

Photoinduced Reactions of Chloranil with Stilbene Derivatives and α,β -Unsaturated Carbonyl Compounds

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Photolysis of chloranil (CA) with *Z*- or *E*-stilbenes **1–5** [(*Z*)- and (*E*)-XC₆H₄CH=CHC₆H₅, X = H, 4-Cl, 3-Cl, 4-Me) in benzene leads to the formation of *trans*-oxetane products **7–13** (80–88% yield) and extensive *Z*- to *E*- (when starting from *Z*-) as well as slight *E*- to *Z*- (when starting from *E*-) isomerizations of the stilbenes. For the monosubstituted stilbenes, two oxetane regioisomers are formed in comparable yields. Similar photolysis in acetonitrile resulted only in the one-way *Z*- to *E*- isomerization of the stilbenes without formation of oxetanes. (*Z*)- and (*E*)-4-Methoxystilbenes do not form oxetane products with CA either in benzene or in acetonitrile, and one-way *Z*- to *E*- isomerization is the only reaction detected. Diphenylvinylene carbonate **6** gave oxetane product **14** with CA in benzene solution. Electron transfer between ³CA* and the alkenes is involved in the cycloaddition and isomerization. Photolysis of CA with ethyl (*E*)- or (*Z*)-cinnamate (*E*-**22** or *Z*-**22**), ethyl 3-nitrocinnamate (*E*-**23** or *Z*-**23**), benzalacetone (*E*-**24** or *Z*-**24**), chalcone (*E*-**25** or *Z*-**25**) and (*E*)-4-fluoro-chalcone (*E*-**26**) in benzene or in acetonitrile gave *trans*-oxetane products **27–31** respectively in good yield (72–95%) and resulted in slight *E*-to-*Z* and considerable *Z*-to-*E* isomerizations without SET-process involvement.

Photoinduced cycloadditions of quinones and halogenoquinones with alkenes take place on the carbonyl group or the ethene double bond of the quinone moiety, giving spirooxetane or cyclobutane derivatives, respectively, depending on the structure of the respective quinone and alkene.^{1–8} The rationalization of the reaction site and regioselectivity in these reactions has drawn much research interest.^{5,7,8} Recent recognition of the fact that a photoinduced electron-transfer process (single-electron transfer, SET) can be involved in some of these reactions and may play an important role in determining the reaction outcome^{7,8} has shed new light on a better understanding of the different site selectivity and regiochemistry seen in these additions in relation to reaction mechanisms. The electron-transfer process has also been found to play important roles in photoinduced *Z*, *E* isomerizations of alkenes in the presence of added electron donors or acceptors, although different mechanisms leading to the isomerization following the initial SET step may operate and may have to be clarified from case to case.^{9–11}

Known results in the field of photoinduced addition reactions of chloranil (CA) with alkenes^{3,12–16} have shown that the reaction modes for CA are more diversified than for benzoquinone (BQ) and its alkyl-substituted derivatives. This is partly the result of the strong electron-acceptor ability of CA, which causes the SET process to be more often involved in the photoinduced reactions with alkenes.

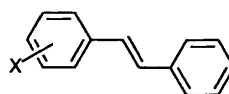
With the aim of further exploring the scope of the reaction and the factors that influence the reaction's outcome, we have investigated the photoinduced reactions of CA with stilbene derivatives **1–5** and α,β -unsaturated carbonyl compounds **22–26**.

Results and Discussion

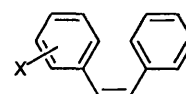
Photoinduced Reactions of CA with Stilbene Derivatives.—Irradiation of CA with (*E*)-, (*E*-**1**) or (*Z*)-stilbene (*Z*-**1**) in benzene solution gave the *trans*-oxetane product **7**.¹⁶ We have found that extensive *Z*-to-*E* and slight *E*-to-*Z* isomerizations

of stilbenes take place during the reaction. As an example, irradiation of a benzene solution of CA (0.02 mol dm⁻³) and *E*-**1** (0.04 mol dm⁻³) gave spirooxetane **7** in 87% yield upon the total conversion of CA and the stilbenes left in excess were 97.4% in *trans* and 2.6% in *cis* as analysed by HPLC. Similar irradiation of CA (0.02 mol dm⁻³) and *Z*-**1** (0.04 mol dm⁻³) in benzene gave compound **7** in 83% yield and the stilbenes in excess were 79% in *trans* and 21% in *cis*. However, when the photolyses were conducted in acetonitrile, formation of oxetane was found to be totally suppressed and the one-way *Z*-to-*E* isomerization became the only reaction detected. Thus, irradiation of an acetonitrile solution of CA (0.02 mol dm⁻³) and *E*-**1** (0.04 mol dm⁻³) with light of $\lambda > 400$ nm under argon for 5 h resulted in a solution containing 99.2% *E*-**1** and 0.8% *Z*-**1**. Similar photolysis of an acetonitrile solution of CA (0.02 mol dm⁻³) and *Z*-**1** (0.04 mol dm⁻³) for 5 h gave a solution containing 68.8% *E*-**1** and 31.2% *Z*-**1**. However, in the isomerizations in acetonitrile, a photostationary state cannot be reached because it was found that during prolonged irradiation both CA and the stilbenes are gradually consumed.

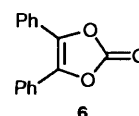
The photoreactions of CA with eight monosubstituted *Z*- and *E*-stilbenes (*E*- and *Z*-**2**, **-3**, **-4** and **-5**) as well as diphenylvinylene carbonate **6** in benzene and acetonitrile were further investigated.



E-**1** X = H
E-**2** X = *p*-Cl
E-**3** X = *m*-Cl
E-**4** X = *p*-Me
E-**5** X = *p*-MeO



Z-**1** X = H
Z-**2** X = *p*-Cl
Z-**3** X = *m*-Cl
Z-**4** X = *p*-Me
Z-**5** X = *p*-MeO



6

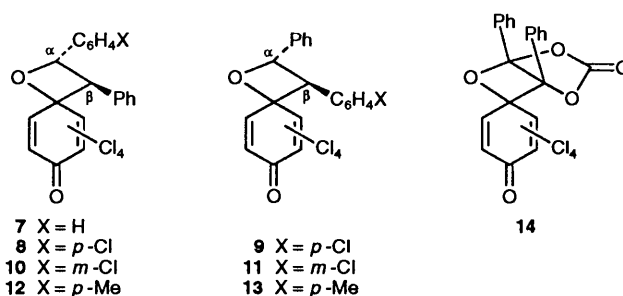
Table 1 Photoinduced reactions between CA and stilbenes^a

Stilbene	$E(D/D^{*+})$ (SCE) ^b	Solvent	ΔG_{ET} (kcal mol ⁻¹)	Irrad. time (t/h)	Products and yields (%) ^c	<i>cis/trans</i> ^d
<i>E</i> -1	1.95	C ₆ H ₆	-3.7	5	7 (87)	2.6/97.4
<i>E</i> -1	1.95	MeCN	-13.8	5		0.8/99.2
<i>Z</i> -1	2.06	C ₆ H ₆	-1.2	5	7 (83)	21.0/79.0
<i>Z</i> -1	2.06	MeCN	-11.3	5		68.8/31.2
<i>E</i> -2	1.98	C ₆ H ₆	-3.0	5	8 (45), 9 (40)	3.3/96.7
<i>E</i> -2	1.98	MeCN	-13.1	5		0.8/99.2
<i>Z</i> -2	2.13	C ₆ H ₆	0.5	5	8 (45), 9 (40)	30.7/69.3
<i>Z</i> -2	2.13	MeCN	-9.7	5		79.2/20.8
<i>E</i> -3	1.57	C ₆ H ₆	-3.5	5	10 (34), 11 (50)	3.7/96.3
<i>E</i> -3	1.57	MeCN	-13.6	5		0.4/99.6
<i>Z</i> -3	1.69	C ₆ H ₆	-0.7	5	10 (34), 11 (54)	29.8/70.2
<i>Z</i> -3	1.69	MeCN	-10.8	5		87.2/12.8
<i>E</i> -4	1.83	C ₆ H ₆	-6.5	5	12 (38), 13 (46)	2.1/97.9
<i>E</i> -4	1.83	MeCN	-16.6	5		0.8/99.2
<i>Z</i> -4	1.95	C ₆ H ₆	-3.7	5	12 (36), 13 (44)	5.2/94.8
<i>Z</i> -4	1.95	MeCN	-13.8	5		82.8/17.2
<i>E</i> -5	1.53	C ₆ H ₆	-13.4	6		0.8/99.2
<i>E</i> -5	1.53	MeCN	-23.5	6		0.5/99.5
<i>Z</i> -5	1.61	C ₆ H ₆	-11.5	6		24.2/75.8
<i>Z</i> -5	1.61	MeCN	-31.7	6		0.7/99.3
6	1.60	C ₆ H ₆	-2.8	5.5	14 (71) ^e	

^a [CA] 0.02 mol dm⁻³, [alkene] 0.04 mol dm⁻³. ^b $E(D/D^{*+})$ for *E*-3, *Z*-3 and 6 was determined by cyclic voltammetry in acetonitrile with tetraethylammonium perchlorate (0.01 mol dm⁻³) as supporting electrolyte vs. SCE reference electrode. $E(D/D^{*+})$ for all the other stilbenes was taken from literature (ref. 10c) and was converted into values vs. SCE by subtracting 0.39 V from the values vs. Ag/AgI. ^c Product quotients 8/9, 10/11 and 12/13 were determined by 500 MHz ¹H NMR spectroscopy. Yield of compound 7 was determined by HPLC. ^d Determined by HPLC upon the total conversion of CA (in benzene) or after photolysis for the indicated time (in acetonitrile). ^e Isolated yield in preparative photolysis.

Irradiation of benzene solutions of CA with each of the stilbenes (*Z* or *E*) except *E*-5 and *Z*-5 with light of $\lambda > 400$ nm gave the corresponding *trans*-oxetane products (8 and 9, 10 and 11, 12 and 13) respectively in high total yields (Table 1). Since the photolyses of either *E*- or *Z*-isomer of the substituted stilbenes 2–4 gave only one stereoisomer of the spirooxetanes and resulted in extensive *Z*-to-*E* isomerization of the *Z*-stilbenes as in the photolyses of CA with the unsubstituted *E*-1 and *Z*-1 to give the *trans*-oxetane 7, *trans*-configurations are similarly assigned for spirooxetanes 8–13. Diphenylvinylene carbonate 6 gave the oxetane 14 in 71% yield. For the monosubstituted stilbenes, two regioisomers were formed in comparable yields. A significant and regular substituent effect on the ratio of the regioisomers was not observed. Some of the regioisomers (9 and 12) can be isolated by stepwise crystallization of the regioisomeric mixture from light petroleum–chloroform and their regiochemistry was assigned by (i) ¹H NMR chemical-shift comparisons: α -H in compound 13 has a slightly higher δ -value (δ 6.70) than in isomer 12 (δ 6.68), and β -H in compound 13 has a slightly lower δ -value (δ 4.93) than in isomer 12 (δ 4.99). On the other hand, δ -values for α -H and β -H in compound 9 (δ 6.67 and 4.95) are slightly lower and higher than that in isomer 8 (δ 6.68 and 4.93), respectively. (ii) The occurrence of the metathetical fragmentation peak in the mass spectrum of the pure isomers 9 (m/z 352) and 12 (m/z 318). In all these photolyses the *cis*-isomer of the spirooxetanes was not found after careful chromatographic separations. Spirooxetanes 7–13 have absorption maxima in the region $\lambda < 300$ nm. Control experiments showed that they are photostable and can stand prolonged irradiation without appreciable consumption when irradiated either alone or in the presence of CA in benzene solution with light $\lambda > 400$ nm. In acetonitrile, irradiation of CA with each of the stilbenes (*Z* or *E*) resulted only in the one-way *Z*-to-*E* isomerization of the stilbenes without formation of the oxetane, as in the case of *E*-1 and *Z*-1. The results are summarized in Table 1.

Stilbene derivatives form charge-transfer complexes (CTCs) with CA, which strongly absorb in the visible region of the



spectrum.¹⁷ The CTC of CA with *E*-1 has a λ_{CT} of 529 nm (ϵ_{CT} 645 cm² mol⁻¹) and a K_{CT} of 1.3 dm³ mol⁻¹.^{17b} Estimation based on the fraction of CA complexed in the presence of the small excess of *E*-1 as used in the photolyses and the ϵ_{CA^-} and ϵ_{CT^-} -values in the region $\lambda > 400$ nm shows that while the CA monomer is the main absorbing species in the photolyses, *E*-1 also absorbs a considerable amount of incident light ($\sim 30\%$). Our own spectroscopic measurements showed that the *Z*-isomers (*Z*-1–*Z*-5) also form CTCs with CA; the λ_{CT} , however, is blue-shifted by ~ 50 nm from that for the corresponding *E*-isomers, in accord with their higher oxidation potentials. However, the addition of the *Z*-isomers in such a small excess as used in the photolyses to a CA solution caused no significant spectral change in the region > 400 nm. In the photolyses of CA with these *Z*-isomers, CA is selectively excited without significant CTC excitation involvement.

The free-energy change of exciplex formation and of electron transfer (for solvent-separated ion-pair formation) in acetonitrile between triplet excited CA and the stilbenes was calculated by use of Weller's equations (1) and (2)¹⁸ where $E(D/D^{*+})$ and $E(A/A^{*-})$ are the oxidation potential of the stilbenes and the reduction potential of CA (-0.02 V, SCE),^{19*}

* SCE = standard calomel electrode.

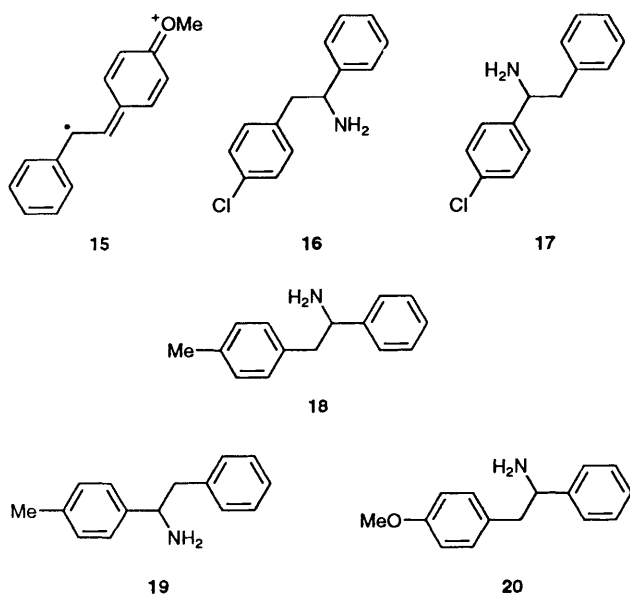
respectively. E^* is the triplet energy of CA (2.12 eV).²⁰ The results are given in Table 1.

$$\text{in benzene, } \Delta G_{\text{ET}} = 23.06 [E(D/D^{+\bullet}) - E(A/A^{\bullet-}) - E^* + 0.38] \text{ kcal mol}^{-1} \quad (1)^\dagger$$

$$\text{in acetonitrile, } \Delta G_{\text{ET}} = 23.06 [E(D/D^{+\bullet}) - E(A/A^{\bullet-}) - E^* - 0.06] \text{ kcal mol}^{-1} \quad (2)^\dagger$$

The ΔG_{ET} s are almost all negative and show that the corresponding electron-transfer processes are, in most cases, exothermic in benzene and in acetonitrile. This suggests that the addition reactions in benzene proceed through highly polar exciplexes or even contact-ion-radical pairs.

The excitation of the CTC together with CA monomer in the photolyses of CA with the *E*-stilbenes also resulted in electron transfer between CA and the alkenes, although, in these cases, very short lived contact-ion-radical pairs (CIP) of singlet multiplicity are formed.²¹



In acetonitrile, dissociation of the triplet ion-radical pair predominates; as a result, the addition product is not formed and *E/Z* isomerizations become the only reactions detected. 4-Methoxystilbenes (*E*- and *Z*-5) do not form an addition product with CA even in benzene solution. Only *E/Z* isomerizations were observed here. Similar inhibition of further reactions of the cation radical of alkenes bearing a *p*-methoxyphenyl group attached to the double bond has also been observed in other SET reactions^{7b,22} and is attributed to the stabilization of the cation radicals by delocalization of the positive charge onto the methoxy-substituted phenyl group in a quinomethane structure such as **15**. In regard to this, it is interesting to note that, in photoinduced aminations of mono-substituted stilbenes sensitized by *p*-dicyanobenzene, two regioisomers were also reported to be formed in comparable amounts when the substituent is *p*-Cl (**16/17** = 1/0.9) or *p*-Me (**18/19** = 1/0.6) and this is related to the distribution of positive charge on the two benzylic positions to similar extents.²³ For *p*-methoxystilbene, delocalization of positive charge from C_α to the methoxy group leads to the inefficient selective amination at the C_β carbon (product **20**).

The oxygen effect on the reaction of CA with *E*-1 was examined. It was found that formation of the oxetane in benzene solution was not interrupted by oxygen purging during the irradiation and no oxidation products were detected, while in acetonitrile the cation radicals of the stilbenes were intercepted by ground-state oxygen to lead to the electron-transfer photooxygenation of substrate *E*-1, with benzaldehyde as the main product. This photooxygenation is similar to the 9,10-dicyanoanthracene (DCA)-sensitized photooxygenations of the stilbenes in acetonitrile²⁴ although superoxide ion is not involved in the CA-sensitized oxygenation because of the endothermic nature of the secondary SET process between $CA^{\bullet-}$ and 3O_2 .²⁵

In the photoinduced *E/Z* isomerizations of alkenes in the presence of added electron-donor or -acceptor sensitizers, several possible mechanisms have been proposed. In cases where the singlet or triplet excited state has an energy lower than the exciplex or the radical-ion pair, isomerization from singlet excited alkenes formed by energy transfer in exciplex¹¹ and from triplet excited alkenes formed by exciplex intersystem crossing (ISC) and dissociation or back-electron transfer of the radical-ion pair²⁶ have been established. In polar solvents, a cation-radical-chain mechanism with free cation radicals of the alkenes as the chain-initiating species may operate.^{10a} Recently, to account for the DCA-sensitized one-way *Z*-to-*E* isomerization of the stilbenes, a cation-radical-chain mechanism involving the dimer cation radical of the stilbenes has been suggested for the isomerization in acetonitrile solution,^{10c} and a singlet version of the Schenck mechanism²⁷ involving a diradical intermediate formed by coupling of the stilbene cation radical and the DCA anion radical is proposed for the isomerizations in benzene solution.^{10b}

The intermediacy of triplet stilbenes in the present photoisomerizations of stilbenes in the presence of CA can be ruled out, based on the following considerations. (i) Populating the triplet stilbene (E_T 45 kcal mol⁻¹ for the phantom triplet state) via back-electron transfer of the ion-radical pairs ($CA^{\bullet-} - E-1^{+\bullet}$) (E_{IP} 36 kcal mol⁻¹) or of the ($CA^{\bullet-} - Z-1^{+\bullet}$) (E_{IP} 39 kcal mol⁻¹)[‡] in acetonitrile is energetically unfavourable; (ii) exothermic non-vertical energy transfer^{28,29} from CA (E_T 49 kcal mol⁻¹)²¹ to lead to the phantom state (E_T 45 kcal mol⁻¹)³⁰ is possible; however, isomerizations from this triplet state should lead to a photostationary state consisting of more than 90% *Z*-1,²⁸ in contradiction to the actually observed one-way *Z*-to-*E* isomerization induced by $^3CA^*$.

Therefore, the photoisomerizations in acetonitrile should proceed by an SET mechanism and with cation radicals of stilbenes as intermediate. This is not only in accord with all the observations mentioned above, but also gains evidence from photo-chemically induced dynamic nuclear polarization (CIDNP) studies of the (CA-stilbenes) systems. In the ¹H NMR spectra of a CD₃CN solution of CA (0.02 mol dm⁻³) and *E*-5 (0.02 mol dm⁻³) during irradiation, the protons of the methoxy group in the isomerized product *Z*-5 show abnormally enhanced absorption (*A*) at δ 3.7, which is consistent with the cation radical mechanism when considering the following parameters determining polarization:³¹ (1) triplet-radical ion pair as precursor for product formation; (2) the stilbene cation radical has a *g*-value of ~2.0026 which is smaller than the *g*-value of 2.0062 for $CA^{\bullet-}$;⁹ (3) the methoxy protons have a positive hyperfine coupling constant with the unpaired electron of the cation radical;⁹ (4) the isomerized product *Z*-5 is formed by escape of the cation radical of the starting material *E*-5 out of the solvent cage followed by rapid electron exchange with neutral alkene molecules in the solution. The methoxy protons of the starting material *E*-5 show a relatively weak polarization in the opposite direction (*E*), leading to a weakening of the original absorption peak. This is because the starting alkene is regenerated by in-cage back-electron transfer of $CA^{\bullet-}$ and

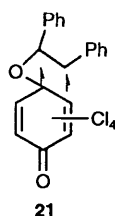
[†] 1 cal = 4.184 J.

[‡] Calculated by $E_{\text{IP}} = 23.06 (E_{\text{I}}^{\text{ox(donor)}} - E_{\text{I}}^{\text{red(acceptor)}})$.

$E-5^{*+}$. In the photo-CIDNP spectra of the (CA-Z-3) system in CD_3CN , main features during irradiation are the enhanced absorptions of the olefinic and a part of the aromatic signals of the starting alkene. In this case, the precursor radical ion pair is still of triplet multiplicity, Δg is still negative, and the starting alkene is regenerated by in-cage back-electron transfer of $CA^{\bullet-}-Z-3^{*+}$ radical ion pair. The electron spin resonance (ESR) hyperfine coupling constant of olefinic and *ortho*, *para* protons of the aromatic ring with the unpaired electron is negative. This leads to the observed polarization.

Besides our investigation on *E-5* and *Z-3* systems, photo-CIDNP phenomena have also been observed for (CA-*E-1*) and (CA-*Z-1*) systems³² and the polarizations are in accord with the SET mechanism.

The ΔG_{ET} in benzene solution and the solvent and oxygen effects on the addition and isomerization reactions showed that polar triplet exciplexes are involved in the addition and isomerization reactions in benzene. Considering the efficient formation of the oxetane product during the reaction, the isomerization is most likely to proceed *via* a Schenck mechanism by bond formation between CA and the stilbene in an exciplex to give a triplet diradical intermediate **21** which has a lifetime long enough to allow internal rotation of the $C_\alpha-C_\beta$ bond to bring the two phenyls from the *cis*- to the more stable *trans*-configuration. The diradical intermediate could then either cyclize to give the *trans*-oxetane product or cleave to give the isomerized alkenes. This mechanism also accounts for the exclusive formation of the *trans*-oxetane product from photo-reactions of CA with either *Z* or *E* stilbenes.



Photoinduced Cycloaddition Reactions of CA with α,β -Unsaturated Carbonyl Compounds.—Similarly to the photo-induced reactions of CA with the stilbene derivatives **1-6**, oxetane-product formation has also been reported in photo-induced reactions of CA with other alkenes of low oxidation potential, such as babaralone,¹⁴ benzvalene¹⁵ and 1,1-dimethylindene.³³ An SET process was also found to be involved in these reactions, as evidenced by either flash photolysis¹⁴ or photo-CIDNP studies.^{33,34}

In order to clarify further the dependence of reaction mode on the structure and oxidation potential of the alkenes, photoinduced reactions of CA with α,β -unsaturated compounds **22-25** (*E* and *Z*) and *E-26* were investigated.

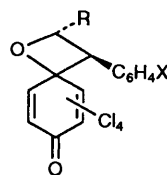


<i>E</i> - and <i>Z-22</i>	X = H, R = CO ₂ Et
<i>E</i> - and <i>Z-23</i>	X = <i>m</i> -NO ₂ , R = CO ₂ Et
<i>E</i> - and <i>Z-24</i>	X = H, R = COMe
<i>E</i> - and <i>Z-25</i>	X = H, R = COPh
<i>E-26</i>	X = <i>p</i> -F, R = COPh

Photolysis of a benzene solution of CA (0.05 mol dm⁻³) with ethyl (*E*)-cinnamate (0.1 mol dm⁻³) with light of $\lambda > 400$ nm under argon purging led to the exclusive formation of the *trans*-oxetane product **27** in 83% yield. Similar photolysis of CA with *Z-22* in benzene also gave the *trans-27* in 89% yield. Slight *E*-to-*Z* (when starting from the *E*) and predominant *Z*-to-*E* (when starting from the *Z*) isomerizations were found to accompany

the addition reactions. However, in sharp contrast with the situation in the photolysis of CA with stilbene derivatives, irradiation of CA with cinnamates *E-22* and *Z-22* in acetonitrile also gave spirooxetane **27** in good yield (Table 2). The structure of product **27** was assigned by spectral and elemental analysis data. In the IR spectrum of compound **27**, the characteristic C-O-C stretching band for oxetane ring occurs at 982 cm⁻¹.¹² The enedione carbonyl group absorption is at 1689 cm⁻¹. The oxetane structure was further confirmed by the fragment peak at m/z 318 in the mass spectrum, which is from the carbonyl-alkene metathetical fragmentation of the cation radical of compound **27**. This peak at m/z 318 also unambiguously revealed the regiochemistry in compound **27**, that is, the β -carbon atom (PhCH=CHCO₂Et) in cinnamate **22** is linked to the carbon atom from the CA carbonyl group.

The regioselectivity found in the oxetane product is consistent with results from considerations of frontier molecular orbital (FMO) interactions of the two reactants. In photochemical reactions, two pairs of FMO interactions should be taken into account:³⁵ (1) Interaction between the lowest singly occupied molecular orbital of the excited species (LSOMO)_{ex} and the highest occupied molecular orbital of the ground-state species (HOMO)_{gr}; (2) Interaction between the highest singly occupied molecular orbital of the excited state (HSOMO)_{ex} and the lowest unoccupied molecular orbital of the ground state (LUMO)_{gr}. However, in the present situation for CA*-**22** reaction, the HSOMO_{CA*}-LUMO_{alkene} should not be important in deciding the regioselectivity of the addition since, in the LUMO of **22**, the atomic orbital coefficients on C_α and C_β are of similar magnitude. On the other hand, the atomic orbital coefficient on C_α in the HOMO of **22** is significantly larger than at C_β .³⁶ In the LSOMO_{CA*}, the atomic orbital coefficient at the carbonyl oxygen atom is much larger than that at the carbonyl carbon atom.³⁷ Therefore, maximum overlap in the LSOMO_{CA*}-HOMO_{alkene} interaction predicts the preferential bonding of the C_β -C_{CA} as is actually found in the oxetane product **27**.



27	X = H	R = CO ₂ Et
28	X = <i>m</i> -NO ₂	R = CO ₂ Et
29	X = H	R = COMe
30	X = H	R = COPh
31	X = F	R = COPh

Photoinduced cycloaddition of CA with ethyl 3-nitrocinnamates (*E*- and *Z-23*), benzalacetones (*E*- and *Z-24*), chalcones (*E*- and *Z-25*) and *E*-4-fluoroalchalcone (*E-26*) were carried out under the same conditions. In all cases, photolyses in benzene and in acetonitrile led to the formation of the corresponding *trans*-oxetane products **27-31** in high yield (Table 2) and resulted in the one-way *Z*-to-*E* isomerization of the alkenes.

Spectroscopic measurements showed that these alkenes did not form strongly absorbing charge-transfer complexes with CA, and addition of the alkenes in the small excess as used in the photolyses to a CA solution did not cause any significant change of the UV spectrum in the region $\lambda > 400$ nm.

Compounds **22-26** are all electron-deficient alkenes. The ionization potentials for *E-22* and *E-25* are 8.55^{38a} and 8.59 eV,^{38b} respectively. Their oxidation potentials were estimated from the ionization-potential data by the empirical eqn. (3)^{38c} to be 2.39 and 2.42 V, respectively. The ΔG_{ET} -values for electron

$$E = (0.71 I_p - 3.68) \text{ V (SCE)} \quad (3)$$

transfer with ³CA* in benzene and in acetonitrile as estimated

Table 2 Photoinduced cycloaddition reactions of CA with α,β -unsaturated compounds **22–26**

Alkene	Solvent	Reaction scale ^a (mmol)		Irrad. time (t/h)	Conversion (%)	Product (yield) ^b (%)
		CA	Alkene			
<i>E</i> - 22	C ₆ H ₆	4.1	11.8	5	97	27 (83)
<i>E</i> - 22	MeCN	2.5	5.4	7	99	27 (89)
<i>E</i> - 22	C ₆ H ₆	1.0	2.0	10	83	27 (89)
<i>E</i> - 22	MeCN	1.1	2.2	10	93	27 (89)
<i>E</i> - 23	C ₆ H ₆	4.9	11.3	15	92	28 (72)
<i>E</i> - 23	MeCN	4.3	9.5	17	91	28 (78)
<i>E</i> - 23	C ₆ H ₆	1.0	2.0	17	48	28 (88)
<i>E</i> - 23	MeCN	1.0	2.0	17	76	28 (83)
<i>E</i> - 24	C ₆ H ₆	4.9	11.1	10	100	29 (80)
<i>E</i> - 24	MeCN	4.9	11.1	11	100	29 (81)
<i>E</i> - 24	C ₆ H ₆	2.4	6.6	7	100	29 (88)
<i>E</i> - 24	MeCN	1.2	3.7	7	100	29 (88)
<i>E</i> - 25	C ₆ H ₆	3.7	7.9	9	91	30 (89)
<i>E</i> - 25	MeCN	4.1	8.7	11	89	30 (90)
<i>E</i> - 25	C ₆ H ₆	0.9	2.1	9	98	30 (81)
<i>E</i> - 25	MeCN	0.8	2.1	9	98	30 (87)

^a CA and the alkene were dissolved in benzene (100 cm³) or in acetonitrile (50 cm³) for photolysis. ^b Based on consumed CA.

by Weller equations (1) and (2) are 15.5 and 5.3 kcal mol⁻¹, respectively, for *E*-**22**, and 16.1 and 6.0 kcal mol⁻¹, respectively, for *E*-**25**. These large positive ΔG_{ET} -values preclude the possibility of SET process involvement in these photocycloaddition reactions. In agreement with this, in the photoreactions of CA with *E*-**25** and *E*-**26**, the formation of oxetane products **30** and **31** were found not to be interrupted by oxygen purging during the reactions, either in benzene or in acetonitrile. The lack of both solvent polarity and oxygen effect in the reaction provided additional support for the absence of SET process involvement in the reactions. CA has a low $\pi\pi^*$ triplet state.³⁷ In accord with this, in photoinduced reactions of CA with alkenes of high oxidation potential, the reaction site has invariably been found to be at the ethene double bond of CA to give cyclobutane products.^{3,12,13} Oxetane product formation in photoinduced reactions of carbonyl compounds of lowest $\pi\pi^*$ triplet state with alkenes is usually inefficient⁴⁰ and occurs only when there is dominant charge-transfer interaction between the carbonyl compound and the alkenes.⁴¹ The latter situation is also exemplified by the photoaddition reactions of CA with the stilbene derivatives **1–6** and other electron-rich alkenes cited above.^{14,15,33} It is also noted that formation of oxetanes from electron-deficient alkenes have mainly been reported in reactions with singlet excited $n\pi^*$ carbonyl compounds.⁴² It is therefore rather unexpected that oxetane products were exclusively formed in the photoreactions of CA with compounds **22–26** which have large positive ΔG_{ET} -values for SET with ³CA*. Accordingly, these reactions disclosed the complexity of the factors that influence the selectivity in reaction site in photoreactions of CA with alkenes. Although a thorough explanation for the reaction site found in the photoinduced cycloadditions of CA with compounds **22–26** cannot be given at this time, steric hindrance for the addition of the alkene toward the dichloro-substituted ethene double bond in CA may be an important factor in driving the reaction site from the ethene double bond to the less hindered carbonyl double bond in CA.

The lack of stereospecificity in the photocycloadditions and the concomitant *Z/E* isomerizations of the alkenes again need the formation of a triplet diradical intermediate such as **21** in order to be accounted for.

In summary, photoinduced reactions of CA with mono-substituted stilbenes **1–6** led to the simultaneous formation of two regioisomeric oxetane products in high total yield, and

resulted in one-way *Z*-to-*E* isomerization of the alkenes via SET mechanisms. The unexpected exclusive formation of oxetane product in high yield for substrates **22–26** shows that, in spite of the fact that CA has a low $\pi\pi^*$ triplet state, spirooxetane products can also be exclusively formed in photocycloadditions of CA with electron-deficient alkenes for which electron transfer with ³CA* is energetically unfavourable. Therefore the electronic configuration of the *T*₁ state of CA, the oxidation potential of the alkenes, and the steric effect on the cycloadditions are among the factors that decide the reaction mode. Although further research on the scope of the reaction and the mechanistic origin of the different reaction modes is still needed, the good yield of the spirooxetane products **27–31** showed that photoinduced cycloadditions of CA with alkenes may be used as versatile synthetic methods for either spirooxetanes or for cyclobutanes, respectively, depending on the structure and the oxidation potential of the alkenes used.

Experimental

M.p.s were measured on a microscopic apparatus and are uncorrected. ¹H NMR were recorded on a JEOL PMX-60 SI spectrometer at 60 MHz or a Bruker AC-500 spectrometer at 500 MHz with SiMe₄ as internal standard and CDCl₃ as solvent unless otherwise stated. *J* Values are given in Hz. IR spectra were taken with a Shimadzu IR 408 or a Nicolet 5DX FT-IR spectrometer; KBr pellets for solid samples, thin films for liquid samples. Mass spectra were recorded with a VG ZAB-MS spectrometer. UV-VIS spectra were run on a Shimadzu UV-240 spectrophotometer. For analytical photolyses, the quantitative analyses of the photolysates were performed on a Varian SY-5000 HPLC instrument with an MCH-5 or an MCH-N-Cap reverse-phase column (15 cm) and with methanol-water mixtures as eluent.

Acetonitrile (CP grade) was refluxed with phosphorus pentoxide and distilled, then was refluxed with anhydrous potassium carbonate and redistilled. Benzene (AR grade) was dried with sodium before use. CA (CP grade) was recrystallized twice from acetone. *E*-**1** (CP grade) was recrystallized twice from ethanol. *Z*-**1** was prepared from *E*-**1** by photoisomerization and was purified by repeated distillation under reduced pressure. HPLC analyses showed that they were 100% pure and were not contaminated by the other isomer. All the other *Z*-stilbenes were prepared by literature procedures.⁴³ The

corresponding *E*-stilbenes were prepared from the *Z*-isomers by being heated with a catalytic amount of iodine at a temperature higher than the m.p. of the *E*-isomer for 0.5 h and subsequent chromatographic separation of the mixture. *E*-2-*E*-5 and *Z*-2-*Z*-5 were similarly purified by repeated recrystallization or distillation before use and their purity was monitored by HPLC. Diphenylvinylene carbonate **6** was prepared by the literature procedure.⁴⁴ Compounds *Z*-22,⁴⁵ *Z*-23,⁴⁵ *Z*-24⁴⁶ and *Z*-25,⁴⁷ were prepared from the corresponding *E*-isomers.

Photo-CIDNP Measurements.—Photo-CIDNP measurements were performed on a Bruker AC 80 MHz NMR spectrometer. A solution of CA (0.02 mol dm⁻¹) and the alkene (0.02 mol dm⁻³) in CD₃CN was purged with dry argon for 4 min to remove dissolved oxygen. The ¹H NMR spectrum of the sample solution was then taken before, during, and after irradiation. A glass filter which cuts off light with λ < 310 nm was used in the irradiation.

General Procedures for Preparative Photolysis.—The light source was a medium-pressure mercury lamp (500 W) in a cooling water jacket which was further surrounded by a layer of filter solution (10% aq. sodium nitrite, 1 cm thickness, λ > 400 nm). The solution of CA and the corresponding alkene was purged with dry argon 0.5 h prior to and throughout the irradiation. The reactions were monitored by HPLC and TLC.

Photolyses of CA with Stilbene Derivatives.—In the preparative photolyses, reaction scales were as follows. For *E*-1, CA (6.2 mmol) and *E*-1 (12.5 mmol) in benzene (125 cm³). For *Z*-1, CA (0.8 mmol) and *Z*-1 (1.6 mmol) in benzene (16 cm³). For *E*-2, *Z*-2, *E*-3, *Z*-3, *E*-4 and *Z*-4, CA (2.5 mmol) and the alkene (3 mmol) in benzene (50 cm³). For **6**, CA (5 mmol) and **6** (7 mmol) in benzene (100 cm³). After the photolysis, the solution was concentrated under reduced pressure to about one-tenth of the original volume, light petroleum (boiling range 60–90 °C) was added and the mixture was kept overnight. The solid product was filtered off, washed with cold benzene, and purified by recrystallization from chloroform–light petroleum (60–90 °C). For the monosubstituted stilbenes **2**–**4**, two regioisomers were obtained as a mixture. The relative ratio of the two regioisomers was determined by 500 MHz ¹H NMR measurements. Some of the isomers (**9** and **12**) could be isolated from the isomeric mixture by stepwise crystallization from chloroform–light petroleum (60–90 °C).

As a typical example, a solution of CA (615 mg, 2.5 mmol) and *Z*-4 (582 mg, 3 mmol) in benzene (50 cm³) was photolysed for 6 h to lead to the total conversion of CA. Concentration of the solution under reduced pressure followed by addition of light petroleum gave the crude solid product (930 mg), which was recrystallized from chloroform–light petroleum to afford a mixture of compounds **12** and **13** (885 mg, 80%).

In the analytical runs, a solution of CA (0.02 mol dm⁻³) and the alkene (0.04 mol dm⁻³) in benzene or in acetonitrile was photolysed for the time indicated in Table 1 and was then subjected to quantitative analysis by HPLC.

5,6,8,9-Tetrachloro-2,3-diphenyl-1-oxaspiro[3.5]nona-5,8-dien-7-one 7. M.p. 150–151 °C (decomp.) (lit.,^{16a} 150 °C); $\nu_{\max}/\text{cm}^{-1}$ 1686, 1604, 1575, 1495, 1126, 1102, 968, 773 and 698; δ (60 MHz) 5.00 (1 H, d, *J* 8.8), 6.72 (1 H, d, *J* 8.8) and 7.3 (10 H, m, ArH); *m/z* 318 (0.4), 180 (base) and 106 (8.1) (Found: C, 56.5; H, 3.1. Calc. for C₂₀H₁₂Cl₄O₂: C, 56.37; H, 2.84%).

5,6,8,9-Tetrachloro-2-(4-chlorophenyl)-3-phenyl-1-oxaspiro[3.5]nona-5,8-dien-7-one 8. Could not be fully separated from isomer **9**; δ (60 MHz) 4.93 (1 H, d, *J* 8.7), 6.68 (1 H, d, *J* 8.7) and 7.28 (9 H, m, ArH); *m/z* 318 (M⁺ – ClC₆H₄CHO).

5,6,8,9-Tetrachloro-3-(4-chlorophenyl)-2-phenyl-1-oxaspiro[3.5]nona-5,8-dien-7-one 9. M.p. 144–146 °C (decomp.); λ_{\max}

(CCl₄)/nm 264 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 19 200) and 295 (13 800); $\nu_{\max}/\text{cm}^{-1}$ 1671, 1600, 1570, 1492, 1278, 1120, 1100, 983, 958, 810, 748, 737 and 695; δ (500 MHz) 4.95 (1 H, d, *J* 8.7), 6.67 (1 H, d, *J* 8.7) and 7.29 (9 H, m, ArH); *m/z* 352 (2.2, M⁺ – C₆H₅CHO), 318 (1.0), 284 (4.3), 244 (20.3) and 214 (base) (Found: C, 52.5; H, 2.7. C₂₀H₁₁Cl₅O₂ requires C, 52.18; H, 2.41%).

5,6,8,9-Tetrachloro-2-(3-chlorophenyl)-3-phenyl-1-oxaspiro[3.5]nona-5,8-dien-7-one 10. Not fully separated from isomer **11**; δ (60 MHz) 4.93 (1 H, d, *J* 8.6), 6.69 (1 H, d, *J* 8.6) and 7.27 (9 H, m, ArH); *m/z* 318 (M⁺ – ClC₆H₄CHO).

5,6,8,9-Tetrachloro-3-(3-chlorophenyl)-2-phenyl-1-oxaspiro[3.5]nona-5,8-dien-7-one 11. Not fully separated from isomer **10**; δ (60 MHz) 4.99 (1 H, d, *J* 8.6), 6.68 (1 H, d, *J* 8.6) and 7.28 (9 H, m, ArH); *m/z* 352 (M⁺ – C₆H₅CHO).

5,6,8,9-Tetrachloro-3-phenyl-2-(p-tolyl)-1-oxaspiro[3.5]nona-5,8-dien-7-one 12. M.p. 162–164 °C (decomp.); $\lambda_{\max}(\text{CCl}_4)/\text{nm}$ 264 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 19 200) and 292 (12 900); $\nu_{\max}/\text{cm}^{-1}$ 1672, 1597, 1567, 1513, 1490, 1446, 1362, 1280, 1117, 1100, 950, 828, 803, 746, 726 and 696; δ (500 MHz) 2.39 (3 H, s, Me), 4.99 (1 H, d, *J* 8.8), 6.68 (1 H, d, *J* 8.8) and 7.27 (9 H, m, ArH); *m/z* 318 (3.3, M⁺ – CH₃C₆H₄CHO), 244 (2.8) and 194 (base) (Found: C, 57.2; H, 3.15. C₂₁H₁₄Cl₄O₂ requires C, 57.30; H, 3.21%).

5,6,8,9-Tetrachloro-2-phenyl-3-(p-tolyl)-1-oxaspiro[3.5]nona-5,8-dien-7-one 13. Not fully separated from isomer **12**; δ (60 MHz) 2.34 (3 H, s, Me), 4.93 (1 H, d, *J* 8.8), 6.70 (1 H, d, *J* 8.8) and 7.26 (9 H, m, ArH); *m/z* 332 (M⁺ – C₆H₅CHO).

2,3,5,6-Tetrachloro-1',5'-diphenylspiro(cyclohexa-2,5-diene-1,7'-2',4',6'-trioxabicyclo[3.2.0]heptane)-3',4'-dione 14. M.p. 136–138 °C (decomp.); $\nu_{\max}/\text{cm}^{-1}$ 1823, 1675, 1597, 1560, 1490, 1448, 1304, 1288, 1215, 1112, 772, 745, 730 and 692; δ (60 MHz) 6.83–7.97 (10 H, m); *m/z* 244 (32), 238 (95) and 165 (base) (Found: C, 52.05; H, 2.2. C₁₂H₁₀Cl₅O₄ requires C, 52.10; H, 2.08%).

Photolysis of CA with α,β -Unsaturated Compounds 22–26.—The reaction conditions are shown in Table 2. After photolysis, the solution was concentrated under reduced pressure and the residue was subjected to chromatographic separation on a silica gel column with light petroleum (60–90 °C)–ethyl acetate mixtures as eluent. The yields of the products are also in Table 2.

Ethyl 5,6,8,9-tetrachloro-7-oxo-3-phenyl-1-oxaspiro[3.5]nona-5,8-diene-2-carboxylate 27. M.p. 137–137.5 °C; $\nu_{\max}/\text{cm}^{-1}$ 1729, 1689, 1602, 1576, 1498, 1450, 1378, 1326, 1284, 1103, 1042, 1016, 982, 840, 738 and 700; δ (60 MHz) 1.40 (3 H, t, Me), 4.37 (2 H, q, CH₂), 5.13 (1 H, d, *J* 8), 5.86 (1 H, d, *J* 8) and 6.72–7.5 (5 H, m, ArH); *m/z* 318 (4.5), 283 (10.4), 176 (28.9) and 131 (base) (Found: C, 48.5; H, 3.2. C₁₇H₁₂Cl₄O₄ requires 48.47; H, 2.87%).

Ethyl 5,6,8,9-tetrachloro-3-(3-nitrophenyl)-7-oxo-1-oxaspiro[3.5]nona-5,8-diene-2-carboxylate 28. M.p. 163–165 °C; $\nu_{\max}/\text{cm}^{-1}$ 1737, 1688, 1581, 1532, 1360, 1278, 1261, 1204, 1102, 1050, 1010, 960, 868, 750, 736, 720 and 680; δ (60 MHz) 1.42 (3 H, t, Me), 4.45 (2 H, q, CH₂), 5.20 (1 H, *J* 8.2), 5.86 (1 H, *J* 8.2) and 7.2–8.2 (4 H, m, ArH); *m/z* 363 (1.6, M⁺ – OHCCO₂C₂H₅), 328 (1.2), 244 (23.7), 207 (33) and 176 (base) (Found: C, 43.8; H, 2.6. C₁₇H₁₁Cl₄NO₆ requires C, 43.71; H, 2.37%).

2-Acetyl-5,6,8,9-tetrachloro-3-phenyl-1-oxaspiro[3.5]nona-5,8-dien-7-one 29. M.p. 148–149 °C; $\nu_{\max}/\text{cm}^{-1}$ 1709, 1682, 1608, 1576, 1500, 1452, 1362, 1276, 1256, 1130, 1102, 1040, 978, 822, 768, 738, 701 and 690; δ (60 MHz) 2.50 (3 H, s, Me), 4.93 (1 H, d, *J* 8.0), 5.67 (1 H, *J* 8.0) and 7.28 (5 H, m, ArH); *m/z* 318 (3.5), 283 (15.2), 2.44 (12.2), 146 (48.6) and 103 (base) (Found: C, 49.2; H, 2.8. C₁₆H₁₀Cl₄O₃ requires C, 49.02; H, 2.57%).

2-Benzoyl-5,6,8,9-tetrachloro-3-phenyl-1-oxaspiro[3.5]nona-5,8-dien-7-one 30. M.p. 176–178 °C; $\lambda_{\max}(\text{CCl}_4)/\text{nm}$ 265 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 17 300) and 291 (7600); $\nu_{\max}/\text{cm}^{-1}$ 1677, 1598, 1575, 1450, 1261, 1252, 1215, 1141, 1105, 968, 951, 873, 749, 732 and 699; δ [60 MHz; (CD₃)₂SO] 5.25 (1 H, d, *J* 8.1),

5.76 (1 H, d, *J* 8.1) and 7.20–8.20 (10 H, m, ArH); *m/z* 244 (20.1), 208 (67.8), 131 (41.9), 103 (45.1) and 77 (base) (Found: C, 55.65; H, 2.6. C₂₁H₁₂Cl₄O₃ requires C, 55.54; H, 2.66%).

2-Benzoyl-5,6,8,9-tetrachloro-3-(4-fluorophenyl)-1-oxaspiro-[3.5]nona-5,8-dien-7-one **31**. M.p. 300 °C (decomp.); $\nu_{\max}/\text{cm}^{-1}$ 1690, 1601, 1577, 1512, 1451, 1401, 1229, 1110, 960, 839, 734 and 694; δ (500 MHz; CD₃CN) 5.47 (1 H, d, *J* 10.2), 6.65 (1 H, d, *J* 10.2) and 6.80–7.90 (9 H, m, ArH); *m/z* 435 (3.6), 244 (33.9), 226 (96.7) and 105 (base) (Found: C, 53.1; H, 2.35. C₂₁H₁₁Cl₄FO₃ requires C, 53.34; H, 2.34%).

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