Photochemical reactions of chloranil with norbornene,† bicyclo[2.1.1]hex-2-ene and cyclopentene. A novel intermolecular photocycloaddition

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Received (in Cambridge, UK) 5th May 1999, Accepted 28th July 1999

The irradiation of chloranil (**CA**), dissolved in benzene, in the presence of norbornene gave the α,β-unsaturated α,γ-dichloro-γ-lactone **1** in 67% yield. Heretofore, such a product had not been observed in a photochemical reaction of **CA** with an alkene. In addition, bicyclo[2.1.1]hex-2-ene and cyclopentene furnished compounds such as **1**. However, conventional products of the reaction of ^{3}**CA** with alkenes were formed in these cases to a considerable extent as well. As the first step *en route* to **1**, a [4 + 2] cycloaddition of ^{3}**CA** onto norbornene is proposed giving rise to a diradical of type **23**, which undergoes the opening of the six-membered ring originating from **CA** with formation of a β-oxoketene of type **20**. The ring closure of the latter with concomitant [1,2] migration of a chlorine atom completes the sequence. On treatment with methanol, the pseudoacid chloride **1** was converted into the pseudoesters **3** and the ester **4**. The structures of **3** and the 2:1 cycloadduct **12** of cyclopentene onto **CA** were analysed by X-ray crystallography.

Introduction

Because of the great variety of possible processes, chloranil (**CA**) is of particular interest with regard to photochemical reactions of quinones with alkenes.[1,2a] In the introduction of the preceding paper,[3] the different types of reactions have been summarised, of which [2 + 2] cycloadditions with formation of cyclobutanes and oxetanes are the most important ones. Also, cycloadditions proceeding with rearrangement play a major part. Using homobenzvalene is a good example of this as its reaction with excited **CA** leads to rearranged cycloadducts exclusively,[3] although the photocycloadditions of methyl phenylglyoxylate, benzil, benzophenone, benzo-1,4-quinone, naphtho-1,4-quinone and cyclopent-2-en-1-one onto this cycloalkene smoothly proceed without rearrangements to give oxetane and cyclobutane derivatives, respectively.[4] In the case of norbornadiene, the reaction with excited **CA** furnished rearranged cycloadducts in addition to oxetane derivatives.[3] This finding motivated us to investigate norbornene, the π bond of which is highly reactive in many types of reactions.[5,6] Furthermore, norbornene may give rise to a rearranged product if a cationic intermediate, a derivative of the 2-norbornyl cation, is involved. As the subunit of a zwitterion, such a cation might be generated, if an electron transfer (ET) from norbornene to the triplet state of **CA** (^{3}**CA**) takes place followed by the appropriate collapse of the radical-ion pair. The probability of an ET can be estimated by using the Weller equation,[7] according to which the free enthalpy of the ET is determined by the energy of ^{3}**CA** (2.13 eV[8]), the reduction potential of **CA** (0.01 V *vs.* SCE[9]), the oxidation potential of the substrate and the solvent polarity. Being 1.95 V,[10] the oxidation potential of norbornene is significantly lower than that of cyclohexene (2.14 V[11]), for which the ET to ^{3}**CA** in benzene was assessed to be endergonic by *ca.* 9 kcal mol^{-1}.[12] Therefore, we considered the ET in the case of norbornene as a realistic possibility ($\Delta G_{ET} \approx 4$ kcal mol^{-1}). The performance of the reaction then led to the surprising result that the adduct possessed an unchanged norbornane skeleton, whereas the moiety stemming from **CA** was rearranged extensively. In order to probe the scope of this reaction type, we studied a number of cycloalkenes, *inter alia* bicyclo[2.1.1]hex-2-ene and cyclopentene.

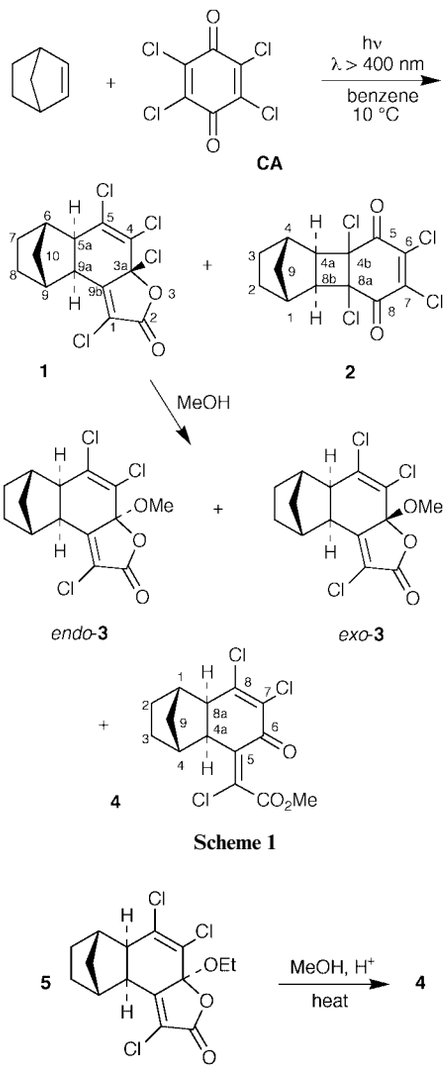
Results

The irradiation of a solution of **CA** and norbornene in benzene at 10 °C furnished a small quantity of the cyclobutane derivative **2** and 67% yield of an isomer (Scheme 1). Its spectra were not in accord with those anticipated for the oxetane derivative **6**, which was isolated from a later experiment (see below). We then noticed the rather ready decomposition of the substance concomitant with a smell of hydrogen chloride in the absence of special precautions. In consequence, we treated the crude product of the photochemical reaction with methanol at rt and obtained after chromatography **2**, the α,β-unsaturated γ-methoxy-γ-lactones *endo*-**3** and *exo*-**3**, as well as an isomer, the ester **4**, in 12, 60, 14 and 9% yield, respectively. The structures of both pseudoesters **3** were established by X-ray diffraction (Fig. 1). Because of the striking similarity of the NMR spectra of *exo*-**3** with those of the major product prior to methanolysis, we assign to the latter the structure of the α,β-unsaturated α,γ-dichloro-γ-lactone **1**.

When the crude product of the photochemical reaction was subjected to ethanolysis, the ethyl pseudoester **5** could be isolated in 54% yield, even without chromatography. On heating in methanol in the presence of sulfuric acid as catalyst, **5** was converted into the ester **4** in 88% yield (Scheme 2).

In order to methanolise the pseudoacid chloride **1** *in situ*, we illuminated a solution of **CA** and norbornene in a 1:1 mixture of benzene and methanol. Indeed, the desired compounds were

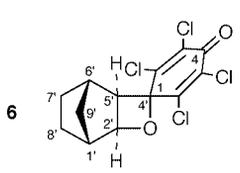
† The IUPAC name for chloranil is tetrachlorobenzoquinone and for norbornene is bicyclo[2.2.1]hept-2-ene.



Scheme 1

Scheme 2

formed, albeit only in poor yields. By chromatography of the crude product, only fractions with substantial impurities could be obtained. From one of them, a 2% yield of the oxetane derivative **6** was isolated.



Photocycloadditions of **CA** onto simple cycloalkenes have so far been described only for cyclooctene[13] and cyclohexene[12] and compounds such as **1** and **2** have not been obtained from these reactions. Therefore, we chose for the next experiment a substrate closely related to norbornene, *i.e.* bicyclo[2.1.1]hex-2-ene. Since the NMR spectra of the crude product indicated the formation of a complex mixture, we made no attempt to isolate a pseudoacid chloride such as **1**, but carried out a methanolysis immediately. By chromatography, a 1:4 mixture of the dicyclobutane derivative **7** and its adduct **8** of hydrogen chloride, the oxetane **9** and the pseudoester **10** were obtained in 16, 22 and 12% yield, respectively (Scheme 3).

Norbornene and bicyclo[2.1.1]hex-2-ene are derivatives of cyclopentene, which is why we irradiated **CA** in the presence of this alkene. The treatment with methanol of the crude product of the cyclopentene reaction at rt did not remove its tendency to decomposition. Only by refluxing in methanol did a mixture

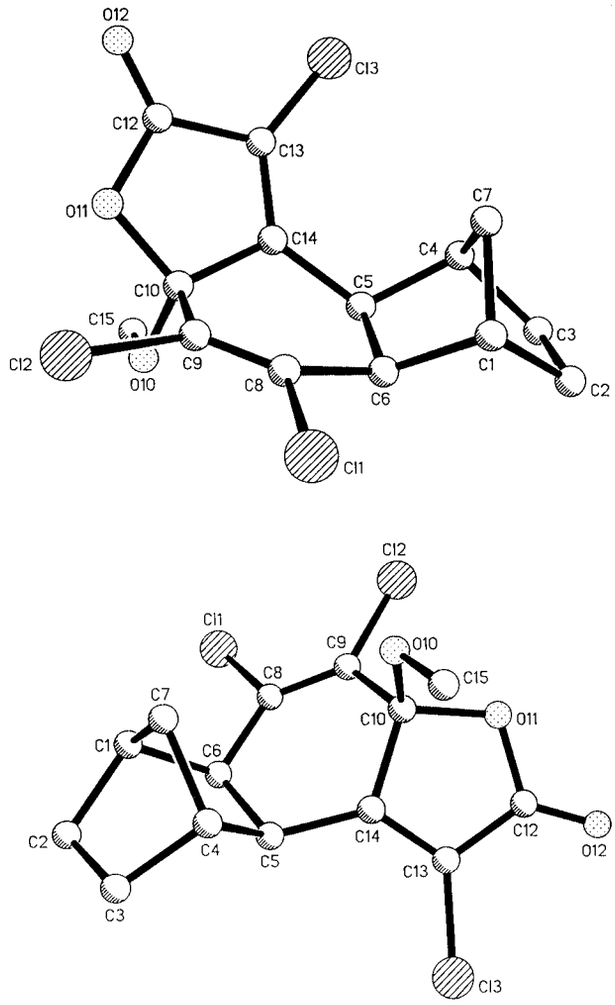
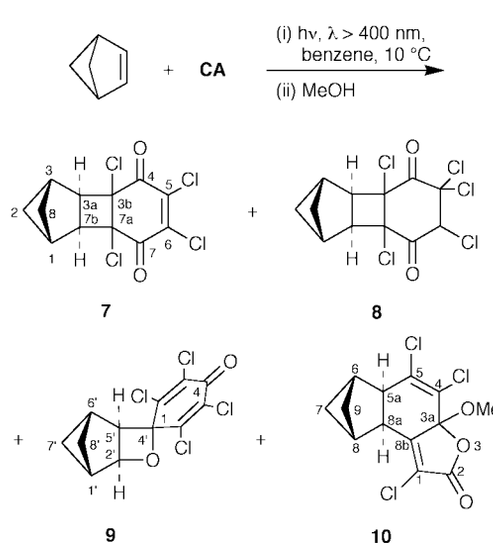


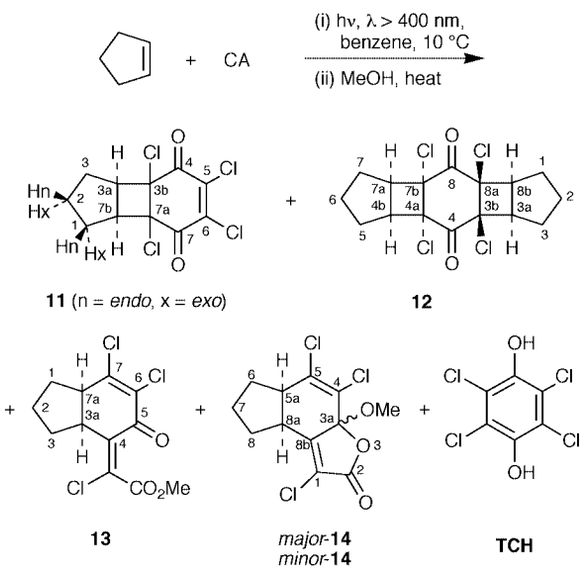
Fig. 1 Molecular structure of the pseudoesters *endo*-**3** (top) and *exo*-**3** (bottom) as determined by X-ray diffraction. The numbering of the atoms does not correspond to the systematic name.



Scheme 3

result that could be separated by chromatography. A 9, 8, 15, 2, 11 and 8% yield of the cyclobutane derivative **11**, the 2:1 adduct **12**, the ester **13**, the pseudoester *minor*-**14**, the pseudoester *major*-**14** and tetrachlorohydroquinone (**TCH**), respectively, were obtained (Scheme 4).

Benzvalene, another cyclopentene derivative, had been subjected to excited **CA** previously.[14] At −30 °C, an oxetane



Scheme 4

derivative was formed exclusively, whereas a small amount of a rearranged adduct emerged at rt as well. However, there was no evidence for a pseudoacid chloride such as **1**. In addition to benzvalene, norbornene, bicyclo[2.1.1]hex-2-ene and cyclopentene, we have also included cyclopropene, cyclobutene, cyclohexene and cyclooctene in our studies.[15] The results will be reported in future publications, but it is noted in advance that the corresponding product of compound **1** was observed only in the case of cyclobutene.

The ^{1}H NMR spectra of the products **1**–**6** clearly document that the reaction with **CA** left the norbornane skeleton intact and that the cycloadditions proceeded at the *exo* face, which is in accord with virtually all reactions of the norbornene double bond.[5,6] Single crystal X-ray analyses prove these facts for compounds **3** (Fig. 1). Their pseudoester subunits reveal a surprising variability of the CO single bond lengths. The distances C10–O10 and C10–O11 (C-3a–OMe and C-3a–O-3 according to the numbering associated with the systematic name) were determined to be 138.7 and 145.3 (*endo*-**3**) or 146.3 pm (*exo*-**3**), respectively. These values deviate considerably from the standard bond length (143 pm[16]), while those of O10–C15 (143.3 or 143.5 pm) are very close to it. The distinction between the cyclobutane **2** and the oxetane **6** was made on symmetry grounds, causing different numbers of signals in the NMR spectra. Furthermore, the chemical shifts clearly indicate the presence (**6**) or the absence (**2**) of a CH–O group. Whether in **2**, the 4a,8b-H and 4b,8a-Cl are bound to the four-membered ring *cis* or *trans* to each other, could not be determined. A characteristic feature of **4** is the presence of two different carbonyl groups, the signals of which in the ^{13}C NMR (δ 164.7, 176.5) and IR spectra (ν_{max} 1741, 1662 cm^{-1}) have to be assigned to an ester and a ketone functionality, both of them α,β-unsaturated.

Based on our experience of bicyclo[2.1.1]hexane derivatives,[17] we recognised this subunit readily by the ^{1}H NMR spectral data of compounds **7**–**10**. Thus, a rearrangement of the olefinic skeleton had not occurred in the reaction with **CA**. In comparison with the data of the products originating from norbornene, the assignment of the structures of **7**, **9** and **10** was straightforward. As in the case of **2**, the configuration of **7** remains unknown, apart from the fact that it has a plane of symmetry. Also the spectral data of **10** do not reveal any information regarding the orientation of the methoxy group. Compared to **7**, the detailed structure of **8** is even more uncertain, as the configuration of the CHCl group could not be elucidated. However, the spectral data strongly support this skeletal constitution.

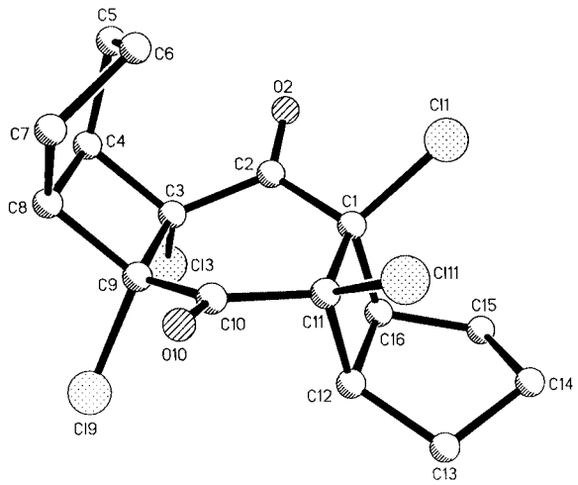
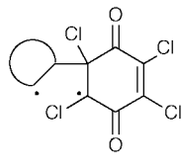


Fig. 2 Molecular structure of the pentacyclic diketone **12** as determined by X-ray diffraction. The numbering of the atoms does not correspond to the systematic name.

For the same reasons as above, complete stereochemical assignments were unfeasible for the cyclopentene-derived products **11** and **14**. In contrast, the configuration as well as the conformation of **12** could be determined by single crystal X-ray analysis (Fig. 2). Accordingly, its bicyclo[3.2.0]heptane moieties take the boat conformation, as the bicyclo[3.1.0]hexane system is known to do.[18] Torsional angles of ≤2° show that the four-membered rings are virtually planar. Further, the carbon atoms of the cyclopentane subunits directly bound to the bridgeheads lie in one plane with the latter with good approximation (torsional angles of *ca.* 2°). From those planes, C6 and C14 (C-6 and C-2, respectively, according to the numbering associated with the systematic name) stick out significantly at the *endo* face of the bicyclo[3.2.0]heptane system as the torsional angles prove: C6–C7–C8–C4, −22.4°; C8–C4–C5–C6, 25.6°; C14–C15–C16–C12, −18.5°; C16–C12–C13–C14, 21.8°. This conformation is probably caused by the interaction between the bridgehead hydrogen atoms and the *exo* hydrogen atoms of the adjacent methylene groups, which would be almost eclipsed within the chair conformation. This becomes substantially staggered in the boat form as is attested by the torsional angles: 39.7° (H4), −36.6° (H8), 35.3° (H12) and −32.5° (H16) (Fig. 2). That this conformation also applies to the solution structure of **12** is manifest in a characteristic splitting of the ^{1}H NMR signals of the eight protons concerned. Since the same fine structure is observed in the spectrum of **11**, its bicyclo[3.2.0]-heptane subunit must adopt the boat conformation as well. In this case, the complete analysis of the eight-spin system showed that $J_{1n,7b}$ (= $J_{3n,3a}$) and $J_{1n,2x}$ (= $J_{2x,3n}$) are not resolved, which is why the relevant torsional angles should have values close to 90° as demanded by the Karplus–Conroy relationship. This is corroborated by the corresponding angles of **12**, which span from 81.9 to 88.9°.

Discussion

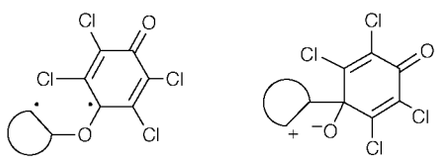
Because of the rapid intersystem crossing, all photochemical conversions of excited **CA** leading to a chemical change of this quinone, start from the triplet state ^{3}**CA**.[19] Major reaction channels with alkenes are hydrogen abstraction, if an allylic hydrogen atom is present, resulting in a triplet radical pair, addition to the double bond, giving rise to a triplet diradical, and ET with formation of a triplet radical-ion pair, if the oxidation potential of the alkene is low enough. As indicated by the production of **TCH**, hydrogen abstraction is involved in the case of cyclopentene, which has precedent in the reactions of cyclohexa-1,3-diene,[20] allyl ethyl ether, indene and cyclohexene.[12]



15

The cyclobutane derivatives **2**, **7** and **11** result from the addition of ^{3}**CA** to the π bond of the respective cycloalkenes, thus there is a [2 + 2]-photocycloaddition of the enone.[2b] As a result, diradicals of type **15** have to be assumed to be intermediates, which collapse to give the four-membered ring after intersystem crossing. Although a number of examples for this kind of cycloaddition onto **CA** have been reported (2-methylpropene, buta-1,3-diene, 2,3-dimethylbuta-1,3-diene,[21] allyl ethyl ether, methyl methacrylate, styrene, α-chlorostyrene, α,*p*-dichlorostyrene[12]), **2**, **7** and **11** are the first cyclobutane derivatives that emerge from **CA** and simple cycloalkenes. For cyclohexene[12] and cyclooctene[13] only 2 : 1 adducts analogous to **12** had been obtained. It is appropiate to mention here that we have also isolated the corresponding 1 : 1 adducts.[15] From the appearance of **12** in addition to **11** we conclude that the latter is an intermediate product *en route* to the former. Obviously, in the same manner as enones,[2b] enediones such as **11** undergo [2 + 2]-photocycloadditions rather readily. The cyclohexane-1,4-dione derivative **8** is probably formed by the addition of hydrogen chloride onto the CC double bond of **7** that results from the methanolysis of the precursor of the pseudoester **10** (see below).

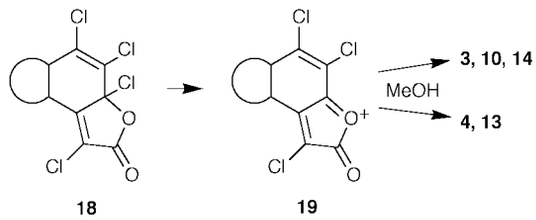
The pathway to the oxetane derivatives **6** and **9** is either that of the Paternò–Büchi reaction with triplet diradicals of the type **16** as intermediates[2c] or *via* the involvement of zwitterions of



16 17

the type **17**. Derived from norbornene or bicyclo[2.1.1]hex-2-ene, the cationic subunit of **17** would certainly be able to rearrange, but in view of the formation of oxetanes from benzvalene[14] and norbornadiene[3] it seems likely that zwitterions **17** do not necessarily take advantage of the possibility to rearrange. The zwitterions **17** would emerge from triplet radical-ion pairs by collapse after intersystem crossing and the latter could result by ET from norbornene or bicyclo[2.1.1]hex-2-ene to ^{3}**CA**. This pathway finds support by the oxidation potentials of cyclopentene (2.03 V *vs.* SCE[10]), norbornene (1.95 V[10]) and bicyclo[2.1.1]hex-2-ene (1.88 V[22]). Whereas the best donor (bicyclo[2.1.1]hex-2-ene) furnished the oxetane derivative **9** as the major product, the poorest donor (cyclopentene) yielded no oxetane at all. In the case of norbornene, a small amount of the oxetane **6** was formed only in a 1 : 1 mixture of benzene and methanol. This is in line with expectations based on the Weller equation,[7b] according to which the free enthalpy of the ET for this rather polar solvent is considerably reduced compared to the value for pure benzene (*ca.* 4 kcal mol^{-1}).

Even if we made no attempt to identify pseudoacid chlorides analogous to **1** in the reaction mixtures obtained from bicyclo[2.1.1]hex-2-ene and cyclopentene, there is no doubt that the pseudoesters **10** and **14** as well as the ester **13** arise from precursors such as **1**, depicted by the general formula **18**. Presumably, the methanolyses of **18** are S_N1 reactions with the cations **19** being the intermediates (Scheme 5). These are attacked by methanol either at the carbon atom of the carbenium–oxonium ion subunit, whereby the ring system is retained and thus the pseudoesters **3**, **10** and **14** result, or at the

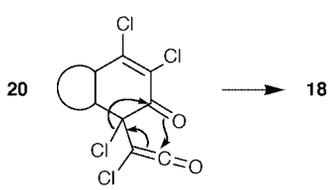


18 19

Scheme 5

carbonyl group of the lactone functionality with opening of the heterocycle and formation of the esters **4** and **13**. As attested by the complete conversion of ethyl pseudoester **5** into the methyl ester **4** (Scheme 2), the esters are thermodynamically more stable than the pseudoesters and hence the latter are formed under kinetic control.

The question now is how the pseudoacid chlorides **18** are generated. The β-oxoketenes **20** seem to be plausible precursors, which can close the five-membered ring by addition of the ketone oxygen atom to the central ketene carbon atom. This step has to be accompanied by a [1,2] migration of the α-chlorine atom and the CC π-bond of the ketene entity. Precedents for such rearrangements of β-oxoketenes to α,β-unsaturated γ-lactones have been described by Miller and coworkers.[23] The intermediacy of the ketene derivative **20** rationalises the poor yields of **3** and **4** on performance of the photochemical reaction in a benzene–methanol mixture, since the trapping of the ketene functionality by methanol should compete with the conversion into **1** (**18**) (Scheme 6).

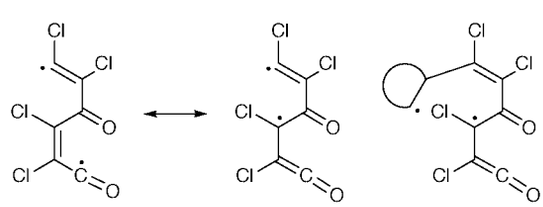


20 18

Scheme 6

The formation of ketenes **20** requires the opening of the **CA** ring. In principle, this could happen at different stages. As the ketenes **20** are isomers of the corresponding cyclobutanes such as **2**, **7** and **11** and oxetanes such as **6** and **9**, their photochemical rearrangement to **20** is basically conceivable. However, these compounds are colourless or pale yellow and thus absorb the light employed (λ > 400 nm) much less efficiently than **CA**. Therefore, photochemical isomerisations of this kind seem unlikely. This view is supported in particular by the high efficiency of the formation of **1**. Moreover, a number of cyclobutanes[12,15,21] and oxetanes[3,12–14] have been prepared from **CA**, but conversions into ketenes and pseudoacid chlorides such as **20** and **18**, respectively, are unknown.

An alternate pathway to be considered is the direct photochemical ring opening of **CA** and the addition of the resulting diradical **21** onto a cycloalkene to give **20** *via* diradicals of the



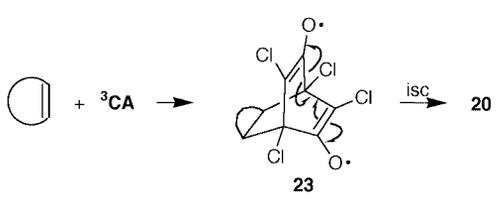
21 22

type **22**. We would expect this course to be favoured in the case of cycloalkenes that are attacked only slowly by ^{3}**CA**. Although a scale of relative rates for reaction with ^{3}**CA** has not been

determined, the tendency should be such as is observed for other reactions, *i.e.* that norbornene reacts quickly while cyclohexene reacts only slowly.[5] Since the experimental findings are at variance with this expectation, as cyclohexene gives no product of the type **18** and norbornene furnishes **1** very efficiently, we exclude this mechanism. Kim *et al.*[24] did report the cleavage of the carbon atom chain of **CA** on irradiation in the presence of hydrogen atom donors such as cyclohexene and proposed the formation of an oxepine derivative, but this result was not confirmed.[12] In view of the mp of 240 °C given for the alleged oxepine derivative,[24] we presume that **TCH** (mp 236–237 °C[25]) had been obtained.

Alternatively, the diradicals **22** could emerge from the diradicals **15** by cleavage of the appropriate CC bond of the subunit originating from **CA**. But there is no obvious reason, why only the diradicals **15** derived from norbornene, bicyclo[2.1.1]hex-2-ene, cyclopentene and cyclobutene should have such a bias.

As mentioned above, norbornene stands out against many other olefins by its high reactivity. In particular, a number of its concerted cycloadditions proceed unusually fast. For the reaction with benzonitrile *N*-oxide, the relative rate constant is *ca.* 6000 times as large as that of cyclohexene and even that of cyclopentene surpasses the latter by a factor of close to 100.[26] Bicyclo[2.1.1]hex-2-ene reacts with 2,4,6-trimethylbenzonitrile *N*-oxide almost as fast as norbornene.[5] The rate ratio for the Diels–Alder reaction of norbornene and cyclohexene with dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate amounts to *ca.* 9000.[5] Since the cycloalkanes giving rise to pseudoacid chlorides **18** seem to be exceptionally suited for concerted cycloadditions, we propose such a process for the reaction with ^{3}**CA**. Simultaneous interactions of the double bonded cycloalkene carbon atoms with C-2 and C-5 of ^{3}**CA** would lead to diradicals **23**, which could rearrange to the β-oxoketenes **20** after intersystem crossing as depicted in Scheme 7. A stepwise generation of



Scheme 7

23 is not likely, because the intermediates involved would have to be the corresponding diradicals **15**, for which no bias is obvious for conversion into **23** in comparison to cyclobutane formation.

Strong support for the diradicals **23** is provided by results of Tsuji *et al.*,[27] who published intramolecular models for the addition of an alkene onto a quinone furnishing a β-oxoketene. Diradicals such as **23** were proposed by the authors to rationalise the outcome.

Experimental

General details

See ref. 4. The internal standard in the NMR spectra was $SiMe_4$. *J* Values are given in Hz. The multiplicities of the signals in the ^{1}H NMR spectra are abbreviated by s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), br (broad) and combinations thereof. Multiplicities in the ^{13}C NMR spectra were determined by a DEPT sequence or by C,H COSY spectra.

General conditions for the photochemical reactions

Thoroughly dried solvents were used. To exclude oxygen, we saturated the solutions of the substrates with nitrogen. Irradiations were carried out by using a pyrex immersion well containing a Hanovia mercury lamp (medium pressure, 450 W), which was surrounded by a glass filter that prevented the passage of light of $\lambda \leq 400$ nm. The progress of the reactions, *i.e.* the consumption of choranil, was monitored by TLC (SiO_2, pentane–ethyl acetate 9 : 1).

Irradiation of chloranil CA in the presence of norbornene—formation of (3aβ,5aα,6β,9β,9aα)-1,3a,4,5-tetrachloro-2,3a,5a,6,7,8,9,9a-octahydro-6,9-methanonaphtho[2,1-*b*]-furan-2-one 1 and (1α,4α,4aβ,8bβ)-4b,6,7,8a-tetrachloro-1,2,3,4,4a,4b,5,8,8a,8b-decahydro-1,4-methanobiphenylene-5,8-dione 2

A solution of **CA** (700 mg, 2.85 mmol) and norbornene (537 mg, 5.70 mmol) in benzene (150 cm^3) was irradiated at 10 °C for 4 h. The solvent was then quickly (15 min) evaporated at 25 °C/15 mmHg and the remaining yellow oil immediately dissolved in the minimum quantity of anhydrous ethyl acetate. On storage of this solution at −35 °C for 5 d, colourless crystals of **1** precipitated (648 mg, 67%), mp 96–98 °C (decomp.) (Found: C, 46.2; H, 2.8. $C_{13}H_{10}Cl_4O_2$ requires C, 45.9; H, 3.0%); ν_{max} (KBr)/cm^{-1} 1803 (C=O), 1650 (C=C), 1605 (C=C); *m*/*z* (EI) 307 (21%), 305 (61), 303 (65), 239 (26), 237 (51), 235 (51), 68 (31), 67 (100), 41 (27), 36 (29); δ_H (400 MHz, $CDCl_3$) 1.33 (1 H, dquint, $J_{10,10}$ 11.3, average of $J_{5a,10}$ and $J_{6,10}$ and $J_{9,10}$ and $J_{9a,10}$ 1.4, *anti*-10-H), 1.44 (1 H, dddd, *J* 12.0 and 8.8 and 5.7 and 2.2) and 1.56 (1 H, ddt, *J* 12.1 and 8.8 and 2.9) (7-H$_\alpha$, 8-H$_\alpha$), 1.68 (1 H, tdd, *J* 12.1 and 5.7 and 3.5) and 1.87 (1 H, tdd, *J* 12.0 and 4.8 and 3.3) (7-H$_\beta$, 8-H$_\beta$), 1.95 (1 H, dquint, $J_{10,10}$ 11.3, average of $J_{6,10}$ and $J_{7\alpha,10}$ and $J_{8\alpha,10}$ and $J_{9,10}$ 2.1, *syn*-10-H), 2.60 (1 H, m) and 2.79 (1 H, br d, *J* 4.8) (6-H, 9-H), 2.86 (1 H) and 3.08 (1 H) (2 × br d, $J_{5a,9a}$ 7.7, 5a-H, 9a-H); δ_C (50 MHz, $CDCl_3$) 27.3, 31.9 (C-7, C-8), 35.9 (C-10), 41.8, 42.0, 42.4, 56.1 (C-5a, C-6, C-9, C-9a), 93.5 (C-3a), 122.4, 126.1, 140.3 (C-1, C-4, C-5), 157.9, 162.3 (C-2, C-9b).

Pseudoacid chloride **1** turned red and hydrogen chloride was evolved at rt in the solid state within 24 h and in $CDCl_3$ solution within 6 h. The ^{1}H NMR spectrum of the yellow oil (see above) indicated the presence of a small amount of **2** (see below) in addition to **1**.

Methanolysis of 1—formation of (3aα,5aα,6β,9β,9aα)-1,4,5-trichloro-2,3a,5a,6,7,8,9,9a-octahydro-3a-methoxy-6,9-methanonaphtho[2,1-*b*]furan-2-one *endo*-3, (3aβ,5aα,6β,9β,9aα)-1,4,5-trichloro-2,3a,5a,6,7,8,9,9a-octahydro-3a-methoxy-6,9-methanonaphtho[2,1-*b*]furan-2-one *exo*-3 and methyl [(1α,4α,4aβ,8aβ)-7,8-dichloro-1,2,3,4,4a,5,6,8a-octahydro-6-oxo-1,4-methanonaphthalen-5-ylidene]chloroacetate 4 as well as isolation of 2

According to the procedure above, a crude mixture of **1** and **2** was prepared from **CA** (1.00 g, 4.07 mmol) and norbornene (766 mg, 8.14 mmol). This mixture (yellow oil) was dissolved in anhydrous methanol (150 cm^3) and left at rt for 24 h. The solvent was then evaporated *in vacuo* and the residue subjected to flash chromatography (SiO_2, pentane–ethyl acetate 25 : 1) at −30 °C. Four fractions, each a yellow oil, were collected, from which crystals were obtained after dissolution in the minimum quantity of ethyl acetate and storage of the solutions at −35 °C. The order of elution was: **2** (164 mg, 12%), **4** (120 mg, 9%), *exo*-**3** (195 mg, 14%), *endo*-**3** (820 mg, 60%).

Compound **2**, yellow crystals, mp 229–230 °C (Found: C, 46.0; H, 3.3. $C_{13}H_{10}Cl_4O_2$ requires C, 45.9; H, 3.0%); ν_{max} (KBr)/cm^{-1} 1709 (C=O), 1552 (C=C); *m*/*z* (CI, isobutane) 347, 345, 343, 341, 339 (MH^+, 3, 11, 47, 100, 82%), 271 (57), 269 (49), 237 (66), 235 (29); δ_H (200 MHz, $CDCl_3$) 0.66 (1 H, dtt, $J_{9,9}$ 12.4, $J_{2\beta,9}$ and $J_{3\beta,9}$ 2.6, $J_{1,9}$ and $J_{4,9}$ 1.3, *syn*-9-H), 1.10 (2 H, m, 2-H$_\beta$, 3-H$_\beta$), 1.26 (1 H, dquint, $J_{9,9}$ 12.4, average of $J_{1,9}$ and $J_{4,9}$ and $J_{4a,9}$ and $J_{8b,9}$ 1.5, *anti*-9-H), 1.54 (2 H, m, 2-H$_\alpha$, 3-H$_\alpha$), 2.62 (2 H, m, 1-H, 4-H), 3.00 (2 H, d, $J_{4a,9anti}$ and $J_{8b,9anti}$ 1.4, 4a-H, 8b-H); δ_C (50 MHz, $CDCl_3$) 26.8 (C-2, C-3), 34.8 (C-9), 36.6 (C-1, C-4),

53.3 (C-4a, C-8b), 67.3 (C-4b, C-8a), 145.3 (C-6, C-7), 181.0 (C-5, C-8).

endo-**3**, colourless crystals, mp 174–175 °C (Found: C, 50.4; H, 3.8. $C_{14}H_{13}Cl_3O_3$ requires C, 50.1; H, 3.9%); ν_{max} (KBr)/cm^{-1} 1785 (C=O), 1652 (C=C), 1615 (C=C); *m*/*z* (EI) 338, 336, 334 (M^+, 0.6, 2.2, 2.3%), 308 (27), 306 (36), 303 (37), 279 (20), 277 (63), 275 (67), 271 (22), 239 (21), 237 (44), 235 (48), 67 (100), 41 (31); δ_H (400 MHz, $CDCl_3$) 1.24–1.33 (2 H, m, 10-H_2), 1.33–1.45 (2 H, m, 7-H_α, 8-H_α), 1.70 (1 H, m) and 1.78 (1 H, m) (7-H_β, 8-H_β), 2.76 and 2.92 (2 × 1 H, 2 × br d, $J_{5a,9a}$ 8.7, 5a-H, 9a-H), 2.85 (1 H, br d, *J* 3.1) and 3.51 (1 H, br d, *J* 4.4) (6-H, 9-H), 3.35 (3 H, s, CH_3); δ_C (50 MHz, $CDCl_3$) 27.4, 29.9 (C-7, C-8), 34.5 (C-10), 36.4, 40.9 (C-6, C-9), 44.3, 52.6 (C-5a, C-9a), 52.1 (CH_3), 101.7 (C-3a), 119.1, 125.2, 139.2 (C-1, C-4, C-5), 153.8 (C-9b), 164.7 (C-2).

exo-**3**, colourless crystals, mp 145–146 °C (Found: C, 49.9; H, 3.9. $C_{14}H_{13}Cl_3O_3$ requires C, 50.1; H, 3.9%); ν_{max} (KBr)/cm^{-1} 1790 (C=O), 1651 (C=C), 1619 (C=C); *m*/*z* (EI) 340, 338, 336, 334 (M^+, 0.1, 1.3, 3.9, 4.1%), 307 (21), 305 (62), 303 (64), 237 (27), 235 (30), 231 (27), 67 (100), 41 (21); δ_H (400 MHz, $CDCl_3$) 1.22 (*anti*-10-H), 1.41 and 1.50 (7-H_α, 8-H_α), 1.67 and 1.82 (7-H_β, 8-H_β), 1.98 (*syn*-10-H), 2.36 and 2.68 (6-H, 9-H), 2.82 and 3.00 (5a-H, 9a-H), 3.34 (3 H, s, CH_3), the multiplicities and the *J* values of the signals of the norbornane subunit are virtually the same as those of **1**; δ_C (50 MHz, $CDCl_3$) 27.7, 31.3 (C-7, C-8), 34.4 (C-10), 41.3, 41.8 (C-6, C-9), 42.1, 55.7 (C-5a, C-9a), 51.7 (CH_3), 101.9 (C-3a), 122.7, 125.7, 139.7 (C-1, C-4, C-5), 154.9 (C-9b), 163.4 (C-2).

Compound **4**, colourless crystals, mp 137–138 °C (Found: C, 50.1; H, 3.6. $C_{14}H_{13}Cl_3O_3$ requires C, 50.1; H, 3.9%); ν_{max} (KBr)/cm^{-1} 1741 (C=O), 1662 (C=O), 1592 (C=C), 1580 (C=C); *m*/*z* (EI) 340, 338, 336, 334 (M^+, 0.2, 2.4, 7.4, 7.6%), 270 (13), 268 (21), 266 (13), 235 (11), 233 (16), 231 (23), 172 (10), 68 (13), 67 (100), 41 (18), 39 (10); δ_H (400 MHz, $CDCl_3$) 1.25 (1 H, dquint, $J_{9,9}$ 11.1, average of $J_{1,9}$ and $J_{4,9}$ and $J_{4a,9}$ and $J_{8a,9}$ 1.3, *anti*-9H), 1.31 (1 H, dquint, $J_{9,9}$ 11.1 average of $J_{1,9}$ and $J_{4,9}$ and $J_{2\beta,9}$ and $J_{3\beta,9}$ 1.8, *syn*-9-H), 1.48–1.60 (2 H, m, 2-H_β, 3-H_β), 1.68 and 1.82 (2 × 1 H, 2 × m, 2-H_α, 3-H_α), 2.37 (1 H, dm, *J* 3.8) and 2.69 (1 H, dm, *J* 4.4) (1-H, 4-H), 2.96 (1 H, br d, $J_{4a,8a}$ 8.3) and 3.06 (1 H, dd, *J* 8.3 and 1.3) (4a-H, 8a-H), 3.90 (3 H, s, CH_3); δ_C (50 MHz, $CDCl_3$) 28.9, 29.6 (C-2, C-3), 33.6 (C-9), 43.7, 45.0 (C-1, C-4), 44.0, 52.5 (C-4a, C-8a), 53.5 (CH_3), 130.8, 133.7, 135.4, 155.3 (C-5, C-7, C-8, *C*ClCO$_2$CH$_3$), 164.7 (*C*O$_2$CH$_3$), 176.5 (C-6).

Ethanolysis of 1—isolation of (3aα,5aα,6β,9β,9aα)-1,4,5-trichloro-3a-ethoxy-2,3a,5a,6,7,8,9,9a-octahydro-6,9-methanonaphtho[2.1-*b*]furan-2-one 5

According to the procedure above, a crude mixture of **1** and **2** was prepared from **CA** (700 mg, 2.85 mmol) and norbornene (537 mg, 5.70 mmol). This mixture (yellow oil) was dissolved in the minimum quantity of anhydrous ethanol. After 24 h at rt, the solution was stored at −35 °C for 7 d. Then colourless crystals of **5** (539 mg, 54%) were collected, mp 187–188 °C (Found: C, 51.2; H, 4.2. $C_{15}H_{15}Cl_3O_3$ requires C, 51.5; H, 4.3%); δ_H (250 MHz, $CDCl_3$) 1.23 (3 H) and 3.58 (1 H) and 3.62 (1 H) (ABX_3 spectrum, $J_{A,B}$ 8.9, $J_{A,X}$ and $J_{B,X}$ 7.0, C_2H_5), chemical shifts and *J* values of the protons of the norbornane subunit are virtually the same as those of *endo*-**3**; δ_C (63 MHz, $CDCl_3$) 15.0 (CH_3), 27.4, 29.9 (C-7, C-8), 34.5 (C-10), 36.4, 40.9 (C-6, C-9), 44.4, 52.5 (C-5a, C-9a), 60.9 (OCH_2), 101.6 (C-3a), 118.8, 125.5, 139.0 (C-1, C-4, C-5), 154.3 (C-9b), 164.8 (C-2).

Methanolysis of 5—preparation of 4

The pseudoester **5** (100 mg, 0.286 mmol) was dissolved in anhydrous methanol (100 cm^3). After addition of concentrated H_2SO_4 (3 drops), the solution was refluxed for 16 h and then concentrated *in vacuo*. The residue was dissolved in dichloromethane and the solution filtered through basic Al_2O_3 of activity III. After concentration of the filtrate *in vacuo*, the residue, a yellow oil, was dissolved in the minimum amount of ethyl acetate. On storage of this solution at −35 °C, colourless crystals of **4** (84 mg, 88%) precipitated, mp 137–138 °C.

(1′α,2′β,5′β,6′α)-2,3,5,6-Tetrachlorospiro[cyclohexa-2,5-diene-1,4′-[3]oxatricyclo[4.2.1.0^{2,5}]nonan]-4-one 6

A solution of **CA** (1.00 g, 4.07 mmol) and norbornene (766 mg, 8.14 mmol) in a mixture of benzene (75 cm^3) and anhydrous methanol (75 cm^3) was irradiated at 10 °C for 5 h. The solvent was then evaporated *in vacuo* and the residue subjected to flash chromatography (SiO_2, pentane–ethyl acetate 25:1). With the exception of **6**, the products obtained were the same as those in the above experiment, in which the compounds, formed by photolysis of the substrates in pure benzene, had been treated with methanol. However, the yields and the purity were very poor. The fraction, following immediately the elution of **2**, was a yellow oil (53 mg), which was dissolved in the minimum quantity of ethyl acetate. On storage at −35 °C, this solution separated **6** (27 mg, 2%) as colourless crystals, mp 167–168 °C (Found: C. 46.2; H, 2.9. $C_{13}H_{10}Cl_4O_3$ requires C, 45.9; H, 3.0%); ν_{max} (KBr)/cm^{-1} 1686 (C=O), 1595 (C=C), 1558 (C=C); *m*/*z* (EI) 346, 344, 342, 340, 338 (M^+, 0.1, 2.6, 13.0, 25.5, 19.9%), 247 (22), 245 (38), 243 (30), 96 (25), 95 (96), 94 (32), 79 (57), 78 (31), 68 (20), 67 (100), 66 (96), 41 (38), 39 (30); δ_H (250 MHz, $CDCl_3$) 0.87–1.04 (2 H, m), 1.44 (1 H, dquint, $J_{9',9'}$ 11.1, average of $J_{1',9'}$ and $J_{2',9'}$ and $J_{5',9'}$ and $J_{6',9'}$ 1.1, *anti*-9′-H), 1.48–1.63 (2 H, m), 2.45 and 2.56 (2 × 1 H, 2 × m, 1′-H, 6′-H), 2.71 (1 H, d, $J_{2',5'}$ 4.8, 5′-H), 3.29 (1 H, dquint, $J_{9',9'}$ 11.1, average of $J_{1',9'}$ and $J_{6',9'}$ and $J_{7'\beta,9'}$ and $J_{8'\beta,9'}$ 2.2, *syn*-9′-H), 5.27 (1 H, br d, $J_{2',5'}$ 4.8, 2′-H); δ_C (63 MHz, $CDCl_3$) 22.2, 28.7, 34.6 (C-7′, C-8′, C-9′), 37.0, 38.8 (C-1′, C-6′), 59.0 (C-5′), 87.7 (C-2′), 89.7 (C-1), 128.3, 129.7 (C-3, C-5), 150.7, 157.1 (C-2, C-6), 170.3 (C-4).

(1α,3α,3aβ,7bβ)-3b,5,6,7a-Tetrachloro-2,3,3a,3b,4,7,7a,7b-octahydro-1,3-methano-1*H*-cyclopenta[3,4]cyclobuta[1,2]-benzene-4,7-dione 7, (1α,3α,3aβ,7bβ)-3b,5,5,6,7a-pentachloro-perhydro-1,3-methanocyclopenta[3,4]cyclobuta[1,2]benzene-4,7-dione 8, (1′α,2′β,5′β,6′α)-2,3,5,6-tetrachlorospiro[cyclohexa-2,5-diene-1,4′-[3]oxatricyclo[4.1.1.0^{2,5}]octan]-4-one 9 and (5aα,6β,8β,8aα)-1,4,5-trichloro-3a,5a,6,7,8,8a-hexahydro-3a-methoxy-6,8-methano-2*H*-indeno[5,4-*b*]furan-2-one 10

A solution of **CA** (1.00 g, 4.07 mmol) and bicyclo[2.1.1]hex-2-ene[28] (800 mg, 9.98 mmol) in benzene (150 cm^3) was irradiated at 10 °C for 6 h. The solvent was quickly evaporated *in vacuo* and the residue immediately dissolved in anhydrous methanol (150 cm^3). After storage at rt for 24 h, the solution was concentrated *in vacuo* and the residue subjected to flash chromatography (SiO_2, pentane–ethyl acetate 25:1). In the order of elution a 1:4 mixture of **7** and **8** (232 mg, 16%), **9** (291 mg, 22%) and **10** (186 mg, 14%) were obtained, each as a yellow oil. On treatment with ethyl acetate each of these oils gave colourless crystals.

7 and **8** as a 1:4 mixture, mp 150–172 °C; ν_{max} (KBr)/cm^{-1} 1785 (C=O), 1759 (C=O), 1707 (C=O), 1548 (C=C); *m*/*z* (CI, isobutane) 369, 367, 365, 363, 361 (MH^+ of **8**, 2, 16, 49, 77, 47%), 331, 329, 327, 325 (MH^+ of **7**, 7, 34, 71, 55), 299 (15), 291 (41), 289 (43), 255 (15), 253 (22), 249 (15), 79 (100); δ_H of **7** (400 MHz, $CDCl_3$) 0.42 (1 H, t, average of $J_{2\beta,8}$ and $J_{8,8}$ 10.6, *syn*-H-8), 0.86 (1 H, dd, $J_{2\beta,8}$ 10.8, $J_{2,2}$ 7.4, 2-H_β), 1.63 (1 H, m, *anti*-8-H), 1.77 (1 H, dt, $J_{2,2}$ 7.4, $J_{1,2}$ and $J_{2,3}$ 2.6, 2-H_α), 2.87 (2 H, m, 1-H, 3-H), 3.38 (2 H, narrow m, 3a-H, 7b-H); δ_H of **8** (400 MHz, $CDCl_3$) 1.01–1.10 (2 H, m, 2-H_β, *syn*-8-H), 1.65 (1 H, dtt, $J_{8,8}$ 9.4, $J_{1,8}$ and $J_{3,8}$ 2.7, $J_{3a,8}$ and $J_{7b,8}$ 1.4, *anti*-8-H), 1.79 (1 H, dt, $J_{2,2}$ 7.3, $J_{1,2\alpha}$ and $J_{2\alpha,3}$ 2.7, 2-H_α), 2.69 and 2.75 (2 × 1 H, 2 × dtd, $J_{1,3}$ 6.9, $J_{1,2\alpha}$ and $J_{1,8anti}$ and $J_{2\alpha,3}$ and $J_{3,8anti}$ 2.7, $J_{1,7b}$ and $J_{3,3a}$ 1.4, 1-H, 3-H), 2.895 and 2.905 (2 × 1 H, 2 × dt, $J_{3a,7b}$ 8.1, $J_{1,7b}$ and $J_{3,3a}$ and $J_{3a,8anti}$ and $J_{7b,8anti}$ 1.4, 3a-H, 7b-H), 5.28 (1 H, s, 6-H); δ_C of **7** (63 MHz, $CDCl_3$) 32.4, 40.2 (C-2, C-8), 40.4,

49.6 (C-1, C-3, C-3a, C-7b), 66.9 (C-3b, C-7a), 145.1 (C-5, C-6), 181.2 (C-4, C-7); δ_C of **8** (63 MHz, $CDCl_3$) 32.0, 39.0 (C-2, C-8), 42.8, 43.4, 44.4, 46.9 (C-1, C-3, C-3a, C-7b), 68.3 (C-6), 73.8, 78.6 (C-3b, C-7a), 91.0 (C-5), 182.1, 195.8 (C-4, C-7).

Compound **9**, mp 146–147 °C (Found: C, 44.0; H, 2.7. $C_{12}H_8Cl_4O_2$ requires C, 44.2; H, 2.5%); ν_{max} (KBr)/cm^{-1} 1682 (C=O), 1595 (C=C), 1556 (C=C); *m*/*z* (EI) 330, 328, 326, 324 (M^+, 3, 12, 24, 19%), 291 (24), 289 (25), 235 (21), 233 (21), 226 (25), 81 (24), 80 (95), 79 (100); δ_H (200 MHz, C_6D_6) −0.11 (1 H, ddd, $J_{7'\beta,8'syn}$ 11.0, $J_{7',7'}$ 7.5, $J_{7'\beta,8'anti}$ 0.8, 7′-H_β), 1.13 (1 H, dt, $J_{7',7'}$ 7.5, $J_{1',7'}$ and $J_{6',7'}$ 2.5, 7′-H_α), 1.25 (1 H, dtq, $J_{8',8'}$ 8.1, $J_{1',8'}$ and $J_{6',8'}$ 2.8, $J_{2',8'}$ and $J_{5',8'}$ and $J_{7'\beta,8'}$ 0.8, *anti*-8′-H), 1.93 (1 H, dq, $J_{1',6'}$ 5.7, average of $J_{5',6'}$ and $J_{6',7'\alpha}$ and $J_{6',8'anti}$ 2.4, 6′-H), 1.98 (1 H, dd, $J_{2',5'}$ 5.3, $J_{5',6'}$ 2.0, 5′-H), 2.21 (1 H, dq, $J_{1',6'}$ 5.7, average of $J_{1',2'}$ and $J_{1',7'\alpha}$ and $J_{1',8'anti}$ 2.6, 1′-H), 2.80 (1 H, dd, $J_{7'\beta,8'}$ 11.0, $J_{8',8'}$ 8.1, *syn*-8′-H), 5.04 (1 H, dd, $J_{2',5'}$ 5.3, $J_{1',2'}$ 2.5, 2′-H); δ_C (50 MHz, $CDCl_3$) 32.4, 38.5 (C-7′, C-8′), 41.3, 42.8 (C-1′, C-6′), 56.2 (C-5′), 84.9 (C-2′), 87.1 (C-1), 128.8, 131.1 (C-3, C-5), 150.7, 157.9 (C-2, C-6), 170.5 (C-4).

Compound **10**, mp 166–167 °C (Found: C, 49.1; H, 3.6. $C_{13}H_{11}Cl_3O_3$ requires C, 48.6; H, 3.5%); ν_{max} (KBr)/cm^{-1} 1788 (C=O), 1652 (C=C), 1616 (C=C); *m*/*z* (EI) 324, 322, 320 (M^+, 4, 11, 10%), 294 (32), 293 (24), 292 (40), 291 (63), 289 (65), 265 (31), 263 (96), 261 (100), 257 (21), 237 (32), 235 (36), 43 (28); δ_H (200 MHz, $CDCl_3$) 0.96 (1 H, dd, $J_{7\alpha,9}$ 10.1, $J_{9,9}$ 8.1, *syn*-9-H), 1.22 (1 H, dd, $J_{7,9syn}$ 10.1, $J_{7,7}$ 7.5, 7-H_α), 1.74 (1 H, dtt, $J_{9,9}$ 8.1, $J_{6,9}$ and $J_{8,9}$ 2.6, $J_{5a,9}$ and $J_{8a,9}$ 1.8, *anti*-9-H), 1.96 (1 H, dt, $J_{7,7}$ 7.5, $J_{6,7}$ and $J_{7,8}$ 3.0, 7-H_β), 2.95 and 3.42 (2 × 1 H, 2 × dtd, $J_{6,8}$ 6.8, average of $J_{6,7\beta}$ and $J_{6,9anti}$ and $J_{7\beta,8}$ and $J_{8,9anti}$ 2.8, $J_{5a,6}$ and $J_{8,8a}$ 1.4, 6-H, 8-H), 3.23 and 3.32 (2 × 1 H, 2 × dt, $J_{5a,8a}$ 8.4, average of $J_{5a,6}$ and $J_{5a,9anti}$ and $J_{8,8a}$ and $J_{8a,9anti}$ 1.6, 5a-H, 8a-H), 3.42 (3 H, s, CH_3); δ_C (63 MHz, $CDCl_3$) 33.4, 38.8 (C-7, C-9), 39.2, 39.8, 42.6, 48.7 (C-5a, C-6, C-8, C-8a), 52.3 (CH_3), 102.6 (C-3a), 119.4, 125.8, 139.5 (C-1, C-4, C-5), 154.8 (C-8b), 164.6 (C-2).

(3aα,7bα)-3b,5,6,7a-Tetrachloro-2,3,3a,3b,4,7,7a,7b-octahydro-1*H*-cyclopenta[3,4]cyclobuta[1,2]benzene-4,7-dione 11, (3aα,3bβ,4aα,4bα,7aα,7bα,8aβ,8bα)-3b,4a,7b,8a-tetrachlorohexadecahydrodicyclopenta[3,4:3′,4′]dicyclobuta[1,2-*a*:1′,2′-*d*]benzene-4,8-dione 12, methyl [(3aα,7aα)-6,7-dichloro-2,3,3a,4,5,7a-hexahydro-5-oxo-1*H*-inden-4-ylidene]chloroacetate 13 and (5aα,8aα)-1,4,5-trichloro-3a,5a,6,7,8,8a-hexahydro-3a-methoxy-2*H*-indeno[5,4-*b*]furans 14

A solution of **CA** (1.00 g, 4.07 mmol) and cyclopentene (554 mg, 8.13 mmol) in benzene (150 cm^3) was irradiated at 10 °C for 4.5 h. The solvent was then quickly evaporated *in vacuo*. Anhydrous methanol (150 cm^3) was immediately 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–ethyl acetate 25:1) at −30 °C. In the order of elution, **11** (112 mg, 9%), **12** (121 mg, 8%), **13** (184 mg, 15%), 27 mg of a mixture containing about 80% of *minor*-**14** (2%) and 281 mg of a mixture consisting of *major*-**14** and tetrachlorohydroquinone **TCH** were each obtained as a colourless oil. Dissolution of the first and the second fraction in the minimum quantity of ethyl acetate and storage of the solution at −35 °C furnished **11** and **12** as crystals. The separation of *major*-**14** and **TCH** was achieved by addition of chloroform (1 cm^3) to the mixture and the removal of the precipitate (**TCH**, 95 mg, 9%) by rapid filtration. The oily residue of the filtrate was virtually pure *major*-**14** (143 mg, 11%).

Compound **11**, mp 135–136 °C (Found: C, 42.5; H, 2.8. $C_{11}H_8Cl_4O_2$ requires C, 42.1; H, 2.6%); ν_{max} (KBr)/cm^{-1} 1702 (C=O), 1559 (C=C); *m*/*z* (CI, isobutane) 321, 319, 317, 315, 313 (MH^+, 0.2, 2.0, 8.3, 18.0, 12.6%), 279 (29), 277 (28), 68 (48), 67 (100); δ_H (400 MHz, $CDCl_3$) 0.92 (1 H, qt, average of $J_{1x,2}$ and $J_{2,2}$ and $J_{2,3x}$ 12.9, $J_{1n,2}$ and $J_{2,3n}$ 6.8, 2-H_n), 1.61 (2 H, m, 1-H_x, 3-H_x), 1.78 (1 H, br dt, $J_{2,2}$ 14.0, $J_{1x,2}$ and $J_{2,3x}$ 7.3, 2-H_x), 1.97 (2 H, br dd, $J_{1,1}$ and $J_{3,3}$ 14.9, $J_{1,2n}$ and $J_{2n,3}$ 6.8, 1-H_n, 3-H_n), 3.53 (2 H, AA′ part of an AA′XX′ spectrum, $J_{3a,7b}$ 8.6, $J_{1x,7b}$ and $J_{3x,3a}$ 8.5, $J_{1x,3x}$ and $J_{1x,3a}$ and $J_{3x,7b}$ not resolved, 3a-H, 7b-H); δ_C (50 MHz, $CDCl_3$) 26.3 (C-2), 28.4 (C-1, C-3), 52.1 (C-3a, C-7b), 68.5 (C-3b, C-7a), 146.2 (C-5, C-6), 181.1 (C-4, C-7).

Compound **12**, mp 200–201 °C (Found: C, 50.1; H, 4.1. $C_{16}H_{16}Cl_4O_2$ requires C, 50.3; H, 4.2%); ν_{max} (KBr)/cm^{-1} 1721 (C=O); *m*/*z* (CI, isobutane) 389, 387, 385, 383, 381 (MH^+, 0.3, 3.1, 15.3, 31.4, 23.2%), 347 (49), 345 (50), 318 (24), 316 (47), 314 (41), 311 (45), 309 (51), 281 (23), 273 (24), 248 (23), 246 (20), 148 (21), 91 (23), 68 (63), 67 (100); δ_H (400 MHz, $CDCl_3$) 0.44 (1 H, qt, average of *J* 13.4, *J* 5.7), 1.47 (2 H, m), 1.71–1.87 (4 H, m), 2.04 (2 H, dd, *J* 14.4, *J* 5.7), 2.11 (1 H, m), 2.17–2.27 (2 H, m), 3.45 and 3.61 (2 × 2 H, 2 × m, 3a-H, 8b-H, 4b-H, 7a-H); δ_C (63 MHz, $CDCl_3$) 25.4, 26.8 (C-2, C-6), 29.2, 30.3 (C-1, C-3, C-5, C-7), 48.2, 52.2 (C-3a, C-8b, C-4b, C-7a), 67.4, 79.8 (C-3b, C-8a, C-4a, C-7b), 193.8 (C-4, C-8).

Compound **13**, oil (Found: C, 46.7; H, 3.8. $C_{12}H_{11}Cl_3O_3$ requires C, 46.6; H, 3.6%); ν_{max} (CCl_4)/cm^{-1} 1750 (C=O), 1682 (C=O), 1609 (C=C); *m*/*z* (EI) 310, 308 (M^+, 0.07, 0.08%), 85 (14), 73 (10), 71 (24), 70 (17), 61 (13), 59 (53), 57 (44), 45 (23), 43 (100), 41 (17); δ_H (400 MHz, $CDCl_3$) 1.47 (1 H, dtt, *J* 12.9, 10.6, 8.6), 1.65–1.84 (2 H, m), 2.13–2.30 (3 H, m), 3.36 (1 H, td, *J* 8.0, 4.5) and 3.52 (1 H, dt, *J* 10.5, 8.0) (3a-H, 7a-H), 3.89 (3 H, s, CH_3); δ_C (50 MHz, $CDCl_3$) 24.0, 30.9, 33.6 (C-1, C-2, C-3), 40.5, 47.0 (C-3a, C-7a), 53.5 (CH_3), 130.4, 133.7, 134.4, 157.6 (C-4, C-6, C-7, *C*ClCO$_2$CH$_3$), 164.6 (*C*O$_2$CH$_3$), 176.3 (C-5).

minor-**14**, oil (impure); ν_{max} (CCl_4)/cm^{-1} 1801 (C=O); δ_H (400 MHz, $CDCl_3$) 1.67 (1 H, m), 1.77–2.12 (4 H, m), 2.28 (1 H, m), 3.25 (1 H, td, *J* 8.5, 6.8) and 3.43 (1 H, td, *J* 9.3, 8.5) (5a-H, 8a-H), 3.35 (3 H, s, CH_3); δ_C (63 MHz, $CDCl_3$) 26.7, 29.7, 29.9 (or 34.0) (C-6, C-7, C-8), 37.4, 50.1 (C-5a, C-8a), 51.9 (CH_3), 101.8 (C-3a), 121.3, 123.9, 140.8 (C-1, C-4, C-5), 155.7 (C-8b), 163.8 (C-2).

major-**14**, oil (Found: C, 46.9; H, 3.8. $C_{12}H_{11}Cl_3O_3$ requires C, 46.6; H, 3.6%); ν_{max} (CCl_4)/cm^{-1} 1800 (C=O), 1694 (C=C); *m*/*z* (EI) 310, 308 (M^+, 4.5, 4.8%), 279 (30), 277 (29), 251 (26), 250 (44), 249 (33), 248 (99), 246 (100), 244 (33), 211 (30), 209 (29), 181 (20), 149 (25), 89 (24), 87 (74), 71 (21), 67 (21), 57 (37), 43 (21), 41 (27); δ_H (400 MHz, $CDCl_3$) 1.51 (1 H, ddt, *J* 12.9, 10.4, 9.0), 1.81 (1 H, m), 1.92–2.10 (2 H, m), 2.27 (1 H, dtd, *J* 12.9, 8.1, 4.0), 2.67 (1 H, m), 3.14 (1 H, dt, *J* 10.5, 8.3) and 3.37 (1 H, ddd, *J* 8.3, 7.3, 3.2) (5a-H, 8a-H), 3.32 (3 H, s, CH_3); δ_C (63 MHz, $CDCl_3$) 24.0, 26.1, 30.9 (C-6, C-7, C-8), 39.9, 50.7 (C-5a, C-8a), 51.5 (CH_3), 102.9 (C-3a), 120.1, 124.2, 139.5 (C-1, C-4, C-5), 154.0 (C-8b), 164.4 (C-2).

X-Ray data for compounds *endo*-3, *exo*-3 and 12‡

***endo*-3.** $C_{14}H_{13}Cl_3O_3$, $M = 335.61$. Orthorhombic, $a = 1450.5(6)$, $b = 1994.8(8)$, $c = 987.9(5)$ pm, $V = 2858(2) \times 10^6$ pm^3, space group *Pbca*, $Z = 8$, $T = 293$ K, $\mu = 0.64$ mm^{-1}; 2986 reflections measured, 2635 unique, giving 2317 with $F > 3\sigma(F)$; $R = 0.041$, $R_w = 0.039$.

***exo*-3.** $C_{14}H_{13}Cl_3O_3$, $M = 335.61$. Triclinic, $a = 962.2(7)$, $b = 1045.7(8)$, $c = 806.1(4)$ pm, $\alpha = 97.55(5)$, $\beta = 112.27(5)$, $\gamma = 98.04(6)°$, $V = 728.0(9) \times 10^6$ pm^3, space group $P\bar{1}$, $Z = 2$, $T = 293$ K, $\mu = 0.63$ mm^{-1}; 3361 reflections measured, 3361 unique, giving 2619 with $F > 3\sigma(F)$; $R = 0.049$, $R_w = 0.043$.

12. $C_{16}H_{16}Cl_4O_2$, $M = 382.11$. Monoclinic, $a = 1268.4(8)$, $b = 1067.7(9)$, $c = 1261.0(10)$ pm, $\beta = 110.39(5)°$, $V = 1601(2) \times 10^6$ pm^3, space group $P2_1/a$, $Z = 4$, $T = 293$ K, $\mu = 0.75$ mm^{-1}; 4061 reflections measured, 3703 unique, giving 3427 with $F > 3\sigma(F)$, $R_{int} = 0.046$; $R = 0.047$, $R_w = 0.049$.

‡ CCDC reference number 207/355.

Acknowledgement

We are grateful to the Fonds der Chemischen Industrie for financial support.

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