Photocycloadditions of Chloranil to Homobenzvalene, Norbornadiene, and Quadricyclane

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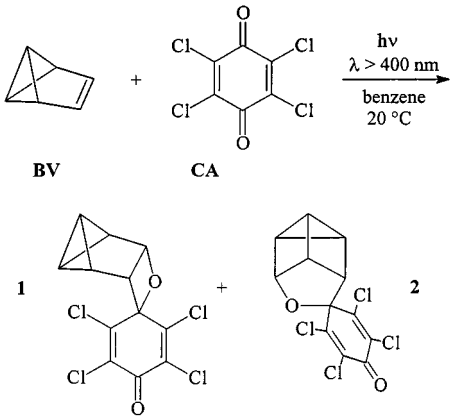
Solutions of chloranil (**CA**) in toluene or benzene have been irradiated in the presence of the C_7H_8 valence isomers homobenzvalene (**HB**), norbornadiene (**N**), and quadricyclane (**Q**). In the case of **HB**, the adducts **3**–**6** were obtained, all of them having a rearranged structure. By a separate irradiation it was shown that **4** is a consecutive product of **3**. The structure of **4** was established by X-ray diffraction analysis. These reactions are most probably initiated by an electron transfer (ET) from **HB** to ^{3}**CA**, continue by bond formation between the radical ions to give the zwitterion **14**, which undergoes Wagner–Meerwein rearrangements, and are completed by ring-closure between the charged centres of the resulting zwitterions. The oxidation potential of **N** is not larger than that of **HB** and the products **8**–**10** may well be formed through an ET to ^{3}**CA**. However, the pathway leading to product **3** most probably involves diradical intermediates. This should also be the case for the adducts **11** and **12**, which were produced upon irradiation of methyl phenylglyoxylate (**PG**) in the presence of **N**. In the case of **Q**, an ET to ^{3}**CA** is again highly likely, followed by a combination of the radical ions to generate the zwitterion **29**, which eventually collapses to produce the oxetane **8** as the sole identifiable product. The photoreactions of **CA** with **N** and **Q** proceeded much less efficiently in acetonitrile solution.

Introduction

Among the quinones, chloranil (**CA**) is of particular importance with regard to photochemical reactions with alkenes[1,2a] because of the great variety of possible processes, several of which may occur simultaneously with a single substrate. Cycloadditions in a 1:1 ratio proceed with formation of cyclobutane derivatives (*trans*-stilbene, acenaphthylene,[3] 2-methylpropene, buta-1,3-diene, 2,3-dimethylbuta-1,3-diene,[4] allyl ethyl ether, methyl methacrylate, styrene, α-chlorostyrene, α,*p*-dichlorostyrene[5]) or with formation of oxetane derivatives [cyclooctene,[6] 1,1-dimethylindene,[7] benzvalene (**BV** → **1**),[8] indene, *trans*-β-bromostyrene,[5] stilbenes, diphenylvinylene carbonate, α,β-unsaturated β-phenylcarbonyl compounds[9]]. In the case of styrene,[3] cyclooctene,[6] and cyclohexene,[5] 2:1 adducts with **CA** containing two cyclobutane subunits are produced. An allylic CH group of 2-methylpropene and 2,3-dimethylbuta-1,3-diene undergoes addition to the C−C double bond of **CA**.[4] The formation of tetrachlorohydroquinone monoethers by 1,6-addition of allylic CH groups takes place with cyclohepta-1,3,5-triene[10] and cyclohexene.[5] The photoreduction of **CA** giving tetrachlorohydroquinone is effected by cyclohexa-1,3-diene,[11] allyl ethyl ether, indene, and cyclohexene.[5] β-Substituted styrenes undergo *cis-trans* isomerization upon irradiation in solution in the presence of **CA**.[9][12] 2,2-Diphenyl-1-methylenecyclopropane,[13] barbaralane,[14] barbaralone,[15] and benzvalene (**BV** → **2**)[8] give rise to products with a rearranged skeleton, invariably possessing a tetrahydrofuran subunit.



Excited **CA** is frequently used as a one-electron acceptor. The formation of the radical cation of **BV** has thus been established by detection of CIDNP signals of **BV** upon irradiation of a solution of **BV** and **CA** in [D_3]nitromethane.[16] Addition products of the substrates were not observed in the course of this experiment. Only later were compounds **1** and **2** isolated and characterized.[8] An irradiated solution of homobenzvalene (**HB**) and **CA** exhibited polarization mainly of a "rearranged species", which eluded identification.[16] Thus, it was a challenge for us to elucidate the reaction product. We extended our study to norbornadiene (**N**) and quadricyclane (**Q**) since these are valence isomers of **HB** and their radical cations, generated by excited **CA**, have been detected through CIDNP[17] and ESR signals.[18a] However, adducts of **N** and **Q** with **CA**

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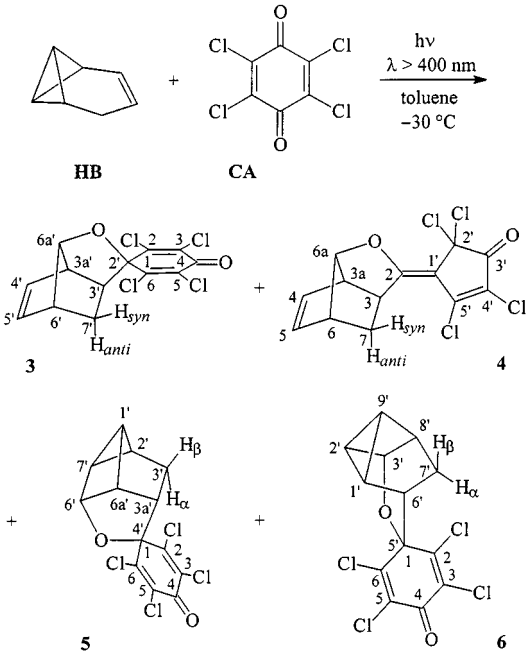
were only suspected[18b] as products of such processes and were neither isolated nor identified.

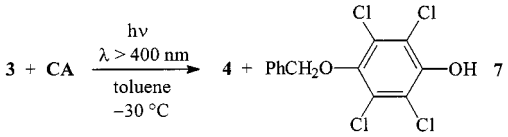
The present work should be viewed in connection with our recent paper on photochemical [2+2] cycloadditions of **HB**. In the reactions described therein, methyl phenylglyoxylate, benzil, benzophenone, and 1,4-benzoquinone gave rise to oxetane derivatives, whereas 1,4-naphthoquinone as well as cyclopent-2-en-1-one yielded cyclobutane derivatives. Rearrangements were either not observed or had to be considered as consecutive processes of the primary photocycloadducts.[19]

Results

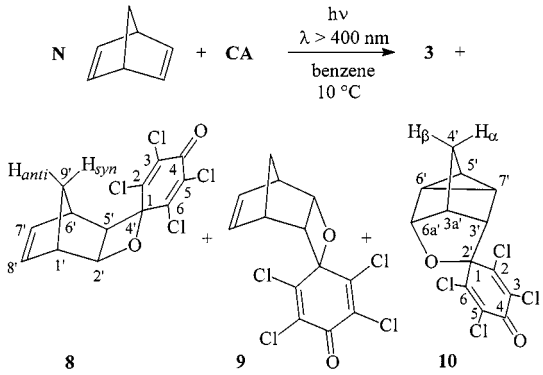
Irradiation of a solution of **CA** (0.017 M) and **HB** (0.026 M) in toluene at −30°C furnished the norbornene derivatives **3** and **4** as well as the pentacyclic compounds **5** and **6** in yields of 26, 15, 2, and 14%, respectively. In addition, the oxetane derivative **8**, the major product of the photocycloaddition of **CA** to norbornadiene (**N**, see below), was obtained in 3% yield. We assume that **8** was derived from a contamination of the **HB** with some **N**. Indeed, the synthesis of **HB**[20] proceeds via 4,5-dichlorohomobenzvalene, the preparation of which may be accompanied by the formation of some *syn*-2,7-dichloronorbornadiene, which should give rise to **N** in the final reductive dechlorination step. NMR-spectroscopic analysis of the **HB** used did not prove the presence of **N**. However, the detection limit was 2% and an **N** content of 1.5% would have been sufficient to generate the actual amount of **8** detected.



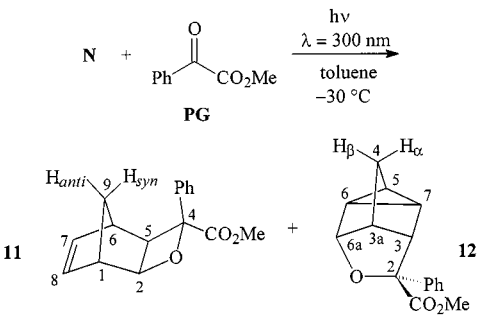
The structure of **4** led us to suspect that this compound could be a consecutive product of **3**. Thus, we irradiated a solution of **CA** and **3** in toluene and **4** was indeed observed. This reaction provided mainly 4-benzyloxy-2,3,5,6-tetrachlorophenol (**7**), which was obtained in an experiment conducted in the absence of **3** in 45% yield.



Photolysis of a mixture of **CA** (0.024 M) and norbornadiene (**N**, 0.048 M) in benzene at 10°C gave the norbornene derivatives **3**, **8**, and **9**, as well as the tricyclene derivative **10**, which were isolated in yields of 7, 43, 16, and 20%, respectively. In contrast, the reaction in acetonitrile solution proceeded much less efficiently, although **CA** was consumed at a similar rate. Only small amounts of **3** and **8** (yields 7 and 5%) could be detected in the complex product mixture, while **9** and **10** were absent.

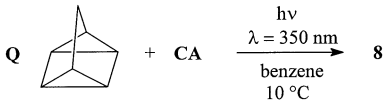


In order to compare the above result with that of a genuine Paternò−Büchi reaction of **N**, we irradiated a mixture of methyl phenylglyoxylate (**PG**) and **N** in toluene solution at −30°C and obtained a 6:1 mixture of the norbornene derivative **11** and the tricyclene derivative **12** in 96% yield.



Irradiation of a solution of **CA** (0.024 M) and quadricyclane (**Q**, 0.048 M) in benzene at 10°C gave rise to the norbornene derivative **8** (36%). Although further products were present, they eluded identification. However, the formation of significant quantities of **3**, **4**, **5**, **6**, **9**, or **10** in this reaction could be excluded. When acetonitrile was used as

solvent, again only **8** could be detected, albeit in rather poor yield.



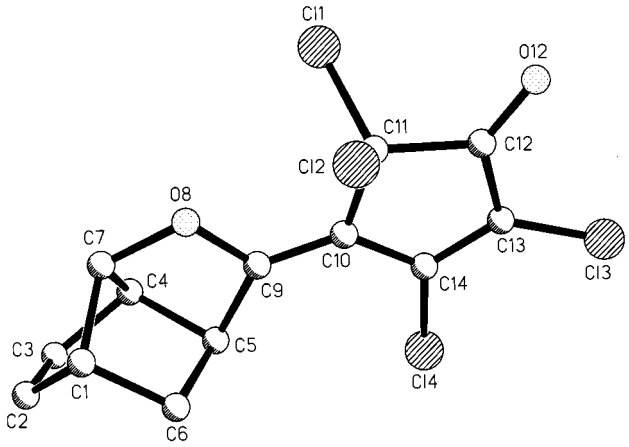


Figure 1. Molecular structure of norbornene derivative **4** as determined by X-ray diffraction; the numbering does not correspond to the systematic name

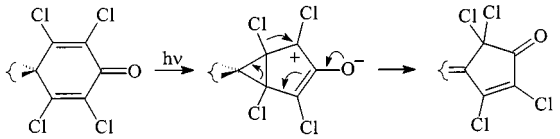
The structure of **4** was elucidated by single-crystal X-ray diffraction analysis (Figure 1). By analogy, the structure of **3** could be established, since the multiplets in the ^{1}H-NMR spectra of **3** and **4**, apart from their different positions, are very similar in appearance. The identification of **6** was somewhat more difficult. The reaction mechanism (see below) led us to expect only **5**, the structure of which is analogous to that of one of the photocycloadducts of tetracyanoethylene with **HB**[21] and to that of the product resulting from the thermal reaction of 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione with **HB**.[22] However, only a minor part of the chromatographic fraction containing the products with saturated hydrocarbon subunits could be characterized as **5** or an isomer thereof with regard to the moiety stemming from **CA**. This was established on the basis of the distinctive fine structure of the signals in the ^{1}H-NMR spectrum. However, in the ^{13}C-NMR spectrum, the signals of the quaternary and chlorine-substituted carbon atoms were not observed as their intensities were too low and hence the cyclohexadienone moiety of **5** could be replaced by an isomeric one, e.g. a methylenecyclopentenone subunit as in **4**. For the major component of this chromatographic fraction, structure **6** is consistent with the analytical and spectral data. In particular, the connectivity of the hydrogen-bearing carbon atoms could be deduced from NOE measurements and a C,H-COSY spectrum.

Structural assignments of the oxetane derivatives **8**, **9**, and **11** were straightforward on the basis of their NMR spectra. Indeed, **8**, as well as **11** and its diastereomer with respect to the configuration of C-4, have been prepared previously by thermal reactions of **Q** with **CA**[23a,23b] and **PG**[23c], respectively. NMR-spectral data also straightforwardly revealed the structures of the tricyclene derivatives **10** and **12**. In particular, the presence of three pairs of signals with the same fine structure in the ^{1}H-NMR spectra (3-H/6a-H, 4-H$_\alpha$/4-H$_\beta$, 6-H/7-H) indicated C_s symmetry of the hydrocarbon subunit.

Discussion

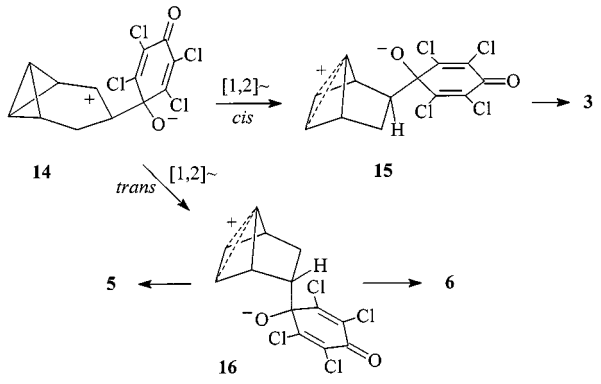
Conducted in toluene solution, the reaction of **HB** shows that this substrate is much more reactive toward excited **CA** than the solvent, although in the absence of **HB** the hydroquinone monobenzyl ether **7** is formed in 45% yield. Ether **7** is also accessible by other routes.[24] That methyl-substituted aromatics, namely *p*-xylene,[25a] hexamethylbenzene, and methylnaphthalenes[25b] add to excited **CA** in a 1,6-fashion to furnish products analogous to **7** is well known and has been studied mechanistically.[25b]

In contrast, the conversion of **3** into **4** has no exact precedent, although light-induced rearrangements of cross-conjugated cyclohexadienones have been widely investigated and utilized synthetically.[2b] The initial step of such processes is the generation of an oxyallyl zwitterion. In the case of **3**, the excitation, probably sensitized by **CA**, should lead to zwitterion **13**. This then undergoes a 1,2-migration of a chloride ion to a cationic centre with concomitant opening of the cyclopropane C−C bond opposite to the carbon atom from which the chloride ion leaves.



The structures of products **3**, **5**, and **6** provide unambiguous evidence for the common intermediacy of **14**, a zwitterion having a tricyclo[4.1.0.0^{2,7}]hept-3-yl cation subunit. Because of its high tendency to undergo rearrangement, the parent cation is unknown. However, solvolyses of suitable esters of tricyclo[4.1.0.0^{2,7}]heptan-3-ol result in *anti*-7-substituted norbornenes, with the 7-norbornenyl cation being the only established intermediate.[26] Thus, Wagner−Meerwein rearrangement of **14** has to be anticipated, which proceeds through migration of a bicyclobutane bridgehead carbon atom, either that *cis*-orientated or that *trans*-orientated in relation to the anionic subunit. From this, two new zwitterions, the diastereomers **15** and **16**, can result. Whereas **15** has only one possibility for covalent bond formation between the charged centres, i.e. that giving rise to **3**, the anionic oxygen atom of **16** can bind to either of the carbon atoms of the two-membered bridge, stabilizing the positive charge, thereby leading to the formation of **5** and **6**.

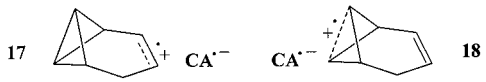
Structural analogues of **3** and **5** result from the photochemical addition of tetracyanoethylene (TCNE) to **HB**.[21] Zwitterionic intermediates corresponding to **14**, **15**, and **16** have to be assumed for these reactions. The mechanistic alternative that has been advanced[21] seems unlikely due to its ad hoc character, while the present proposal relies on



precedent in considering the rearrangement of the cationic moiety (see above). Thermal reactions of **HB** and several of its derivatives with 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (PTAD) furnish structural analogues of **5**, but none of **3**.[22][27] This excludes the intermediacy of zwitterionic species related to **15** and supports that of species related to **16**, which are believed to evolve from aziridinium imides that result directly from a homobenzvalene molecule and PTAD. Lacking a free carbocationic centre, these aziridinium imides, in contrast to **14**, have only one possibility for rearrangement, i.e. only the bicyclobutane bridgehead carbon atom arranged *trans* in relation to the nitrogen atoms is amenable to a [1,2] migration.[22] The question as to why **16** makes use of both modes of ring closure (to give **5** and **6**), whereas the corresponding zwitterions derived from TCNE and PTAD prefer only one mode, remains open at present. The product formed on irradiation of **CA** in the presence of benzvalene (**BV**) at 20°C contains only a small fraction of compound **2**, which is the lower homologue of **5**. The major product, oxetane **1**, is even formed exclusively when the reaction is conducted at −30°C.[8] These findings can be rationalized in terms of two alternative mechanisms: either the zwitterion related to **14** is only involved in the less important of two competing pathways or, if even **1** emerges from this zwitterion, it must be much less prone to rearrangement than **14**.

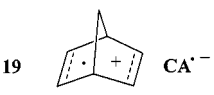
Apart from **14**, other conceivable intermediates cannot plausibly explain the formation of **3**, **5**, and **6**. As evidenced by [2+2] photocycloadditions of **HB**,[19] the relevant diradical would not rearrange, but would rather undergo conversion into an oxetane derivative. Moreover, attack of excited **CA** at the bicyclobutane system of **HB** would furnish products of other types, as exemplified by the radical addition of phenylsulfane[28] and electrophilic additions (H^+, $AcOHg^+$, halogens)[29] to **HB**.

As a precursor for **14**, the radical-ion pair **17** seems appropriate, which could arise from **HB** and the triplet state of **CA** (^{3}CA) by electron transfer (ET). After inter-system crossing, **17** could collapse to give **14**. The formation of ^{3}CA proceeds via singlet-excited **CA**, which has been observed directly in a recent study and was shown to convert into ^{3}CA with a rate constant of ca. 10^{11} s^{-1}.[30] We were unable to detect an electron donor−acceptor (EDA) complex of **CA** with **HB**. However, toluene, the solvent used for the present reaction, is known to form such a species (K = 1.37 L mol^{-1} in cyclohexane).[31] On irradiation, this EDA complex may well directly generate a singlet radical-ion pair as in the cases of the EDA complexes of anisole,[30] hexamethylbenzene, and several methylnaphthalenes.[25b] On the other hand, this process may not be of any consequence because of the rapid return to the ground state by efficient back-ET.[30] The excitation of free **CA** should be the major source of ^{3}CA, toward which **HB** is a much better electron-donor than toluene, resulting in the formation of **17**.

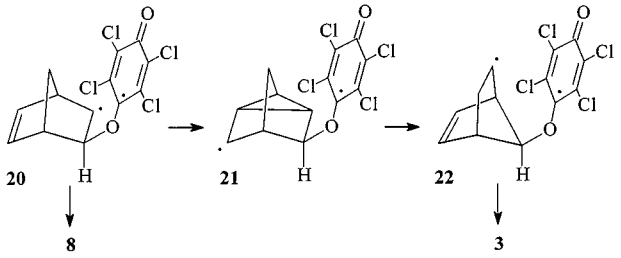


Owing to the low polarity of the solvent used (toluene), **17** has to be classified as a contact radical-ion pair (charge-transfer exciplex).[32a] The driving force for the generation of radical-ion pairs can be estimated by means of the Weller equation.[32] Chinese authors[5][9] have applied this relationship to photocycloadditions of **CA**. Besides the solvent polarity, three quantities determine the free enthalpy of the ET: the energy of ^{3}CA (2.13 eV[33]), the reduction potential of **CA** (0.01 V vs. SCE[34]), and the oxidation potential of the substrate. The first oxidation potential of **HB** was estimated to be 1.54 V vs. SCE,[22] a value that relates to the removal of an electron from the central bicyclobutane bond[35] leading to the radical-ion pair **18**. However, this species cannot serve as intermediate en route to **3**, **5**, and **6**, as evidenced by the behavior of the radical cation generated from tricyclo[4.1.0.$0^{2,7}$]heptane.[36] The second oxidation potential of **HB** is associated with the removal of an electron from the π orbital and can be calculated as 1.83 V vs. SCE from the second ionization potential, determined by photoelectron spectroscopy,[35] by using the same procedure as for the estimation of the first. In this way, the ΔG value for the formation of **17** is calculated to be +0.7 kcal mol^{-1}. Accordingly, the ET from the π orbital of **HB** to ^{3}CA is almost thermoneutral and is thus quite possible thermodynamically. The peculiar proposal that the donor transfers an electron from an orbital more stable than the HOMO may be justified by the better alignment with the acceptor π orbital (^{3}CA is considered to be in a ππ* state[5][37]) of the **HB** π than with its highest σ orbital.

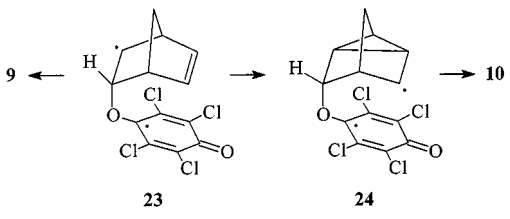
In the absence of **HB**, the generation of a triplet radical-ion pair from ^{3}CA and toluene is unlikely, since, based on the oxidation potential of toluene (ca. 2.40 V vs. SCE[38]), the Weller equation gives a ΔG_{ET} value of +13.8 kcal mol^{-1}. Therefore, the formation of **7** should proceed in a manner different from that whereby the corresponding monoethers derived from hexamethylbenzene and methylnaphthalenes are formed, where a sequential ET and proton transfer result in free radicals, which furnish the products on combination after inter-system crossing.[25b] As the precursors of **7**, the free radicals should derive directly from ^{3}CA and toluene.



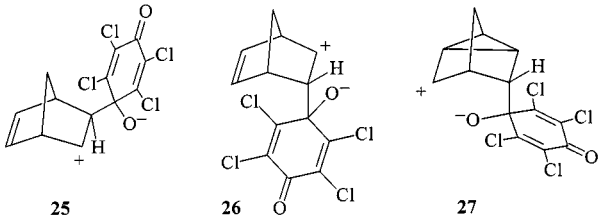
Norbornadiene (**N**) has an oxidation potential of 1.54 vs. SCE,[39a] which is equal to the first oxidation potential of **HB**. Thus, the Weller equation characterizes the ET from **N** to ^{3}CA as clearly exergonic ($\Delta G_{ET} = -5.5$ kcal mol^{-1} in benzene). Indeed, the radical-ion pair **19** was observed in [D_3]acetonitrile through the CIDNP signals of **N**.[17] The question then arises as to whether the addition of **CA** to **N** in benzene proceeds via **19**. The zwitterion **15**, the precursor of **3** when **HB** is used as the substrate, cannot result from **19** by any plausible pathway. A formal homolytic cleavage of the bond connecting the C_7H_8 and **CA** moieties in **15** gives rise to a radical-ion pair, the cation of which is rearranged compared to that of **19**. However, access to such a cation would involve the radical cation of **Q** (**28**) as an intermediate. Since the conversion of **19** to **28** is endergonic,[39b] which is why only the reverse process has been observed,[17] and, moreover, the reaction of **Q** with ^{3}CA does not furnish **3**, the possibility that **3** might be formed via zwitterion **15** can be ruled out.



Instead, diradical **22**, generated from **20** via **21** by rearrangement, seems likely to be the intermediate en route from **N** to **3**. Diradical **20** could result either from **19** by collapse, with annihilation of the charges, or by addition of ^{3}CA to **N** akin to the first step of a Paternò–Büchi reaction. The transformation of **20** to **21** would proceed in competition with the ring closure of **20** to give the oxetane **8**, the major product of the reaction. These routes to **3** and **8** have a precedent in the pathways followed upon irradiation of 1,4-benzoquinone in the presence of **N** in benzene solution, which also furnishes four adducts structurally analogous to **3** and **8**–**10**.[40] For this reaction in [D_3]acetonitrile, the intermediacy of the diradicals **20** and **22** has been established from CIDNP signals of the products corresponding to **3** and **8**.[41]

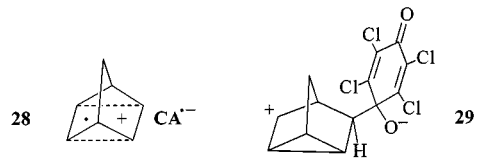


Whereas the norbornadiene skeleton has to be attacked from the *exo* side to give **20** en route to **3** and **8**, the *endo* face is the target in the pathway leading to the adducts **9** and **10**, with the diradicals **23** and **24** being possible intermediates. The photochemical addition of methyl phenylglyoxylate (**PG**) to **N**, a genuine Paternò–Büchi reaction giving **11** and **12**, should proceed via diradicals such as **20**, **23**, and **24**. Products of the types **3**, **8**/**11**, and **10**/**12** have also been obtained upon irradiation of benzophenone in the presence of **N**.[42]



An alternative route to the products **8**, **9**, and **10** might involve the zwitterionic intermediates **25**, **26**, and **27**, respectively. However, the formation of **3** from **N** via **25** would seem highly unlikely, since the cationic homoallyl → cyclopropylcarbinyl (cf. **29**) → homoallyl rearrangement of **25** would generate a zwitterion with a connectivity that would lead to a product in which the endocyclic oxygen atom and the cyclohexadienone moiety were transposed compared to the arrangement in **3**.

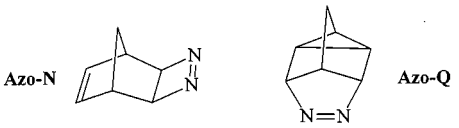
The finding that adduct **3** is formed in both benzene and acetonitrile in the same yield supports the intermediacy of nonpolar species without interference of polar ones such as radical-ion pairs or zwitterions. On the other hand, the decrease in the yields of **8**, **9**, and **10** from 43, 16, and 20% to 5, 0, and 0%, respectively, on changing the solvent from benzene to acetonitrile indicates the sensitivity of the pathways generating these products to solvent polarity. This leads to the hypothesis that the radical-ion pair **19** is the source of **9**, **10**, and the major amount of **8** in benzene. In this medium, **19** has to be a contact-ion pair,[32a] which rapidly collapses to give the zwitterions **25** and **26** after intersystem crossing. The direct addition of ^{3}CA to **N**, resulting in diradical **20**, the precursor to **3** and a small amount of **8**, is a parallel reaction of minor importance. However, this is the only adduct-forming process in acetonitrile, since **19** now becomes a solvent-separated ion pair. Because of the large distance between the ions, its collapse to **25** and **26** is inefficient and it is depleted by nonspecific processes such as reactions with the solvent. The precipitation of a substance of uncertain composition provides evidence to support this assumption.



The low oxidation potential of **Q** (0.91 V vs. SCE[39a]) is a perfect prerequisite for an ET to ^{3}CA. Estimation of the free enthalpy for this process in benzene using the Weller equation[32] gives a value of −20.1 kcal mol^{-1}. In fact, CIDNP signals of **Q** and **N**[17] and a time-resolved ESR spectrum[18a] observed upon irradiation of a [D_3]acetonitrile solution of **Q** and **CA** prove the existence of the radical-ion pair **28** as a species distinctly different from **19**. The

collapse of **28** to give a zwitterion can only occur as attack of the anion at the rear side of one of the partial bonds of the cation, thereby generating **29**, which furnishes **8**, the sole product characterized, either directly or via zwitterion **25**. This route accounts for the fact that products **9** and **10** were not found, in contrast to the reaction of **N**. Further, the absence of **3** rules out the intermediacy of diradical **21** instead of **29**. It is interesting to note that, in line with the present process, the photochemical reaction of 1,4-benzoquinone with **Q** does not produce significant amounts of compounds analogous to **9** or **10**.[40] However, in addition to the oxetane derivative corresponding to **8**, the tetrahydrofuran derivative corresponding to **3** is observed,[40] with both products arising via diradicals analogous to **20**−**22**, as has been demonstrated by CIDNP studies.[41]

The decrease in the yield of **8** on changing the solvent from benzene (38%) to acetonitrile (ca. 3%) has to be ascribed to the different nature of **28** in these solvents, i.e. contact vs. solvent-separated ion pair. Owing to the greater distance between the ions, the latter is consumed mainly by processes other than collapse to zwitterion **29**.



By irradiation of **CA** in [D_3]acetonitrile in the presence of 3,4-diazatricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene (**Azo-N**) and 3,4-diazatetracyclo[6.1.0.$0^{2,6}$.$0^{5,9}$]non-3-ene (**Azo-Q**), other sources of the radical-ion pairs **19** and **28** have recently been studied.[18b] CIDNP signals of **N** and **Q** prove that **Azo-N** gives rise to **19** and **28**, whereas only **19** results from **Azo-Q**. The figures illustrating these findings display further signals, which could not be interpreted by the authors.[18b] With the present ^{1}H-NMR spectra at hand, we assign the signals in emission seen at δ = 6.2, 5.9, and 4.9 in the case of **Azo-Q** to the oxetane **8**.

Conclusion

On irradiation of **CA** in [D_3]acetonitrile in the presence of **N** and **Q**, only CIDNP signals of **N** in the first case and those of **N** and **Q** in the second case have been observed,[17] but adduct formation has only been suspected.[18b] We have now obtained various adducts in good yields by conducting the reaction in benzene. The use of acetonitrile as solvent resulted in a dramatic decrease in the yields. In the case of **HB**, interpretation of the CIDNP signals could not be accomplished.[16] These signals probably originated from one or several of the **CA** adducts characterized in this work. In the light of the established product structures, further CIDNP studies would seem in order to elucidate the reaction mechanisms. In this respect, the present study leaves many questions open. Whereas the additions of **HB** and **Q** to **CA** most probably proceed via radical-ion pairs and zwitterions, two competing pathways are proposed for the reaction of **N** in benzene. One of them also starts with radical-ion pair formation, while the other is initiated by direct addition of ^{3}CA to **N** resulting in a diradical. The former process does not seem to yield adducts in acetonitrile solution.

Experimental Section

Instrumentation: See ref.[19]

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 either by means of a Pyrex immersion well containing a Hanovia mercury lamp (medium pressure, 450 W) surrounded by a glass filter to prevent passage of light of $\lambda \leq 400$ nm, or in a Rayonet photochemical reactor RPR-100 (λ = 300 or 350 nm) in a Pyrex vessel. The progress of the reactions, i.e. the consumption of chloranil or methyl phenylglyoxylate, was monitored by TLC [SiO_2, pentane (P) or light petroleum (LP)/ethyl acetate (EA), 9:1]. Purification of the crude chloranil adducts was carried out by flash chromatography (denoted simply as chromatography) using mixtures of P or LP and EA as eluants.

Irradiation of Chloranil (CA) in the Presence of Homobenzvalene (HB): A solution of **CA** (500 mg, 2.03 mmol) and **HB**[20] (286 mg, 3.10 mmol) in toluene (120 mL) was irradiated (λ > 400 nm) at −30°C for 6 h. The solvent was then evaporated at 30°C/20 Torr. Chromatography of the residue at −30°C (basic Al_2O_3, activity III, P/EA, 14:1) afforded three fractions (described in order of elution): (i) 201 mg (29%) of a 9:1 mixture of 2,3,5,6-tetrachloro-3′,3a′,6′,6a′-tetrahydrospiro[cyclohexa-2,5-diene-1,2′-[3,6]-methano[2*H*]cyclopenta[*b*]furan]-4-one (**3**) and (1′*α*,2′β,5′β,6′*α*)-2,3,5,6-tetrachlorospiro[cyclohexa-2,5-diene-1,4′-[3]oxatricyclo-[4.2.1.$0^{2,5}$]non[7]en]-4-one (**8**); (ii) 150 mg of a yellow oil containing 2,3,5,6-tetrachlorospiro[cyclohexa-2,5-diene-1,5′-[4]oxatetracyclo-[4.3.0.$0^{2,9}$.$0^{3,8}$]nonan]-4-one (**6**) as the major component along with small amounts of **3**, 2,3,5,6-tetrachlorohexahydrospiro[cyclohexa-2,5-diene-1,4′-[1,2,6]methenocyclopenta[*c*]furan]-4-one (**5**) and impurities; (iii) 102 mg (15%) of (*Z*)-2-[2,2,4,5-tetrachloro-3-oxocyclopent-4-en-1-ylidene]-3,3a,6,6a-tetrahydro-3,6-methano-2*H*-cyclopenta[*b*]furan (**4**) as a yellowish solid with m.p. 174−176°C after recrystallization from LP/EA. The components of fraction (i) were obtained as pure compounds (**3** and **8**) from an experiment with norbornadiene (see below). Fraction (ii) was further purified by chromatography (basic Al_2O_3, activity III, P/EA, 35:1, −30°C) to give a yellow oil, which was dissolved in a small quantity of EA. On storage of this solution at −35°C, colorless crystals with m.p. 183−185°C separated (112 mg, 16%), which were shown to be an 8:1 mixture of **6** and most probably **5**. − **4:** IR (KBr): $\tilde{\nu}$ = 1732 cm^{-1} (C=O), 1647 (C=C), 1514. − MS (70 eV); *m/z* (%): 342, 340, 338, 336 (1.5, 7.5, 16, 12) [M^+], 303 (15), 301 (16), 237 (10), 92 (26), 91 (49), 66 (14), 65 (100), 63 (10), 55 (85), 39 (49). − ^{1}H NMR ($CDCl_3$): δ = 1.52 (dd, $J_{7,7}$ = 12.1, $J_{3,7}$ = 6.2 Hz, *anti*-7-H), 1.80 (dd, $J_{6,7}$ = 5.1 Hz, *syn*-7-H), 2.99 (dddt, $J_{5,6}$ = 3.4, $J_{6,6a}$ = 2.6, $J_{4,6}$ = $J_{3a,6}$ = 1.0 Hz, 6-H), 3.33 (m, 3a-H), 3.78 (dd, $J_{3,3a}$ = 1.6 Hz, 3-H), 4.82 (t, $J_{3a,6a}$ = 2.6 Hz, 6a-H), 5.81 (ddd, $J_{4,5}$ = 6.1, $J_{3a,4}$ = 3.2 Hz, 4-H), 6.33 (ddd, $J_{3a,5}$ = 0.8 Hz, 5-H); the assignments are based on the similarity of the fine structure of the signals to that seen in the spectrum of **3**. − ^{13}C NMR ($CDCl_3$): δ = 32.8 (C-7), 38.3 (C-3), 44.0 (C-6), 54.1 (C-3a), 74.6 (C-2′), 94.3 (C-6a), 108.4 (C-1′), 122.3 (C-4′), 125.8 (C-4), 137.7 (C-5), 156.0 (C-5′), 170.4 (C-2), 184.1 (C-3′); the assignments of the signals of the CH and CH_2 carbon atoms were made on the basis of a C,H-COSY spectrum. − $C_{13}H_8Cl_4O_2$ (338.0): calcd. C 46.19, H 2.39; found C

45.95, H 2.33. – **5** and **6** as an 1:8 mixture: IR (KBr): $\tilde{\nu}$ = 1681 cm^{-1} (C=O), 1558 (C=C). – MS (70 eV); *m/z* (%): 342, 340, 338, 336 (0.1, 0.8, 1.7, 1.3) [M^+], 107 (22), 92 (48), 91 (100), 81 (26), 79 (10), 66 (62), 65 (31), 39 (26). – $C_{13}H_8Cl_4O_2$ (338.0): calcd. C 46.19, H 2.39; found C 46.03, H 2.36. – **5:** ^{1}H NMR ($CDCl_3$/C_6D_6): δ = 2.03/0.90 (m, 7′-H), 2.07/1.36 (td, $J_{1',2'} = J_{1',7'}$ = 4.5, $J_{1',6a'}$ = 2.5 Hz, 1′-H), 2.30–2.45/1.45–1.57 (3′-H_β), 2.61/1.45–1.57 (br. d, $J_{3',3'}$ = 14.0 Hz, 3′-H_α), 2.73/1.63 (br. dd, $J_{3'\beta,3a'}$ = 9.8, $J_{3a',6a'}$ = 6.0 Hz, 3a′-H), 3.48/2.72 (dddd, $J_{6',6a'}$ = 7.9, $J_{6a',7'}$ = 3.5 Hz, 6a′-H), 4.96/4.48 (dd, $J_{6',7'}$ = 3.2 Hz, 6′-H); the missing absorption (2′-H) and those signals for which a range is specified are superimposed by the multiplets of **6**. – ^{13}C NMR (C_6D_6): δ = 13.9 (C-1′), 24.7, 26.2 (C-2′,7′), 35.3 (C-3′), 48.2 (C-6a′), 57.4 (C-3a′), 76.7 (C-6′); assignments are based on a DEPT spectrum and on data for model compounds (see text); the intensities of the signals of the quaternary carbon atoms were too low to permit their detection. – **6:** ^{1}H NMR ($CDCl_3$): δ = 1.57 (m, 1 H), 1.88 (m, 1 H), 2.29–2.45 (m, 4 H), 2.91 (m, 1 H), 4.48 (m, 1 H). – ^{1}H NMR (C_6D_6): δ = 0.81 (ddd, $J_{7',7'}$ = 12.2, $J_{6',7'}$ = 6.2, $J_{7',8'}$ = 1.8 Hz, 7′-H_β), 1.02 (≈ qt, $J_{1',2'}$ = 5.9, $J_{1',6'} = J_{1',9'}$ = 4.6, $J_{1',3'} = J_{1',8'}$ = 1.1 Hz, 1′-H), 1.47 (ddd, $J_{6',8'}$ = 2.0 Hz, 6′-H), 1.55 (≈ td, $J_{2',9'}$ = 3.7, $J_{8',9'}$ = 2.3 Hz, 9′-H), 1.77 (≈ dtt, $J_{2',3'}$ = 3.6, $J_{2',7'\alpha} = J_{2',8'}$ = 1.3 Hz, 2′-H), 2.00 (ddd, $J_{7'\alpha,8'}$ = 2.1 Hz, 7′-H_α), 2.15 (≈ dsept, $J_{3',8'}$ = 6.8 Hz, 8′-H), 3.95 (ddd, 3′-H); the assignments were made on the basis of decoupling experiments and NOE measurements. – ^{13}C NMR (C_6D_6): δ = 20.7 (C-1′), 21.6 (C-9′), 24.7 (C-2′), 35.4 (C-7′) 42.8 (C-8′), 50.7 (C-6′), 67.4 (C-3′), 81.8 (C-1), 128.8, 129.8 (C-3,5), 159.1, 159.6 (C-2,6), 171.0 (C-4); the assignments were made on the basis of a C,H-COSY spectrum.

X-ray Diffraction Analysis of 4:[43] Data were collected from a suitable crystal of **4** of approximate dimensions of 0.35 × 0.30 × 0.85 mm with a Nicolet R3m/V diffractometer (Mo-K_α radiation, graphite monochromator). Cell dimensions were refined from 22 reflections *hkl*: *a* = 1605.8(7) pm, *b* = 1361.8(7), *c* = 642.3(3), β = 97.55(3)°, *V* = 1392(1) × 10^6 pm^3, monoclinic, space group $P2_1/a$, *Z* = 4, $\rho_{calcd.}$ = 1.613 g cm^{-3}. A total of 3226 unique intensities were measured in the range θ = 1.75–27.5° using the Wyckoff scan technique, of which 2136 were considered observed [$F_o > 3\,\sigma(F_o)$]. A semiempirical absorption correction was applied (ψ scan). The structure was solved and refined on *F* using direct methods and the program SHELXTL-PLUS, respectively. All non-hydrogen atoms were refined anisotropically, while a riding model was employed in the refinement of the hydrogen-atom positions; R = 0.068, R_w = 0.055, $w = 1/\sigma^2(F)$.

Conversion of 3 into 4 by Irradiation of CA in the Presence of 3: A solution of pure **3** (50 mg, 0.15 mmol, see below) and **CA** (100 mg, 0.41 mmol) in anhydrous toluene (100 mL) was irradiated (λ > 400 nm) at −30°C for 4 h. The solvent was then evaporated in vacuo. The ^{1}H-NMR spectrum of the residue showed the characteristic signals of **3** and **4** in an intensity ratio of 1:2, as well as strong signals attributable to 4-benzyloxy-2,3,5,6-tetrachlorophenol (**7**) and impurities.

Irradiation of CA in Toluene: A solution of **CA** (1.00 g, 4.07 mmol) in toluene (150 mL) was irradiated (λ > 400 nm) at −5°C for 20 h. The toluene was then evaporated in vacuo and the residue was purified by chromatography (SiO_2, P/EA, 9:1) to give **7** (621 mg, 45%) as an oil, which was dissolved in EA. Storage of this solution at −35°C afforded colorless crystals with m.p. 144–145°C (142–143.5°C[24c]). – ^{13}C NMR ($CDCl_3$): δ = 75.3 (CH_2), 119.0, 127.6, 146.1, 146.3 (HOC_6Cl_4O), 128.53, 128.57 (*o*-,*m*-C), 128.64 (*p*-C), 135.8 (*i*-C).

Irradiation of CA in Benzene in the Presence of Norbornadiene (N): A solution of **CA** (700 mg, 2.85 mmol) and **N** (525 mg, 5.70 mmol) in benzene (120 mL) was irradiated (λ > 400 nm) at 10°C for 5 h. The solvent was then evaporated in vacuo. Chromatography (SiO_2, P/EA, 25:1) of the residue at −30°C gave, in order of elution, **3** (70 mg, 7%), **8** (416 mg, 43%), (3′α,3a′β,5′α,6′α,6a′β)-2,3,5,6-tetrachlorohexahydrospiro[cyclohexa-2,5-diene-1,2′-[3,5,6]methenocyclopenta[*b*]furan]-4-one (**10**, 189 mg, 20%), and (1′α,2′α,5′α,6′α)-2,3,5,6-tetrachlorospiro[cyclohexa-2,5-diene-1,4′-[3]oxatricyclo[4.2.1.$0^{2,5}$]non[7]en]-4-one (**9**, 152 mg, 16%) as yellow oils. Dissolution of these in the minimum volume of EA and storage of the solutions at −35°C furnished colorless crystals in each case. – **3:** M.p. 214–215°C. – IR (KBr): $\tilde{\nu}$ = 1682 cm^{-1} (C=O), 1559 (C=C). – MS (70 eV); *m/z* (%): 342, 340, 338, 336 (0.1, 0.4, 0.8, 0.7) [M^+], 92 (36), 91 (65), 81 (100), 79 (10), 77 (10), 66 (61), 65 (20), 53 (10), 39 (21). – ^{1}H NMR ($CDCl_3$): δ = 0.96 (ddd, $J_{7',7'}$ = 13.3, $J_{3',7'}$ = 5.6, $J_{6a',7'}$ = 0.8 Hz, *anti*-7′-H), 2.28 (ddd, $J_{3',3a'}$ = 1.8, $J_{3',6a'}$ = 0.5 Hz, 3′-H), 2.45 (br. dd, $J_{6',7'}$ = 5.2 Hz, *syn*-7′-H), 2.90 (ddq, $J_{5',6'}$ = 3.4, $J_{3a',6'} = J_{6',6a'}$ = 1.8 Hz, 6′-H), 3.89 (m, 3a′-H), 4.45 (br. t, $J_{3a',6a'}$ = 2.5 Hz, 6a′-H), 5.64 (ddd, $J_{4',5'}$ = 6.1, $J_{3a',4'}$ = 3.4, $J_{4',6'}$ = 1.4 Hz, 4′-H), 6.38 (ddd, $J_{3a',5'}$ = 0.5 Hz, 5′-H); the assignments were made on the basis of decoupling experiments and NOE measurements. – ^{13}C NMR ($CDCl_3$): δ = 30.7 (C-7′), 45.9 (C-6′), 50.4 (C-3a′), 54.4 (C-3′), 92.1 (C-1), 96.5 (C-6a′), 124.7 (C-4′), 128.3, 129.8 (C-3,5), 139.9 (C-5′), 157.0, 157.9 (C-2,6), 171.8 (C-4); the assignments were made on the basis of a C,H-COSY spectrum. – $C_{13}H_8Cl_4O_2$ (338.0): calcd. C 46.19, H 2.39; found C 45.75, H 2.06. – **8:** M.p. 164–165°C [ref.[23a] 160°C (dec.); ref.[23b] 210°C (dec.)]. – The spectral data are in accord with literature values:[23a,23b] IR (KBr): $\tilde{\nu}$ = 1678 cm^{-1} (C=O), 1557 (C=C). – MS (70 eV); *m/z* (%): 342, 340, 338, 336 (0.4, 1.8, 3.8, 3.0) [M^+], 245 (11), 107 (17), 92 (41), 91 (78), 87 (10), 66 (100), 65 (23), 39 (22). – ^{1}H NMR ($CDCl_3$): δ = 1.56 (d quint, $J_{9',9'}$ = 9.8, $J_{1',9'} = J_{2',9'} = J_{5',9'} = J_{6',9'}$ = 1.2 Hz, *anti*-9′-H), 2.60 (dt, $J_{2',5'}$ = 5.0, $J_{5',6'}$ = 0.8 Hz, 5′-H), 3.10, 3.34 (2 × d quint, $J_{1',8'} = J_{6',7'}$ = 3.2, $J_{1',2'} = J_{1',6'} = J_{1',9'syn} = J_{6',9'syn}$ = 1.3 Hz, 1′,6′-H), 3.15 (br. d, *syn*-9′-H), 4.99 (dt, 2′-H), 5.94, 6.24 (2 × dd, $J_{7',8'}$ = 5.6 Hz, 7′,8′-H). – ^{13}C NMR ($CDCl_3$): δ = 42.8 (t, C-9′), 42.9, 45.5 (2 × d, C-1′,6′), 54.7 (d, C-5′), 82.5 (d, C-2′), 84.5 (s, C-1), 128.7, 130.9 (2 × s, C-3,5), 133.5, 140.8 (2 × d, C-7′,8′), 150.6, 157.9 (2 × s, C-2,6), 170.4 (s, C-4). – $C_{13}H_8Cl_4O_2$ (338.0): calcd. C 46.19, H 2.39; found C 46.54, H 2.44. – **9:** M.p. 156–158°C. – IR (KBr): $\tilde{\nu}$ = 1682 cm^{-1} (C=O), 1556 (C=C). – MS (70 eV); *m/z* (%): 340, 338, 336 (0.1, 0.3, 0.2) [M^+], 92 (25), 91 (45), 66 (100), 65 (12), 39 (11). – ^{1}H NMR ($CDCl_3$): δ = 1.03 (dtt, $J_{9',9'}$ = 9.6, $J_{1',9'} = J_{6',9'}$ = 1.5, $J_{7',9'} = J_{8',9'}$ = 0.8 Hz, *syn*-9′-H), 1.76 (dt, $J_{1',9'} = J_{6',9'}$ = 1.5 Hz, *anti*-9′-H), 3.13, 3.27 (2 × m, 1′,6′-H), 3.36 (dd, $J_{2',5'}$ = 6.8, $J_{5',6'}$ = 4.8 Hz, 5′-H), 5.50 (dd, $J_{1',2'}$ = 4.6 Hz, 2′-H), 6.34, 6.37 (2 × br. d, $J_{7,8}$ ≈ 6 Hz, 7′,8′-H). – ^{13}C NMR ($CDCl_3$): δ = 45.2, 47.1 (2 × d, C-1′,6′), 49.5 (t, C-9′), 58.3 (d, C-5′), 82.8 (d, C-2′), 86.2 (s, C-1), 127.9, 130.3 (2 × s, C-3,5), 137.0, 137.3 (2 × d, C-7′,8′), 153.1, 158.7 (2 × s, C-2,6), 171.1 (s, C-4). – $C_{13}H_8Cl_4O_2$ (338.0): calcd. C 46.19, H 2.39; found C 46.62, H 2.40. – **10:** M.p. 201–203°C. – IR (KBr): $\tilde{\nu}$ = 1682 cm^{-1} (C=O), 1560 (C=C). – MS (70 eV); *m/z* (%): 340, 338, 336 (0.2, 0.3, 0.3) [M^+], 303 (12), 301 (13), 92 (79), 91 (100), 66 (20), 65 (12), 39 (11). – ^{1}H NMR ($CDCl_3$): δ = 1.33 (1 H), 1.56–1.77 (4 H), 2.51 (1 H), 3.01 (1 H), 4.75 (1 H). – ^{1}H NMR (C_6D_6): δ = 0.58 (dddd, $J_{6',7'}$ = 5.5, $J_{5',7'}$ = 4.9, $J_{3',7'}$ = 2.1, $J_{3a',7'}$ = 0.8 Hz, 7′-H), 0.87 (tq, $J_{5',6'}$ = 4.9, $J_{3a',5'} = J_{4'\alpha,5'} = J_{4'\beta,5'}$ = 1.3 Hz, 5′-H), 0.92, 1.01 (2 × dt, $J_{4',4'}$ = 11.3, $J_{3a',4'}$ = 1.5 Hz, 4′-H_2), 1.01 (m, 6′-H), 1.30 (t, $J_{3',3a'}$ = 2.1 Hz, 3′-H), 2.33 (br. s, 3a′-H), 4.18 (t, $J_{3a',6a'} = J_{6',6a'}$ = 2.5 Hz, 6a′-H). – ^{13}C NMR (C_6D_6): δ = 14.5 (C-7′), 16.1 (C-5′), 17.5 (C-6′), 28.3 (C-4′), 39.4 (C-3a′), 62.4 (C-3′), 86.3 (C-1), 87.4 (C-6a′), 129.3, 130.1 (C-3,5), 156.6, 157.1 (C-2,6), 170.5 (C-4); the assignments were made on the basis of a C,H-COSY spectrum. –

$C_{13}H_8Cl_4O_2$ (338.0): calcd. C 46.19, H 2.39; found C 46.51, H 2.47.

Irradiation of CA in Acetonitrile in the Presence of N: A solution of **CA** (500 mg, 2.03 mmol) and **N** (3.75 g, 40.7 mmol) in acetonitrile (200 mL) was irradiated with several light bulbs (total power 700 W) at 10°C for 3 h. Some colorless insoluble material was then allowed to precipitate overnight and the remaining clear solution was further irradiated at 10°C for 1 h. The insoluble material (46 mg) was collected by filtration, but its ^{1}H-NMR spectrum did not reveal its identity. The filtrate was concentrated in vacuo and purification of the residue by chromatography (SiO_2, LP/EA, 20:1) afforded **3** and **8** (80 mg, 12%) as a 1.5:1 mixture containing some minor impurities. When the reaction was conducted with a fivefold lower concentration of **N**, the yield dropped to 4%.

Irradiation of Methyl Phenylglyoxylate (PG) in the Presence of Norbornadiene (N): A solution of **PG** (700 mg, 4.26 mmol) and **N** (786 mg, 8.53 mmol) in toluene (150 mL) was irradiated (λ = 300 nm) at −30°C for 48 h. The solvent was then evaporated at 30°C (bath)/15 Torr. At 100−135°C (kugelrohr)/0.01 Torr, 1.05 g (96%) of a colorless oil was distilled from the residue. ^{1}H-NMR-spectroscopic analysis showed this oil to be a 6:1 mixture of methyl (1α,2β,4β,5β,6α)-4-phenyl-3-oxatetracyclo[4.2.1.0^{2,5}]non-7-ene-4-carboxylate (**11**) and methyl (2α,3β,3aα,5β,6β,6aα)-hexahydro-2-phenyl-3,5,6-methenocyclopenta[*b*]furan-2-carboxylate (**12**). Medium-pressure liquid chromatography (540 mm × 52 mm SiO_2 column, 0.020−0.045 mm, 15 bar, P/EA, 25:1) of 500 mg of the mixture furnished pure **11** (278 mg) as a colorless oil, which, after dissolution in dichloromethane/pentane, yielded crystals of m.p. 57−59°C. − **11** and **12** as a 6:1 mixture: MS (70 eV); *m/z* (%): 256 (0.3) [M^+], 198 (12), 197 (79), 179 (15), 167 (11), 159 (17), 105 (100), 103 (16), 92 (10), 91 (42), 77 (44), 66 (88), 65 (13), 51 (11), 39 (10). − $C_{16}H_{16}O_3$ (256.3): calcd. C 74.98, H 6.29; found C 75.06, H 6.79. − **11**: IR (CCl_4): $\tilde{\nu}$ = 1756 cm^{-1}, 1733 (C=O). − ^{1}H NMR ($CDCl_3$): δ = 1.16 (dquint, $J_{9,9}$ = 9.5, $J_{1,9}$ = $J_{2,9}$ = $J_{5,9}$ = $J_{6,9}$ = 1.3 Hz, *anti*-9-H), 1.65 (br. d, *syn*-9-H), 2.85 (m, 6-H), 2.99 (dt, $J_{2,5}$ = 5.3, $J_{5,6}$ = 1.2 Hz, 5-H), 3.03 (m, 1-H), 3.73 (s, CH_3), 4.65 (dt, $J_{1,2}$ = 1.2 Hz, 2-H), 5.87 (dd, $J_{7,8}$ = 5.7, $J_{1,8}$ = 3.2 Hz, 8-H), 6.18 (dd, $J_{6,7}$ = 3.1 Hz, 7-H), 7.22−7.44 (m, C_6H_5); the configuration and signal assignments were made on the basis of NOE measurements. The previous assignment[23c] was hampered by the fact that a mixture of diastereomers had to be investigated, which were present in a ratio close to 1:1. − ^{13}C NMR ($CDCl_3$): δ = 41.1, 45.4, 45.5 (3 × d, C-1,5,6), 41.2 (t, C-9), 52.9 (q, CH_3), 80.2 (d, C-2), 83.4 (s, C-4), 125.3 (d, *o*-C), 127.5 (d, *p*-C), 128.0 (d, *m*-C), 132.8, 139.1 (2 × d, C-7,8), 137.4 (s, *i*-C), 174.2 (s, C=O). − **12**: ^{1}H NMR ($CDCl_3$): δ = 0.74 (dddd, $J_{6,7}$ = 5.8, $J_{5,7}$ = 5.0, $J_{3,7}$ = 2.1, $J_{3a,7}$ = 0.7 Hz, 7-H), 1.20 (dddd, $J_{5,6}$ = 5.0, $J_{6,6a}$ = 2.2, $J_{3a,6}$ = 0.6 Hz, 6-H), 1.28 (tq, $J_{3a,5}$ = $J_{4\alpha,5}$ = $J_{4\beta,5}$ = 1.4 Hz, 5-H), 1.70 (t, 4-H_2), 2.19 (br. s, 3a-H), 3.23 (t, $J_{3,3a}$ = 2.1 Hz, 3-H), 3.68 (s, CH_3), 4.56 (dd, $J_{3a,6a}$ = 2.9 Hz, 6a-H), 7.22−7.44 (m, *m*-,*p*-H), 7.58 (m, *o*-H); the configuration and signal assignments were made on the basis of NOE experiments. − ^{13}C NMR ($CDCl_3$): δ = 12.4, 15.3, 15.4 (3 × d, C-5,6,7), 29.8 (t, C-4), 40.9 (d, C-3a), 52.1 (d, C-3), 52.5 (q, CH_3), 84.7 (d, C-6a), 86.8 (s, C-2), 125.6 (d, *o*-C), 127.4 (d, *p*-C), 140.6 (s, *i*-C); the signals of *m*-C and C=O are superimposed by those of **11**.

Irradiation of CA in the Presence of Quadricyclane (Q): A solution of **CA** (700 mg, 2.85 mmol) and **Q** (525 mg, 5.70 mmol) in benzene (120 mL) was irradiated (λ = 350 nm) at 10°C for 5 h. The solvent was then evaporated in vacuo. Chromatography (SiO_2, LP/EA, 25:1) of the residue at −30°C gave, after crystallization from EA, 350 mg (36%) of pure **8**. Although the ^{1}H-NMR spectrum of the crude product (before chromatography) indicated further components, none of these could be identified. Notably, signals of compounds **3**, **4**, **5**, **6**, **9**, and **10** were not observed.

Irradiation of CA in Acetonitrile in the Presence of Q: A solution of **CA** (300 mg, 1.22 mmol) and **Q** (1.33 g, 14.4 mmol) in acetonitrile (70 mL) was irradiated with several light bulbs (total power 1000 W) at 10°C for 45 min. Some colorless insoluble material was then allowed to precipitate overnight and the remaining clear solution was further irradiated at 10°C for 1 h. The insoluble material (128 mg) was collected by filtration, but its ^{1}H-NMR spectrum did not reveal its identity. The filtrate was concentrated in vacuo and the residue was analysed by NMR spectroscopy. The oxetane **8** was the sole identifiable product. By using an internal standard, its yield was estimated to be ca. 3%.

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