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PAPER

Photocycloadditions of tetrachloro-1,4-benzoquinone (chloranil) onto cyclobutene and cyclopropene. Expected and unexpected products†

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Solutions of chloranil (**CA**) in chlorobenzene were irradiated in the presence of cyclobutene and cyclopropene. Cyclobutene gave rise to two conventional 1 : 2 cycloadducts onto the dichloroethene subunits of **CA** and an α,β-unsaturated α,γ-dichloro-γ-lactone. Heating of the crude product in methanol converted the lactone into an α,β-unsaturated methyl γ-oxocarboxylate (25% yield) and a large amount of the major 1 : 2 cycloadduct, which contains chlorocyclobutane entities, into a cyclopropylcarbinyl chloride derivative (24% yield). An entirely new product type was the result in the case of cyclopropene. After treatment of the crude product with methanol a tetracyclic acetal containing a cyclopentanone and a dihydropyran subunit was isolated in 36% yield. Apparently, **CA** had taken up two molecules of cyclopropene. One of the resulting cyclopropane entities must have undergone a rearrangement en route to the final product.

Introduction

Reactions of quinones with alkenes have been an area of continuous interest in organic photochemistry.[1] Those of chloranil (**CA**) are notable because of the great diversity of possible processes. Owing to the rapid intersystem crossing, all conversions of excited **CA** that lead to chemical change of **CA** start from the triplet state (^{3}**CA**).[2] The most important reaction types of ^{3}**CA** with alkenes have been summarised in the introduction of our recent publication.[3a] Here we restrict ourselves to a brief review of results pertinent to the reactions described in this work, that is, to the three processes that a monocyclic monoalkene may undergo with ^{3}**CA**. Whereas *cis*- and *trans*-cyclooctene exclusively undergo a [2 + 2] cycloaddition onto a dichloroethene subunit,[3a] cyclohexene, dissolved in benzene, further gives rise to the photoreduction of chloranil (**CA**) with formation of tetrachlorohydroquinone and its monocyclohexenyl ether.[3a,4] In addition to the generation of two dichlorocyclobutane derivatives and the photoreduction, a third reaction type is exhibited by cyclopentene, as a tetrachlorobenzofuranone derivative results. En route to the latter product, probably a [4 + 2] cycloaddition proceeds, in which ^{3}**CA** serves as substrate with 4 π electrons.[3a,b]

Even if the angle strain of the ethene moiety of cyclopentene is only very small, it could be the deciding factor for the formation of the tetrachlorobenzofuranone derivative. The results with the more strained cyclopentenes norbornene and bicyclo[2.1.1]hex-2-ene[3b] support this assumption. On the other hand, *trans*-cyclooctene does not bring about a tetrachlorobenzofuranone in spite of its relatively high strain energy of 15.3 kcal mol^{-1},[5] but only a [2 + 2] cycloadduct onto a dichloroethene subunit of **CA**.[3a] The reason could be the different origin of the strain in comparison to the situation in cyclopentene, namely the pyramidalisation of the ethene moiety, which may not promote the unusual reactivity. To examine whether or not an enhanced angle strain relative to that of cyclopentene will increase the portion of the tetrachlorobenzofuranone product, we irradiated **CA** in the presence of cyclobutene and cyclopropene. With these cycloalkenes, an electron transfer onto ^{3}**CA**, as it proceeds or can be assumed with substrates of a low oxidation potential,[3c,4,6] was not expected, since the estimation of the oxidation potentials on the basis of first the vertical ionisation potentials[7] (cyclobutene: 9.43,[8] 9.59 eV;[9] cyclopropene: 9.86,[8] 9.82 eV[9]) gives values considerably higher than those of cyclopentene and cyclohexene (first vertical ionisation potentials: 9.18 eV and 9.12 eV,[8] respectively). And in the latter cases, at most the photoreduction of **CA** can be considered as a process initiated by an electron transfer from the cycloalkene onto ^{3}**CA**.[4]

Results and discussion

At variance with the reactions recently described by us,[3a] benzene could not be utilised as solvent, because the irradiations of **CA** in the presence of cyclobutene and cyclopropene should be carried out at temperatures below 0 °C due to the volatility of

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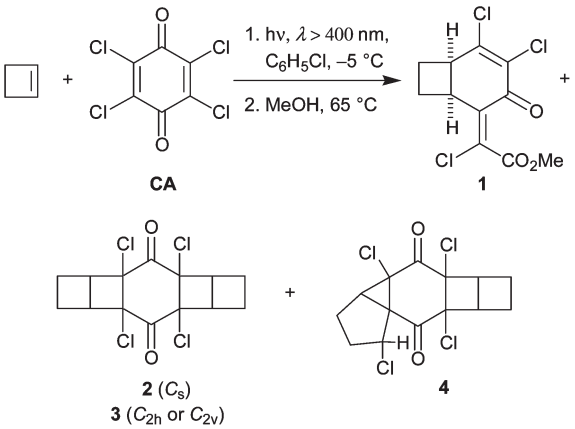
† Dedicated to Professor Waldemar Adam on the occasion of his 75th birthday.



Scheme 1 Compounds isolated after the photochemical reaction of chloranil (**CA**) with cyclobutene and the treatment of the crude product with methanol.

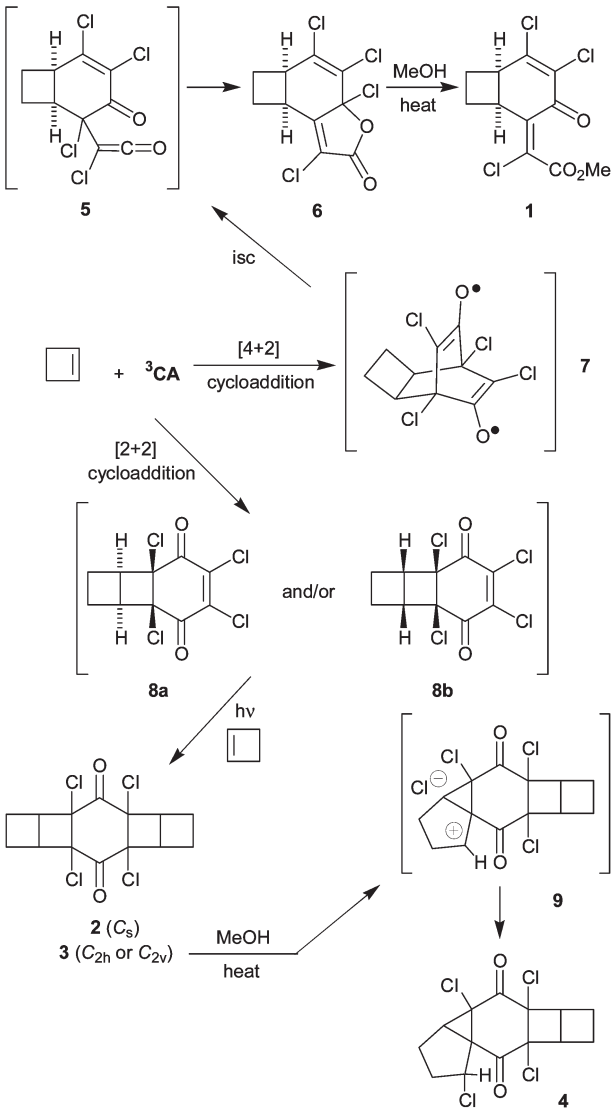
these cycloalkenes. Since toluene reacts readily with ^{3}**CA**,[3c] it could not be used, which is why we chose chlorobenzene.

1. Cyclobutene

The reaction was performed at −5 °C with a medium-pressure mercury lamp 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. After the complete consumption of **CA**, chlorobenzene was evaporated at 35 °C/15 mmHg and the residue refluxed in methanol. In this way, a possibly formed tetrachlorobenzofuranone derivative, which should be a pseudoacid chloride, would be transformed to a pseudoester or an ester.[3b]

Indeed, after the evaporation of the methanol, the methyl ester **1** was isolated by flash chromatography in 25% yield. In addition to it, the 1 : 2 cycloadducts **2** and **3** of **CA** as well as their unsymmetrical isomer **4** (Scheme 1) were obtained in 6, 10 and 24% yield, respectively. The identity of these products is based on their NMR spectroscopic data, and there the comparison with the values of analogous products plays an important part. In the case of **1**, these are the corresponding methyl esters derived from norbornene and cyclopentene[3b] and with **2** and **3** the 1 : 2 cycloadducts of cyclopentene,[3b] cyclohexene and *cis*-cyclooctene.[3a]

In the NMR spectra of the crude product prior to methanolysis, only the signals of **3** and another compound were clearly discernible. We take the latter for the tetrachlorobenzofuranone derivative **6** (Scheme 2), which should have yielded the ester **1** on treatment with methanol. The ratio of **3** : **6** amounted to 1.4 : 1. That the absorptions of the 1 : 2 cycloadduct **2** could at best be suspected, was probably caused by the small quantity (6% isolated yield), which gave rise only to an insufficient signal-to-noise ratio. Although **3** was isolated in a small yield as well (10%), its bands appeared with a good signal-to-noise ratio in the spectra of the crude product. This is ample evidence for the conversion of **3** into **4** to a substantial extent on heating in methanol. This rearrangement takes advantage from the decrease of the ring strain energy, since a bicyclo[3.1.0]hexane emerges



Scheme 2 The mechanism for the formation of the compounds on irradiation of chloranil (**CA**) in the presence of cyclobutene followed by heating of the crude product in methanol.

from a bicyclo[2.2.0]hexane moiety. The parent hydrocarbons are different by 20.8 kcal mol^{-1} with respect to their standard heat of formation.[10]

In all probability, this isomerisation proceeded by the heterolytic dissociation of a C–Cl bond of **3** with concomitant Wagner–Meerwein rearrangement furnishing the contact ion pair **9** (Scheme 2), which is a derivative of the cyclopropylcarbinyl cation. The collapse of **9** then led to the isolated compound **4**, the possible configurations and conformations of which are discussed below. In spite of the presence of the nucleophile methanol, only the rearrangement product **4** was detected and no methanolysis product. However, a small amount of the methyl ether corresponding to **4** could have been overlooked in the workup.

The reverse isomerisation, that is, the formation of cyclobutyl chloride from cyclopropylcarbinyl chloride on solvolysis of the latter had been observed a long time ago.[11] A more recent

example for internal return after the reorganisation of the carbon atom skeleton is the generation of *endo*-2-norbornyl mesylate as major product of ethanolysis and hydrolysis of 2-norpinyl mesylate.[12]

The formation of the tetrachlorobenzofuranone derivative **6** should have proceeded on a route analogous to that proposed for the production of the corresponding compounds from norbornene, bicyclo[2.1.1]hex-2-ene and cyclopentene.[3a,b] Thus, cyclobutene would have undergone a [4 + 2] cycloaddition with ^{3}**CA** and afforded the triplet diradical **7**, which would have been subject to opening of the ring originating from **CA** after intersystem crossing to give the α-chloro-β-oxoketene derivative **5** (Scheme 2). The closure of a five-membered ring by addition of the ketone oxygen atom onto the central ketene carbon atom of **5** and the [1,2] migration of the α chlorine atom then could have completed the pathway to **6**.

In comparison to the reaction of cyclopentene, the percentage of the [4 + 2] cycloaddition of cyclobutene onto ^{3}**CA** is not increased. Thereby, the argument advanced in the introduction that this reaction type could be supported by the angle strain of the ethene subunit of cyclopentene, norbornene and bicyclo [2.1.1]hex-2-ene is not invalidated, however, since this quantity of cyclobutene is not much higher than that of cyclopentene. This can be estimated from the total strain energies of cyclopentene and cyclopentane (5.9 and 6.3 kcal mol^{-1}) on the one hand and cyclobutene and cyclobutane (29.8 and 26.2 kcal mol^{-1}) on the other.[5]

Though we speculated in an earlier paper[3b] that the [4 + 2] cycloaddition of ^{3}**CA** onto cyclopentene and its derivatives was concerted, the mechanism has not yet been shown and the distinction between concerted and two step radical processes has not yet been proved. Cyclobutene would support a concerted reaction, since it adds onto dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate in a concerted [4 + 2] cycloaddition 14 times as fast as cyclopentene and still with one third of the rate of norbornene.[13] Also, cyclohexene and *cis*-cyclooctene, which react significantly slower than cyclopentene with the tetrazine,[13] would not militate against concertedness of the [4 + 2] cycloaddition onto ^{3}**CA**, as they furnish only [2 + 2] cycloadducts and no product of the [4 + 2] mode.[3a] However, *trans*-cyclooctene severely questions concertedness of the [4 + 2] cycloaddition onto ^{3}**CA**, since it combines over 1000 times as fast as norbornene with the tetrazine[13] and yet does not give a product formed *via* a [4 + 2] cycloaddition onto ^{3}**CA**.[3a]

The stereochemical alternatives of the 1 : 2 cycloadducts **2** and **3** are the same as in the case of cyclopentene as substrate for ^{3}**CA**. At variance with the reaction of cyclohexene,[3a] an antarafacial cycloaddition can be excluded on the grounds of ring strain of the potential product. Thus, as conceivable precursors for **2** and **3**, the 1 : 1 cycloadducts **8a** and **8b** (Scheme 2) have to be discussed, in which the six-membered and the terminal four-membered ring are located *trans* and *cis*, respectively, at the central cyclobutane subunit. However, we observed neither **8a** nor **8b**. Apparently, the excitation of these compounds by the light used and the subsequent reaction with the excess of cyclobutene occurred more readily than the corresponding processes of the 1 : 1 cycloadducts of **CA** with cyclopentene, cyclohexene and *cis*-cyclooctene under similar conditions. There, 1 : 1 cycloadducts were observed and some of them even isolated.[3a,b]

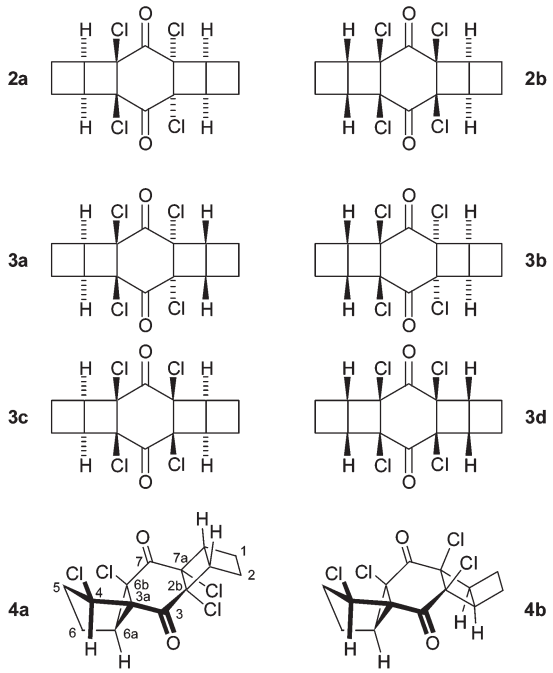


Fig. 1 Possible configurations of the photocycloadducts **2** and **3** of **CA** onto cyclobutene and of the product **4** resulting from the rearrangement of **3**.

Possibly, the reaction of excited **8a** and/or **8b** with cyclobutene proceeds even faster than that of ^{3}**CA**.

With **8a** and **8b** being the possible precursors, the diastereomers **2a** and **2b** have to be considered as the C_s symmetric 1 : 2 cycloadduct (Fig. 1). The difference between the two consists in the relative arrangement of the bicyclo[2.2.0]hexane moieties at the cyclohexanedione core, which is *trans* in **2a** and *cis* in **2b**. The formation of **2b** could be at a disadvantage with that of **2a**, since cyclobutene would have to approach the excited **8a** or **8b** from the *endo* side, which is sterically strongly hindered by the bicyclo[2.2.0]hexane part. The configuration of **2a** is analogous to that of the sole 1 : 2 cycloadduct of cyclopentene, which has been analysed by X-ray diffraction.[3b]

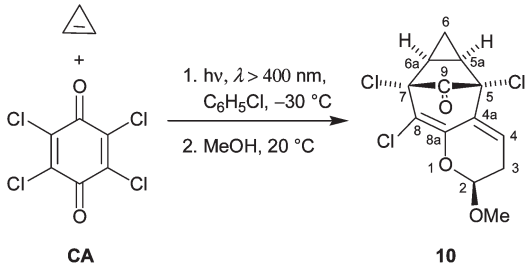
In the case of the C_{2h} or C_{2v} symmetric 1 : 2 cycloadduct, the four diastereomers **3a–3d** are possible (Fig. 1). As with the comparison of **2a** and **2b**, we favour **3a** and **3b** because of the *trans* annulation of the bicyclo[2.2.0]hexane systems at the cyclohexanedione core over **3c** and **3d**, although there is no experimental evidence for this assumption. However, the most likely configuration of the rearrangement product **4** puts stereochemical restrictions on the precursor **3** (see below).

The ^{1}H NMR spectrum of **4** contains characteristic information on the steric arrangement of the bicyclo[3.1.0]hexane system. Causing a doublet with the coupling constant of 5.4 Hz, the proton at the three-membered ring, therefore, interacts only with the *exo* proton of the proximal methylene group. This pattern is typical for the boat conformation of the bicyclo[3.1.0]hexane skeleton,[14] which has been known for the parent hydrocarbon for a long time.[15,16] The multiplicity of the signal of the CHCl group is revealing as well, as it is a triplet with a line distance of 9.2 Hz. Thus, this proton is coupled equally strongly with both protons of the neighbouring methylene group. This situation is

in accord only with the *exo* position of this proton at the bicyclo[3.1.0]hexane system, since, as an *endo* proton, it would exhibit a resolved interaction exclusively with the *endo* proton of the neighbouring methylene group.[14]

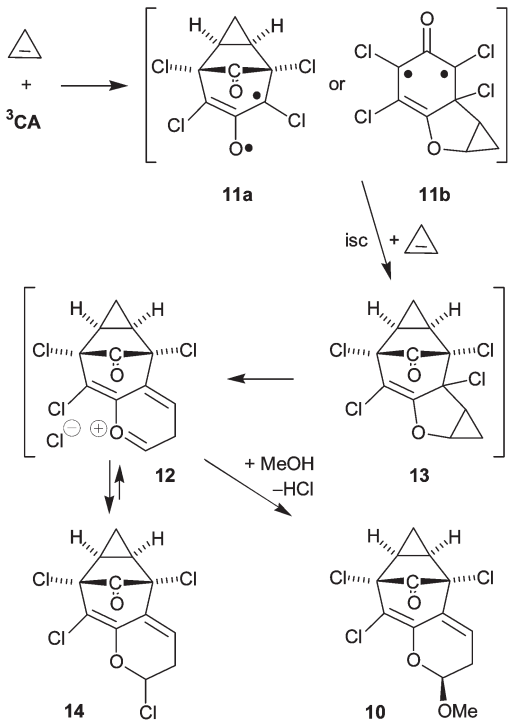
Based on these findings, configuration and conformation of the bicyclo[3.1.0]hexane subunit of **4** are determined as illustrated by the formulas **4a** and **4b** in Fig. 1. The chlorine atom at the cyclopropane moiety must be located *endo*, since, owing to the carbonyl groups and the annulation of two small rings, the six-membered ring is rather rigid and cannot be annulated *trans* at the cyclopropane moiety due to intolerable ring strain. In consequence, chlorine and hydrogen atom at the cyclopropane entity must be arranged *trans*. If it is further taken into account that the configuration of the migrating centre is retained in the Wagner–Meerwein rearrangement, only those isomers **3** have to be considered as precursors of **4** that have a *trans* relationship between a chlorine atom and the hydrogen atom next to it, that is, **3a** and **3c**. In contrast, the rearrangement of **3b** and **3d** would lead to the *trans* annulation of the five- or six-membered ring at the cyclopropane moiety. As discussed above, we favour **3a** and, hence, **4a** over **3c** and **4b**, respectively.

Our imagination of the reorganisation of **3a** or **3c** starts with an inspection of the bond common to the two cyclobutane subunits of a bicyclo[2.2.0]hexane system. Because of the angle strain, the electron density is bent out of the straight line between the respective carbon nuclei on the side opposite to the chlorine atoms. This electron pair should have attacked a chlorine-bearing carbon atom and displaced the chlorine atom from the rear, resulting in the cyclopropylcarbinyl cation within the ion pair **9** (Scheme 2). Without the necessity to change the face of the ring system, the chloride ion now should have been bound by the carbocationic centre giving rise to **4a** or **4b** (Fig. 1). Overall, the migrating CH group and the chloride ion, hence, would have undergone a [1,2] transposition. The present rearrangement is closely related to the conversion of *endo*-6-chlorobicyclo[3.1.0]hexane into 3-chlorocyclohexene.[17]



CA 10

Scheme 3 The compound **10** isolated after the photochemical reaction of chloranil (**CA**) with cyclopropene and the treatment of the crude product with methanol.



Scheme 4 Mechanistic proposals for the photochemical reaction of chloranil (**CA**) with cyclopropene and the methanolysis of the initial product.

2. Cyclopropene

The irradiation of **CA** in the presence of cyclopropene was carried out under the same conditions as in the case of cyclobutene, except that now the temperature was kept at −30 °C. After the complete consumption of **CA**, the major amount of the solvent chlorobenzene was quickly evaporated at 35 °C/15 mmHg, the residue immediately dissolved in methanol and the mixture left at 20 °C for 24 hours. By flash chromatography, the tetracyclic acetal **10** (Scheme 3) was then isolated as the sole product in 36% yield. Its structure was determined by X-ray diffraction.[18]

The ^{1}H NMR spectrum of the crude product prior to methanolysis indicated a complex mixture, whose main component we take for the α-chloro ether **14** (Scheme 4), which should have been the precursor to **10**. In particular, chemical shifts and coupling constants of four signals are very similar to those of the cyclopropane protons of **10**. In addition, the multiplets at δ 6.24 and 6.39 should originate from the olefinic proton and the CHCl group. Only the bands of the allylic methylene group cannot be identified unambiguously.

As the skeleton of **10** testifies, **CA** took up two cyclopropene molecules by the excitation. One of them retained the three-membered ring, whereas the other, with inclusion of a chlorine-bearing carbon atom, underwent the rearrangement to a homoallyl system. Such a reorganisation is typical for cyclopropylcarbinyl subunits carrying a leaving group. In the first section, we have quoted the transformation of the unsubstituted cyclopropylcarbinyl chloride to chlorocyclobutane, parallel to which homoallyl chloride is generated.[11] In this way, the homoallyl chloride **14** should have been formed from the cyclopropylcarbinyl chloride **13**, namely by heterolytic dissociation and opening of the three-membered ring giving rise to the ion pair **12** (Scheme 4), the collapse of which should have resulted in **14**. The conversion of the α-chloro ether **14** into the acetal **10** is considered to be an S_N1 substitution with the ion pair **12** again being the intermediate. The ease of the isomerisation **13** → **14**,

which did occur already under the conditions of the photochemical reaction (−35 °C) or the workup (up to 35 °C), has probably its cause in the oxygen atom bound to the cyclopropane moiety and being a good electron donor. In consequence, the cation of **12** is a carbenium–oxonium ion and thus highly stabilised.

To rationalise the formation of **13**, we propose the diradicals **11a** and **11b**, which should have been generated by addition of one cyclopropene molecule onto ^{3}**CA** and should have furnished **13** by reaction with a second one. Thus, a single excitation of **CA** would have led to the taking up of two cyclopropene molecules. Owing to the triplet nature of the reacting **CA**,[2] an intermediate **11a** or **11b** should have resulted as a triplet diradical. En route to **13**, an intersystem crossing would then have been required.

Both **11a** and **11b** are derivatives of the oxyallyl diradical. In the case of **11b**, a vinyl group extends the π-electron system. Recently, the unsubstituted oxyallyl diradical was observed spectroscopically for the first time. It is characterised by only a small energy gap between the singlet and the triplet state, with the former being the more stable one by 1.3 kcal mol^{-1}.[19] Also, this finding was compared to the results of previous and the most recent theoretical studies.[19,20]

The resonance structures of **11a** and **11b** in Scheme 4 have been chosen such that they illustrate the formation of **13** by a [3 + 2] cycloaddition each with cyclopropene. The reaction of ^{3}**CA** with cyclopropene to give **11a** or **11b** is also a [3 + 2] cycloaddition. Such processes of ^{3}**CA** are unknown heretofore. Compared with that, [3 + 2] cycloadducts of oxyallyl systems with 1,3-dienes[21] and vinyl ethers[22] were obtained and shown to be of the cyclopentanone and α-methylenetetrahydrofuran types. A quantum chemical investigation of the reaction between the uncharged oxyallyl and 1,3-butadiene indicated, for the [3 + 2] cycloaddition, the route to an α-methylenetetrahydrofuran as the most favourable pathway.[23]

It is interesting to note that oxyallyl intermediates can be generated photochemically from cross-conjugated cyclic dienones.[24] This class of compounds is related to quinones, such as **CA**. In particular, a transient oxyallyl with a bicyclic skeleton can be trapped on irradiation of 2,7-cyclooctadienone in the presence of vinyl ethers to give tricyclic norbornanones and oxatriquinanes.[22,24]

Conclusions

On employment of cyclobutene, we have discovered the first alkene that is not a derivative of cyclopentene and yet undergoes a [4 + 2] cycloaddition with ^{3}**CA**. With opening of the ring originating from **CA**, this reaction is believed to yield the tetrachlorobenzofuranone derivative **6** and, from it by the action of methanol, the isolated product, namely the α,β unsaturated methyl γ-oxocarboxylate **1**. In addition to **1**, a C_s and a C_{2h} or C_{2v} symmetric 1 : 2 cycloadduct (**2** and **3**, respectively) onto the ethene subunits of **CA** were obtained as well as the rearrangement product **4** of **3**. Most probably promoted by the polar solvent methanol, this rearrangement brought about a cyclopropylcarbinyl chloride from a chlorocyclobutane. In the case of the 1 : 2 cycloadducts of **CA** with the higher cycloalkenes cyclopentene, cyclohexene and cyclooctene, such a transformation was not observed.

An entirely new reaction type was found by irradiation of **CA** in the presence of cyclopropene. After the methanolysis of the crude product, the tetracyclic acetal **10** was isolated. It is believed that two subsequent [3 + 2] cycloadditions of cyclopropene onto ^{3}**CA** furnished the pentacyclic intermediate **13**, which underwent a ring expansion to give the 2-chlorodihydropyran **14**. Dissolved in methanol, the latter was subject to an S_N1 substitution with formation of **10**.

Because of the product mixture, the photocycloaddition of cyclobutene onto **CA** will probably not gain preparative importance. However, the single product obtained in the case of cyclopropene could be of interest as starting material for syntheses, in particular, as cyclopropene is easily accessible in quantity.[25] Additionally, a number of cyclopropene derivatives are readily prepared in useful amounts[26] and can be envisaged for the synthesis of substituted derivatives of **10**.

The most interesting aspect of this work and the previous studies on this subject[3a,b,27] is the puzzling reactivity of ^{3}**CA** with alkenes that do not transfer a single electron to ^{3}**CA**. The [2 + 2] cycloaddition onto a dichloroethene subunit proceeds most frequently. In addition to that, the [4 + 2] cycloaddition involving the positions 2 and 5 of ^{3}**CA** takes place with cyclopentenes and cyclobutene and is the major reaction by far in the case of norbornene. Finally, a [3 + 2] cycloaddition onto either the positions 2 and 6 or an oxygen and a proximal chlorine-bearing carbon atom of ^{3}**CA** was exclusively observed in the case of cyclopropene. It is very possible that these three addition types start with a common first step, that is, the making of a C–C bond resulting in a triplet diradical. These species would then collapse to give rings of different size according to the kind of alkene. There is an alternative first step conceivable only in the case of cyclopropene, as a C–O bond could initially be formed en route to the possible intermediate **11b**. Quantum chemical calculations could greatly contribute to an understanding of these phenomena.

Experimental

General details and general conditions for the photochemical reactions

See ref. 3*a*.

Irradiation of chloranil (CA) in the presence of cyclobutene

In a photolysis vessel, a solution of **CA** (1.00 g, 4.07 mmol) in anhydrous chlorobenzene (150 cm^3) was saturated with nitrogen and then cooled to −30 °C. Having been stored in a freezer under nitrogen, cyclobutene[28] (440 mg, 8.14 mmol) was added. The mixture was then irradiated by utilising a pyrex immersion well containing a Hanovia mercury lamp (medium pressure, 450 W), which was surrounded by a glass filter supposed to prevent the passage of light of $\lambda < 400$ nm, at −5 °C. After **CA** had been completely consumed (6 h), the solvent was quickly (15 min) evaporated at 35 °C (bath)/15 mmHg and the remaining yellow oil was immediately refluxed in anhydrous methanol (150 cm^3) over 18 h. The mixture was then concentrated *in vacuo* and the

Table 1 Proton–proton coupling constants of **1**, with which the simulation of the multiplets gives an excellent match with the experimental fine structure

Chemical shifts (δ/ppm)	Coupling constants (Hz) with the protons at δ				
	2.196	2.550	2.670	3.560	4.030
2.124	9.8	3.1	−11.8	3.0	−0.9
2.196		−11.6	9.8	−1.1	9.3
2.550			9.4	2.0	9.0
2.670				9.5	0.0
3.560					8.1

residue subjected to flash chromatography (SiO_2, pentane–ethyl acetate 25 : 1). Four fractions, a yellow oil each, were collected, from which crystals were obtained after dissolution in the minimum quantity of ethyl acetate and storage of the solutions at −30 °C. The order of the elution was: (2aα,2bα,3aβ,3bα,5aα,5bβ,6aα,6bα)- **2a** or (2aα,2bβ,3aβ,3bβ,5aβ,5bβ,6aβ,6bα)-2b,3a,5b,6a- tetrachlorododecahydrodicyclobuta[1,2:1′,2′]dicyclobuta[3,4-*a*:3′,4′-*d*]benzene-3,6-dione **2b** (81 mg, 6%), (2a*S*,2b*R*,3a*S*,4*S*,6a*R*,6b*R*,7a*S*,7b*R*)-*rel*- **4a** or (2a*R*,2b*S*,3a*S*,-4*S*,6a*R*,6b*R*,7a*R*,7b*S*)-*rel*-2b,4,6b,7a-tetrachlorodecahydro(cyclopenta[1,2]cyclopropa)(cyclobuta[1′,2′]cyclobuta)[2,3-*a*:3′,4′-*d*]-benzene-3,7(1*H*)-dione **4b** (348 mg, 24%), methyl (*E*)-[(2aα,6aα)-5,6-dichloro-2,2a,4,6a-tetrahydro-4-oxocyclobutabenzen-3(1*H*)-ylidene]chloroacetate **1** (296 mg, 25%) and (2aα,2bβ,3aα,3bβ,5aβ,5bα,6aβ,6bα)- **3a** or (2aα,2bα,3aβ,3bβ,5aβ,5bβ,6aα,6bα)- **3b** or (2aα,2bβ,3aβ,3bα,5aα,5bβ,6aβ,6bα)- **3c** or (2aα,2bα,3aα,3bα,5aα,5bα,6aα,6bα)-2b,3a,5b,6a- tetrachlorododecahydrodicyclobuta[1,2:1′,2′]dicyclobuta[3,4-*a*:3′,4′-*d*]benzene-3,6-dione **3d** (151 mg, 10%).

Compound **1**, colourless solid (the formation of crystals lasted 4 weeks), mp 99–101 °C (Found: C, 45.0; H, 3.1. $C_{11}H_9Cl_3O_3$ requires C, 44.7; H, 3.1%); ν_{max} (KBr)/cm^{-1} 2994m, 2958m, 2936m, 1732s, 1668s, 1601s, 1581s, 1451m, 1435s, 1334m, 1305s, 1285s, 1268s, 1247m, 1242m, 1211s, 1200m, 1122m, 1050s, 1029m, 970m, 934w, 882m, 852w, 808w, 774w, 751m, 734m, 660m, 642m and 622m; δ_H (400 MHz; $CDCl_3$) 2.124 (1 H, m) and 2.670 (1 H, m) (CH_2), 2.196 (1 H, m) and 2.550 (1 H, m) (CH_2), 3.56 (1 H, m, CH), 3.91 (3 H, s, CH_3) and 4.03 (1 H, m, CH). The fine structure of the multiplets is distinctive, but cannot be described in simple terms due to higher order effects. Therefore, we have simulated the shape of the multiplets by using the gNMR program.[29] The coupling constants listed in Table 1 furnish an excellent match and, thus, testify to a significant folding of the cyclobutane subunit. δ_C (63 MHz; $CDCl_3$) 26.1 (CH_2), 26.3 (CH_2), 33.8 (CH), 41.9 (CH), 53.5 (CH_3), 130.8 (CCl), 132.2 (CCl), 133.8 (CCl), 156.4 (C-3), 164.6 (CO_2CH_3) and 175.5 (C-4); *m*/*z* (EI, 70 eV) 298, 296, 294 (M^+, 5, 16, 17%), 270 (26), 268 (78), 266 (83), 253 (23), 251 (24), 235 (28), 233 (63), 231 (100), 227 (22), 203 (20), 181 (24), 179 (24), 174 (28), 172 (43) and 59 (32).

Compound **2**, colourless crystals, mp 172–174 °C (Found: C, 47.7; H, 3.3. $C_{14}H_{12}Cl_4O_2$ requires C, 47.5; H, 3.4%); ν_{max} (KBr)/cm^{-1} 2985w, 2963w, 2942w, 2930w, 1732s, 1726s, 1182m, 1099m, 1071w, 1036w, 1019w, 751w and 669w; δ_H (250 MHz; $CDCl_3$) 1.79 (2 H, m), 2.37–2.77 (6 H, m), 3.38 (2 H, m) and 3.67 (2 H, m); δ_C (63 MHz; $CDCl_3$) 23.4 (CH_2), 23.5 (CH_2), 43.4 (CH), 47.6 (CH), 68.9 (CCl), 81.3 (CCl) and 192.8 (CO); *m*/*z* (EI, 70 eV) 354 (M^+, 0.1%), 175 (15), 143 (30), 141 (91), 115 (25), 113 (34), 105 (22), 78 (20), 77 (100), 53 (24), 51 (35) and 39 (22).

Compound **3**, colourless crystals, mp 170–171 °C (Found: C, 47.2; H, 3.2. $C_{14}H_{12}Cl_4O_2$ requires C, 47.5; H, 3.4%); ν_{max} (KBr)/cm^{-1} 3010w, 2994w, 2958m, 1731s, 1722s, 1436w, 1266w, 1259m, 1163m, 1139m, 1102m, 1067m, 1054m, 1015m, 942w, 925m, 915w, 810w, 693m and 673m; δ_H (250 MHz, $CDCl_3$) 2.42–2.69 (8 H, m) and 3.63 (4 H, m); δ_C (63 MHz; C_6D_6) 22.2 (CH_2), 42.2 (CH), 76.9 (CCl) and 192.1 (CO); *m*/*z* (EI, 70 eV) 321, 319, 317 (M^+ − Cl, 4, 11, 12%), 267 (22), 266 (20), 265 (55), 263 (60), 239 (26), 238 (22), 237 (69), 235 (73), 233 (22), 231 (34), 149 (20), 143 (24), 141 (52), 115 (20), 113 (24), 105 (23), 77 (79), 75 (23), 54 (100), 51 (41) and 39 (26).

Compound **4**, colourless crystals, mp 213–214 °C (Found: C, 47.9; H, 3.2. $C_{14}H_{12}Cl_4O_2$ requires C, 47.5; H, 3.4%); ν_{max} (KBr)/cm^{-1} 2986m, 2948m, 2931m, 2856w, 1726s, 1700s, 1458w, 1320w, 1308w, 1287w, 1260m, 1245w, 1231w, 1209m, 1156m, 1067w, 1058w, 1006w, 946w, 938m, 928m, 907m, 855w, 710m and 616w; δ_H (400 MHz; $CDCl_3$) 2.28 (1 H, m), 2.36–2.61 (7 H, m), 3.25–3.33 (2 H, m), 3.64 (1 H, d, *J* 5.4, H on cyclopropane moiety) and 5.16 (1 H, t, *J* 9.2, CHCl); δ_C (63 MHz; $CDCl_3$) 20.9 (CH_2), 21.1 (CH_2), 26.2 (CH_2), 33.6 (CH_2), 38.8 (CH), 40.3 (CH), 44.9 (CH), 58.3 (CHCl), 58.8, 66.2, 69.6 and 70.7 (3 CCl and C_q), 189.6 and 193.5 (2 CO); *m*/*z* (EI, 70 eV) 356, 354, 352 (M^+, 0.2, 0.4, 0.3%), 321, 319, 317 (M^+ − Cl, 7, 24, 24), 283 (23), 281 (34), 253 (20), 247 (20), 245 (44), 217 (28), 209 (29), 181 (23), 153 (22), 143 (21), 141 (67), 115 (20), 113 (22), 105 (40), 77 (100) and 51 (40).

In the NMR spectra of the crude product prior to methanolysis, only the signals of chlorobenzene, **3** and a third component could be unambiguously discerned. We take the latter for the pseudoacid chloride **6**, which should be converted into the methyl ester **1** by methanol; δ_H of the third component (250 MHz; $CDCl_3$) 1.70–3.80 (several m); δ_C of the third component (63 MHz; $CDCl_3$) 22.0 (CH_2), 26.7 (CH_2), 32.0 (CH) and 49.4 (CH); the signals of the carbon atoms without a hydrogen atom were not observed due to too low intensities.

Irradiation of chloranil (CA) in the presence of cyclopropene

In a photolysis vessel, a solution of **CA** (800 mg, 3.25 mmol) in anhydrous chlorobenzene (150 cm^3) was saturated with nitrogen and then cooled to −30 °C. Cyclopropene was prepared by treatment of allyl chloride (23.0 g, 301 mmol) with sodium amide (12.0 g, 308 mmol) according to Closs and Krantz.[25a] It was driven out of the generator flask by a slight stream of nitrogen, conducted through 2 N sulfuric acid (to remove ammonia) and a tube containing phosphorous pentoxide (to remove water) and led into the solution of **CA** by a pvc tube. After the introduction of cyclopropene had taken place for 10 min, the mixture was irradiated by utilising a pyrex immersion well containing a Hanovia mercury lamp (medium pressure, 450 W), which was surrounded by a glass filter supposed to prevent the passage of light of $\lambda < 400$ nm, at −30 °C. Initially, cyclopropene caused a clouding (probably a precipitate of **CA**), but the mixture became

clear again until the end of the cyclopropene addition (2 h). After **CA** had been completely consumed (6 h of irradiation), the mixture was quickly (15 min) concentrated to a volume of about 10 cm^3 at 35 °C (bath)/15 mmHg, then immediately treated with anhydrous methanol (150 cm^3) and kept at 20 °C for 24 h. Evaporation of the methanol *in vacuo* and flash chromatography (SiO_2, pentane–ethyl acetate 9 : 1) of the residue at −30 °C furnished (2α,5β,5aβ,6aβ,7β)-5,7,8-trichloro-3,5,5a,6,6a,7-hexahydro-2-methoxy-5,7-methano-2*H*-cyclopropa[4,5]cyclohepta[1,2-*b*]pyran-9-one **10** (375 mg, 36%) as an oil, which gave colourless crystals, mp 148–150 °C, after treatment with a small quantity of ethyl acetate (Found: C, 48.2; H, 3.3. $C_{13}H_{11}Cl_3O_3$ requires C, 48.55; H, 3.45%); ν_{max} (KBr)/cm^{-1} 3085w, 3072w, 3002w, 2960m, 2940m, 2910w, 2900w, 2845w, 1788s, 1584m, 1451m, 1442m, 1420m, 1392m, 1373m, 1352m, 1338m, 1232m, 1222m, 1182m, 1172m, 1150m, 1142m, 1128m, 1113s, 1086m, 1068s, 1060s, 1022s, 1010s, 984s, 955m, 940s, 915s, 878s, 855m, 839m, 822s, 818s, 792w, 762w, 751m and 737m; δ_H (200 MHz; $CDCl_3$) 0.78 (1 H, dt, *J* 7.9 and 3.9, 6-H_α), 1.14 (1 H, dt, *J* 7.9 and 7.1, 6-H_β), 2.04 (1 H, ddd, *J* 7.6, 7.1 and 3.8) and 2.63 (1 H, ddd, *J* 7.6, 7.1 and 4.0) (5a-H and 6a-H), 2.48 (1 H, ddd, *J* 18.6, 5.6 and 2.0) and 2.68 (1 H, ddd, *J* 18.6, 4.3 and 3.4) (3-H_α and 3-H_β), 3.42 (3 H, s, CH_3), 5.16 (1 H, ddd, *J* 4.3, 2.0 and 0.6, 2-H) and 6.14 (1 H, ddd, *J* 5.6, 3.4 and 0.6, 4-H); δ_C (50 MHz; $CDCl_3$) 11.3 (C-6), 27.1 and 32.0 (C-5a and C-6a), 30.0 (C-3), 56.0 (CH_3), 75.2 and 76.6 (C-5 and C-7), 98.6 (C-2), 115.9 (C-8), 118.5 (C-4), 130.7 (C-4a), 143.3 (C-8a) and 192.2 (C-9); *m*/*z* (EI, 70 eV) 326, 324, 322, 320 (M^+, 1, 10, 30, 31%), 285 (10), 255 (10), 253 (15), 249 (15), 227 (11), 225 (14), 199 (12), 162 (11), 115 (14), 71 (79), 58 (100) and 45 (17).

The ^1H NMR spectrum of the crude product prior to methanolysis indicated the presence of a complex mixture, whose major component, apart from chlorobenzene, was most likely the α-chloro ether **14**; δ_H (250 MHz; $CDCl_3$) 0.84 (1 H, dt, *J* 7.9 and 3.9) and 1.21 (1 H, dt, *J* 7.9 and 7.1) (6-H_2), 2.16 (1 H, ddd, *J* 7.7, 7.1 and 3.7) and 2.69 (1 H, ddd, 7.7, 7.1 and 4.1) (5a-H and 6a-H), 6.24 (1 H, ddd, *J* 6.6, 2.6 and 1.0) and 6.39 (1 H, dt, *J* 4.3 and 1.2) (2-H and 4-H); because of several multiplets in the pertinent region, the signals of the 3-CH_2 group could not be unambiguously localised, but the most likely chemical shifts are δ 2.90 and 3.00.

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