The first one consisted of **18** [838 mg, 22%; in addition to the configurations shown in Scheme 7, further possible configurations are (6aα,6bα,7aα,7bα,13aβ,13bα,14aα,14bα) and (6aα,6bβ,7aβ,7bβ,13aα,13bβ,14aβ,14bα)], the second of **6** (212 mg, 7%), the third of the two isomers **19** as a 2:1 mixture (689 mg, 24%), and the forth of **TCH** (112 mg, 6%). Because of the extremely low solubility of **TCH** in the eluant, the amount of **TCH** actually formed may have been larger than the one isolated. The first three fractions were recrystallised from LP/EA, whereby **6**, **18**, and the major one of the isomers **19** were obtained pure.

**Compound 6:** M.p. 131–132 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.39 (dddd, $J$ = 12.7, 10.0, 5.6, 4.2 Hz, 1 H), 1.85 (tdd, $J$ = 12.7, 6.5, 4.5 Hz, 1 H), 2.00–2.35 (m, 6 H), 3.60 (ddd, $J$ = 12.5, 8.7, 5.5 Hz, 1 H, 1′-H), 5.14 (ddd, $J$ = 10.0, 8.7, 5.5 Hz, 1 H, 8′-H), 5.55 (ddd, $J$ = 10.5, 9.4, 7.1 Hz, 1 H), 5.71 (ddd, $J$ = 10.7, 8.5, 7.1 Hz, 1 H) ppm. $^{13}$C NMR (63 MHz, $CDCl_3$): $\delta$ = 21.0, 23.2, 23.7, 32.0 ($CH_2$), 53.0 (C-1′), 84.8 (C-8′), 85.7 (C-1), 129.1, 130.2 (HC=CH), 129.9, 130.7 (C-3, C-5), 151.6, 152.4 (C-2, C-6), 169.8 (C-4) ppm. IR (KBr): $\tilde{\nu}$ = 3016 (w), 2938 (m), 2861 (w), 1686 (s), 1607 (w), 1578 (s), 1459 (m), 1394 (w), 1278 (m), 1111 (s), 996 (w), 975 (m), 962 (m), 911 (w), 877 (w), 826 (w), 790 (w), 754 (m), 742 (m), 728 (s), 671 (w) cm$^{-1}$. MS (EI, 70 eV): *m*/*z* (%) = 358, 356, 354, 352 (0.1, 0.6, 1.0, 0.8) $[M]^+$, 323, 321, 319, 317 (0.4, 2.3, 7.7, 7.8) $[M - Cl]^+$, 248 (15), 246 (15), 245 (12), 108 (51), 107 (17), 93 (44), 91 (11), 87 (12), 81 (27), 80 (100), 79 (95), 78 (12), 77 (12), 67 (91), 66 (28), 55 (11), 54 (94), 53 (13), 41 (33), 39 (26). $C_{14}H_{12}Cl_4O_2$ (354.1): calcd. C 47.49, H 3.42; found C 47.50, H 3.28.

**Compound 18:** M.p. 195–197 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.10–1.41 (m, 2 H), 1.68–1.83 (m, 2 H), 1.90–2.30 (m, 12 H), 2.72 (ddd, $J$ = 11.8, 9.5, 6.1 Hz, 1 H), 2.80 (ddd, $J$ = 11.6, 9.8, 5.9 Hz, 1 H), 2.92 (td, $J$ = 11.8, 4.3 Hz, 1 H), 2.97 (td, $J$ = 11.7, 4.8 Hz, 1 H), 5.54–5.71 (m, 4 H) ppm. $^{13}$C NMR (63 MHz, $CDCl_3$): $\delta$ = 22.5, 22.7, 23.2, 23.4, 27.9, 28.31, 28.33, 28.6 ($CH_2$), 45.2, 48.0, 52.9, 53.6 (saturated CH), 70.5, 73.1, 76.1, 78.8 (CCl), 129.8, 130.0 (double intensity), 130.2 (olefinic CH), 191.7, 192.8 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 3017 (m), 2941 (m), 2910 (m), 2852 (w), 1727 (s), 1465 (m), 1439 (m), 1205 (m), 1186 (m), 1129 (m), 1088 (w), 1068 (m), 1010 (w), 875 (w), 756 (w), 734 (m), 671 (m) cm$^{-1}$. MS (EI, 70 eV): *m*/*z* (%) = 464, 462, 460 (0.3, 0.7, 0.5) $[M]^+$, 392 (20), 391 (21), 390 (32), 389 (23), 108 (49), 107 (99), 93 (32), 91 (42), 81 (20), 80 (43), 79 (100), 78 (21), 77 (37), 67 (53), 54 (28), 41 (37), 39 (26). $C_{22}H_{24}Cl_4O_2$ (462.2): calcd. C 57.17, H 5.23; found C 56.88, H 5.20.

**Major Isomer 19:** M.p. 113–115 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 2.19 (m, 1 H), 2.29–2.45 (m, 3 H), 2.64–2.86 (m, 2 H), 5.48–5.71 (m, 4 H), 5.80 (ddd, $J$ = 12.0, 5.5, 1.5 Hz, 1 H), 5.91 (s, 1 H, OH) ppm. $^{13}$C NMR (63 MHz, $CDCl_3$): $\delta$ = 27.93, 27.95, 34.8 ($CH_2$), 82.4 (HCO), 119.0, 127.5 (CCl), 125.6, 129.4, 129.47, 129.54 (HC=CH), 145.7, 145.8 (aromatic CO) ppm. IR (KBr): $\tilde{\nu}$ = 3433 (m, br.), 3020 (w), 2937 (w), 2876 (w), 2827 (w), 1436 (s), 1388 (s), 1320 (m), 1279 (m), 1203 (m), 1168 (w), 1033 (w), 986 (w), 967 (w), 939 (m), 902 (m), 880 (w), 816 (w), 791 (w), 717 (w), 668 (w) cm$^{-1}$. MS (EI, 70 eV): *m*/*z* (%) = 254, 252, 250, 248, 246 (0.2, 2, 9, 17, 14) $[C_6H_2Cl_4O_2]^+$, 107 (50), 106 (46), 105 (12), 91 (48), 79 (100), 78 (30), 77 (15), 41 (14). $C_{14}H_{12}Cl_4O_2$ (354.1): calcd. C 47.49, H 3.42; found C 47.30, H 3.53.

**Minor Isomer 19:** $^{13}$C NMR (63 MHz, $CDCl_3$): $\delta$ = 23.1, 28.0, 29.0, 29.4 ($CH_2$, one of the 4 signals is from an impurity), 83.1 (HCO), 118.9, 127.4 (CCl), 128.3, 128.7, 128.8, 129.4, 130.2 (HC=CH, one of the 5 signals is from an impurity), 145.6, 146.1 (aromatic CO) ppm.

**Observation of 2,3,4a,10b-Tetrachloro-4a,4b,5,6,9,10,10a,10b-octahydrobenzo[3,4]cyclobuta[1,2]cyclooctene-1,4-dione (17):** A solution of **CA** (2.00 g, 8.13 mmol) and **COD** (880 mg, 8.13 mmol) in benzene (220 mL) was illuminated at 10 °C by several light bulbs (Osram, total power 700 W) for 8 h. The solvent was then evaporated in vacuo. A $^{13}C$ NMR spectrum of the crude product indicated the presence of significant amounts of both isomers **19** and a small quantity of **6**. Signals of further important components were ascribed to two isomers **17**, whereas no evidence for **18** was found. Although **6** and **19** were removed from the mixture by flash chromatography ($SiO_2$; LP/EA, 20:1), an analytically pure sample of **17** could not be obtained. Also, attempts to separate the isomers **17** failed. Number and intensities of the signals in the $^{13}C$ NMR spectrum indicate that a symmetrical compound **17** and an unsymmetrical one were present in a ratio of 1:2. Red oil. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.0–3.4 (several m with the major one between $\delta$ = 1.9 and 2.3 ppm), 5.5–5.7 (m, 2 H) ppm. $^{13}C$ NMR (63 MHz, $CDCl_3$): $\delta$ = 22.4, 23.3, 24.4, 25.2, 27.8, 28.6 ($CH_2$), 47.8, 50.6, 52.1 (saturated CH), 69.4, 70.0, 76.1 (saturated CCl), 129.2, 130.0 (double intensity) (HC=CH), 145.0, 145.6 (olefinic CCl; 1 signal is missing, possibly due to too low intensity), 180.3, 180.5, 181.2 (CO) ppm.

**Irradiation of CA in the Presence of Cyclohexene (CH)**

**Isolation of 4b,5a,9b,10a-Tetrachlorohexadecahydrobenzo[3,4]cyclobuta[1,2-*b*]biphenylene-5,10-dione (9), 2,3,5,6-Tetrachloro-4-(cyclohex-2′-en-1′-yloxy)phenol (10), and (4aα,4bα,8aβ,8bα)-2,3,4a,8b-Tetrachloro-4a,4b,5,6,7,8,8a,8b-octahydrobiphenylene-1,4-dione (20a):** A solution of **CA** (1.00 g, 4.07 mmol) and **CH** (669 mg, 8.14 mmol) in benzene (150 mL) was irradiated at 10 °C by a medium-pressure mercury lamp (Hanovia, 450 W) by utilising a Pyrex immersion well containing a glass filter, which surrounded the lamp and was supposed to prevent the passage of light with $\lambda < 400$ nm, for 12 h. The solvent was then evaporated in vacuo, and the residue was subjected to flash chromatography ($SiO_2$; pentane/EA, 25:1). In the order of elution, **9** [496 mg, 30%; ref.[5] 20%; in addition to the configurations shown in Scheme 8, further possible configurations are (4aα,4bα,5aα,5bα,9aβ,9bα,10aα,10bα) and (4aα,4bβ,5aβ,5bβ,9aβ,9bα,10aβ,10bα)], **20a** (140 mg, 10%, slightly contaminated by **9** and other components), and **10** (261 mg, 20%) were obtained as oils. Dissolution of these oils in the minimum amount of EA and storage of the solutions at –35 °C gave rise to colourless crystals in all three cases.

In a second experiment, the irradiation was carried out as above, but, after the removal of the benzene, the residue was refluxed in methanol overnight. Thereafter, the same products as above were observed and no compounds containing a methoxy group.

In addition to elemental analyses, Xu et al.[5] reported $^1H$ NMR and IR spectroscopic as well as MS data for **9** and **10**. Since these data are not extensive and seem to be not very precise, we add our data.

**Compound 9:** M.p. 204–206 °C (ref.[5] 212–214 °C). $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.10–2.00 (m, 16 H), 2.61–2.81 (m, 2 H), 3.09–3.31 (m, 2 H) ppm. $^{13}C$ NMR (63 MHz, $CDCl_3$): $\delta$ = 21.2, 21.6, 23.1, 23.6, 24.9, 25.1, 27.0, 27.6 ($CH_2$), 44.8, 46.0, 47.6, 55.3 (CH), 69.2, 71.9, 76.6, 82.6 (CCl), 190.6, 195.1 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2950 (s), 2870 (m), 1730 (s), 1455 (m), 1192 (w), 1170 (w), 1158 (w), 1137 (w), 1121 (m), 1099 (w), 1028 (w), 958 (w), 918 (w), 898 (m), 811 (w), 849 (w), 688 (m) $cm^{-1}$. MS (EI, 70 eV): *m*/*z* (%) = 414, 412, 410, 408 (0.1, 0.6, 1.3, 0.7) $[M]^+$, 379, 377, 375, 373 (1, 9, 27, 27) $[M – Cl]^+$, 340 (16), 339 (33), 338 (25), 337 (44), 301 (19), 273 (15), 169 (15), 105 (17), 91 (17), 82 (36), 81 (100), 79 (28), 77 (32), 67 (68), 55 (19), 53 (16), 41 (39), 39 (17).

**Compound 10:** M.p. 101–102 °C (ref.[5] 105–107 °C). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.62 (m, 1 H), 1.81 (m, 1 H), 1.92–2.08 (m, 3 H), 2.15 (m, 1 H), 4.72 (m, 1 H, HCO), 5.89 (s, 1 H, OH), 5.89 (ddt, *J* = 10.1, 3.7, 1.8 Hz, 1 H), 6.01 (dddd, *J* = 10.1, 4.0, 3.0, 1.0 Hz, 1 H) (HC=CH) ppm. $^{13}C$ NMR (63 MHz, $CDCl_3$): $\delta$ = 18.7, 25.1, 28.8 ($CH_2$), 78.2 (HCO), 118.9, 127.7 (CCl), 125.8, 133.1 (HC=CH), 145.6, 146.0 (aromatic CO) ppm. IR (KBr): $\tilde{\nu}$ = 3440 (m, br.), 3040 (w), 2950 (m), 2910 (w), 2880 (w), 2840 (w), 1691 (w), 1681 (w), 1439 (s), 1390 (s), 1358 (w), 1333 (w), 1322 (m), 1282 (m), 1205 (m), 1173 (w), 1162 (w), 1119 (w), 1003 (m), 941 (m), 922 (m), 911 (m), 889 (w), 881 (m), 736 (w), 719 (m) $cm^{-1}$. MS (EI, 70 eV): *m*/*z* (%) = 295, 293, 291 (0.8, 2.0, 2.1) $[M – Cl]^+$, 250 (10), 248 (26), 246 (35), 244 (19), 211 (17), 209 (17), 89 (11), 87 (33), 81 (95), 80 (100), 79 (35), 53 (12), 41 (12).

**Compound 20a:** M.p. 118–119 °C. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.20–1.45 (m, 3 H), 1.60–2.05 (m, 5 H), 2.12 (m, 1 H), 2.70 (m, 1 H) ppm. $^{13}C$ NMR (63 MHz, $CDCl_3$): $\delta$ = 24.9, 25.2, 27.2, 27.7 ($CH_2$), 51.3, 52.6 (CH), 68.7, 78.4 (saturated CCl), 145.4, 145.8 (olefinic CCl), 179.8, 181.3 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2965 (m), 2945 (m), 2880 (m), 2855 (m), 1701 (s), 1680 (m), 1559 (s), 1459 (w), 1449 (m), 1252 (m), 1222 (m), 1195 (m), 1150 (m), 1136 (m), 1120 (w), 1062 (m), 1050 (w), 1029 (m), 950 (m), 935 (w), 923 (w), 889 (w), 780 (w), 733 (m), 721 (m), 713 (m) $cm^{-1}$. MS (EI, 70 eV): *m*/*z* (%) = 297, 295, 293, 291 (4, 32, 100, 100) $[M – Cl]^+$, 246 (29), 244 (20), 211 (23), 209 (25), 87 (44), 81 (52), 67 (39), 55 (24), 43 (29), 41 (31). $C_{12}H_{10}Cl_4O_2$ (328.0): calcd. C 43.97, H 3.07; found C 45.38, H 3.18.

**Observation of (4aα,4bα,8aα,8bα)- or (4aα,4bβ,8aβ,8bα)-2,3,4a,8b-Tetrachloro-4a,4b,5,6,7,8,8a,8b-octahydrobiphenylene-1,4-dione (20b):** A solution of **CA** (1.00 g, 4.07 mmol) and **CH** (334 mg, 4.07 mmol) in benzene (250 mL) was irradiated at 20 °C in a Rayonet photochemical reactor RPR-100 ($\lambda$ = 350 nm) for 4.5 h. After evaporation of the benzene in vacuo, the remaining buff oil was subjected to flash chromatography ($SiO_2$; LP/*tert*-butyl methyl ether, 9:1). In the order of elution, **20b** (125 mg, 9%), **20a** (107 mg, 8%) and **10** (234 mg, 18%) were obtained as oils, which still contained impurities to the extent of about 10%.

**Compound 20b:** $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.18–1.41 (m, 4 H), 1.52–1.93 (m, 4 H), 3.24 (m, 2 H) ppm. $^{13}C$ NMR (63 MHz. $CDCl_3$): $\delta$ = 21.3, 22.3 ($CH_2$), 44.3 (CH), 69.4 (saturated CCl), 146.4 (olefinic CCl), 180.9 (CO) ppm.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