An Extremely Short-lived 1,4-Biradical as Intermediate in the Photocycloaddition Reactions of Triplet State Aromatic Thiones with Allenes

Johan Kamphuis and Hendrik J. T. Bos
Department of Organic Chemistry, State University Utrecht Croesestraat 79, 3532 AD Utrecht, The Netherlands
Robert J. Visser, Bert H. Huizer, and Cyril A. G. O. Varma*
Department of Chemistry, State University of Leyden, Gorlaeus Laboratories, P.O. Box 9502, 2300 RA Leyden, The Netherlands

The photochemical reaction of xanthene-9-thione, thiobenzophenones, and thioxanthene-9-thione with allenes has been studied by initiating the reaction with a 308 nm laser flash and by following transient u.v.–visible optical absorptions on a nanosecond time scale. In the wavelength range $320 < \lambda < 800$ nm there is only a transient absorption arising from the thione in its lowest triplet state $T_1(n\pi^*)$. The rate constant k_a for quenching of the thione in this state by allenes is determined from Stern–Volmer plots. A 1,4-biradical which appears as a reaction intermediate could be scavenged with *NN'*-dimethyl-4,4'-bipyridinium dichloride (methyl viologen, MV). The yield of the methyl viologen radical cation MVRC resulting from scavenging has been determined as a function of the concentration of MV. A lifetime of 90 ps follows from this for the 1,4-biradical (**8**). The short lifetime is attributed to a large spin density on the sulphur atom from both unpaired electrons, causing efficient local spin–orbit coupling. Both the logarithm of the rate constant k_t for the disappearance of the aromatic thione in the thermal reaction with an allene and log k_a depend linearly on the ionization energy of the allene. Previous suggestions that the 1,4-biradical has a triplet state exciplex as precursor are rejected on the basis of the similarity of these relations and because of the fact that there is no difference in the effect on k_a and k_t caused by deuteriation of the allene.

Photochemical cycloaddition reactions of carbonyl compounds have been studied extensively since the turn of the century.[1] The Paterno–Büchi reaction,[2] which involves the addition of an olefin to an electronically excited ketone, is attracting much attention because of its synthetic utility and its mechanism.[3] It has been suggested that a 1,4-biradical appears as an intermediate in the reaction and that it has a charge-transfer exciplex as precursor.[4] However, most of the evidence for the exciplex and for the 1,4-biradical on the reaction pathway has been provided in indirect ways.[4,5] Laser flash techniques have been applied to detect biradicals in these reactions by scavenging them with methyl viologen (MV).[6] In the case of the photoreaction of benzophenone with dioxene a transient electronic absorption band could be assigned to a 1,4-biradical.[7]

Systematic research on photocycloaddition reactions of thiocarbonyl compounds with olefins and acetylenes has yielded much information on the regiospecifity and mechanism for thiocarbonyl compounds in their electronically excited singlet and triplet states. De Mayo *et al.*[8] and Ohno *et al.*[9] studied the photochemical cycloaddition reaction of thiones with alkenes and some acetylenes and concluded that an exciplex or a 1,4-biradical or both appear as reaction intermediates, although they did not observe these species directly. The (2 + 2) cycloaddition reactions of thiones, in their lowest electronically excited triplet state (T_1), with a number of acetylenes has been studied by Bos *et al.*[10] The explanation of the observed regioselectivity in these reactions has been based on the rule that the products are derived from the energetically most stable biradical. The photochemical reaction of (±)-bornane-2-thione with bis(methylthio)acetylene resulted in the formation of an α,β-unsaturated dithioester and a vinylic sulphide. The latter product is taken as evidence for intramolecular γ-hydrogen abstraction within a 1,4-biradical.[11]

Turro *et al.*[12] measured the rate constant for the quenching of the phosphorescence of aromatic thiones by several olefins and alkynes. From the observed linear dependence of the logarithm of the quenching rate constant on the ionization potential of the quencher, they conclude that the quenching leads to a complex with little charge-transfer character.

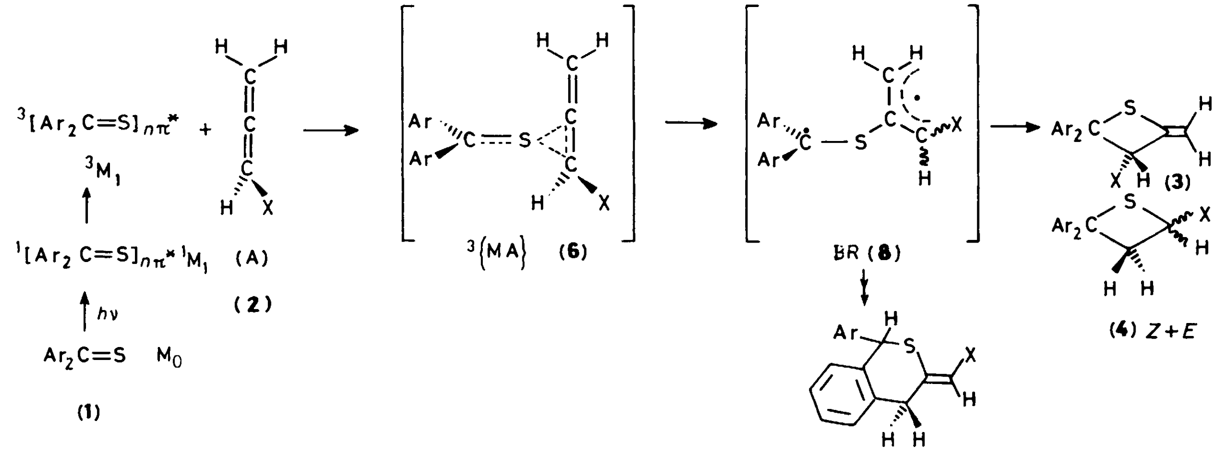
In this paper we deal with the question of whether an exciplex or a 1,4-biradical or both appear as intermediates in the photochemical reaction of aromatic thiones with allenes.

The cycloaddition products formed in the reaction have been identified previously.[13,14] The products are in general the thietanes (**3**) and (**4**) formed by (2 + 2) cycloaddition and sometimes also the thiopyran derivative (**5**) formed by (4 + 2) cycloaddition (see Scheme 1). The formation of these products might be explained on the basis of Scheme 1, in which the exciplex (**6**), the 1,4-biradical (**7**), and the allylic 1,4-biradical (**8**) are proposed as intermediates. The particular photochemical reactions studied are those of xanthene-9-thione (**1**), thiobenzophenones (**9a**—**l**), and thioxanthene-9-thione (**10**) with allenes (**2a**—**l**), acetylenes (**11a,b**) and butatriene (**12**).

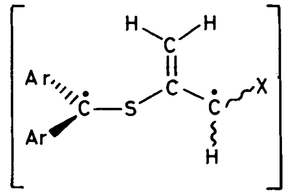
We report time-resolved spectroscopic measurements of the quenching of the lowest triplet state of thiones by allenes and of the rate of repopulation of the ground state of a thione after u.v. excitation. Although no transient absorptions from reaction intermediates other than the triplet-state thione could be observed, the scavenging of an intermediate by methyl viologen is observable. The kinetics of the scavenging reaction yield the lifetime of the intermediate. These results, put together with those obtained from studies of the thermal reactions of thiones with allenes, lead to the conclusion that the scavenged intermediate is a 1,4-biradical, which does not have an exciplex as its precursor.[15]

Experimental

The photochemical reactions were initiated by exciting the aromatic thione with a pulse from a XeCl excimer laser with wavelength 308 nm and duration *ca.* 10 ns full width at half maximum. The laser beam entered the cell with a rectangular



Scheme 1.



(7)

cross-section of *ca.* 2 cm width and 0.3 cm height. The number of laser photons entering the sample cell per pulse has been determined with a solution of the photochromic compound Aberchrome 540 in toluene as actinometer[16] in the cell. The actinometer solution in the sample cell was stirred between successive laser pulses. After a total of 30 laser pulses the change in optical density of the actinometer solution at 494 nm was measured on a spectrophotometer and then used to calculate the number of photons. At full intensity of the laser this number was equal to 5.4 × 10^{15} photons per pulse.

Laser-induced transient optical absorptions $OD_\lambda(t)$ of solutions were studied in a manner described previously.[17] The probing beam traversed the excited region of the solution lying immediately behind the entrance window for the laser beam. The probing beam with a cross-section of 0.3 × 0.3 cm was perpendicular to both the direction of the laser beam and the short axis of the cross-section of the laser beam and traversed a 2 cm long excited region. In all cases $OD_\lambda(t)$ could be fitted numerically to the form $OD_\lambda(t) = OD_\lambda(0) \exp(-kt)$.

In most cases the compounds were dissolved in CH_2Cl_2 and the concentration of aromatic thiones was such that they caused an optical density at 308 nm of *ca.* 1.0 over a pathlength of 1 cm. The samples were deoxygenated by passing nitrogen through the solution containing only the thione as solute until the lifetime of its triplet–triplet absorption did not change any more. Then the allene was introduced into the deoxygenated solution of the thione.

NN'-Dimethyl-4,4'-bipyridinium dichloride (methyl viologen, MV) has been used in solutions in CH_3CN–water (9:1 v/v), containing 9.4 × 10^{-5}M-xanthene-9-thione and 6.6 × 10^{-2}M-phenylallene, in order to scavenge the 1,4-biradical intermediate in the photocycloaddition reaction.[6] The concentrations of MV were varied between 2.9 × 10^{-5} and 1.8 × 10^{-4}M. The scavenging of the biradical resulted in the formation of the radical cation of methyl viologen (MVRC), which has an absorption band at 603 nm.

A solution of xanthene-9-thione in CH_2Cl_2 with an excess of the optically active allene (+)-PhCH=C=C(H)Me ($[\alpha]^{20}_{546}$ 32.3°, in CH_2Cl_2, 28% enantiomeric excess) was irradiated continuously at −80 °C with a broad spectral band of light between 540 and 640 nm. After completion of the reaction, the excess of allene and the cycloaddition products were separated by preparative h.p.l.c. [Kieselgel 60, eluant hexane–CH_2Cl_2 (3:1)]. The unconsumed allene retained its optical activity ($[\alpha^{20}_{546}]$ 31 ± 1° in CH_2Cl_2). The mixture of products dissolved in CH_2Cl_2 showed $[\alpha^{20}_{546}]$ 0.5 ± 0.2°.

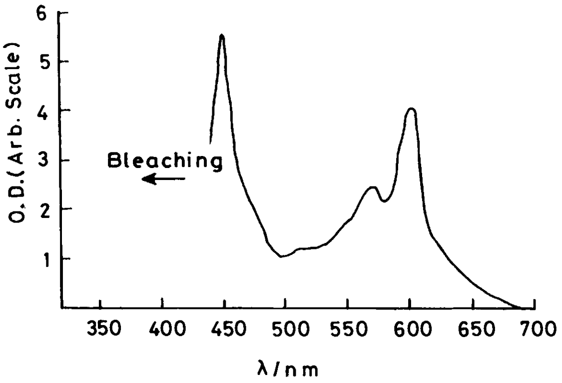


Figure 1. Transient optical absorption spectrum of xanthene-9-thione in CH_2Cl_2 attributed to T_1–T_n electronic transitions. The wavelength region where bleaching of S_0–S_n absorptions is observable is indicated

The syntheses of the starting compounds for the photoreactions have been published.[13,14] All solvents were of spectroscopic quality (Merck Uvasol).

Results and Discussion

In general thioketones have widely separated electronic absorption bands and therefore easily allow selective excitation of different excited electronic singlet states.[18] Bimolecular reactions of molecules in states above the first excited singlet state S_1, are rare, because the lifetime of these states is very short. However, thiones provide a clear example of intermolecular reactions from S_2.[18,19] Cycloaddition products are formed when allenes react with thiones, which have been excited into S_1.[13,14]

These reactions have been supposed to proceed *via* the lowest electronically excited triplet state.[13] Excitation of the thiones with the excimer laser brings them in their electronically excited state S_2.[20] It is therefore necessary to determine whether the cycloaddition products are then also only formed after encounter of an allene and a triplet state thione. To this end the laser-induced transient absorption of xanthene-9-thione is

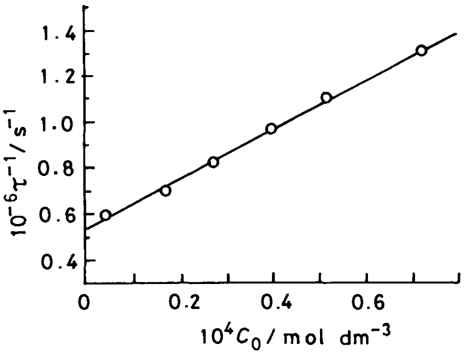


Figure 2. Effect of self-quenching on the lifetime τ of the lowest triplet state of xanthene-9-thione in toluene shown as a function of the initial concentration C_0 of the solute in its ground state

$$^3M + {}^3M \xrightarrow{k_d} {}^nM_2 \xrightarrow{k \approx \infty} {}^3M + M_0 \ (n = 1,3,5)$$

$$^3M + M_0 \xrightarrow{k_d} 2M_0$$

$$^3M \xrightarrow{1/\tau_T^0} M_0$$

Scheme 2.

studied as a function of the concentration of allene present in the solution. Figure 1 shows the transient absorption spectrum induced in a deoxygenated solution of xanthene-9-thione in CH_2Cl_2, which does not contain any of the allene. The decay is single exponentially and the lifetime is 750 ns, just as at other wavelengths in the spectrum. The lifetime of the spectrum in Figure 1 is equal to that determined for the phosphorescence at 680 nm of the same liquid solution excited with the same laser pulse. Therefore the transient spectrum has to be attributed to xanthene-9-thione in its lowest triplet state (T_1).

Both the transient absorption spectrum and the phosphorescence of the liquid solution may be quenched by allenes. Stern–Volmer plots fot the quenchings for instance by 3-methylbuta-1,2-diene (1,1-dimethylallene) yield quenching rate constants which are equal for both. From this we conclude that the first chemical step in the photocycloaddition reaction is the encounter of an allene with the thione in its triplet state T_1.

When the concentration C_0 of the thioketone, existing in the solution prior to the laser excitation, is increased the lifetime τ_T of the molecules arriving in the state T_1, as a result of laser excitation is reduced. Figure 2 shows that the Stern–Volmer plot of $1/\tau_T$ *versus* C_0 may be described by a relation of the form (1) where τ_T^0 is the triplet-state lifetime in the absence of self-

$$1/\tau_T = (1/\tau_T^0) + k_sC_0 \qquad (1)$$

quenching. If the mechanism of self-quenching involves only deactivation of triplet-state thione molecules (^3M) by ground-state thioketone molecules (M_0),[18] a linear dependence of $1/\tau_T$ on $(C_0 - C_T)$ rather than on C_0 is expected. The laser pulse creates an initial concentration of triplet molecules $C_T(0)$, which turns out to be as large as $C_0/3$ when determined by actinometry.

The observed behaviour has to be explained by introducing triplet–triplet annihilation as an additional quenching mechanism and by taking the rate constant for this process equal to that for the quenching by ground-state molecules (Scheme 2). Anticipating that this will be the case when the rate of both processes is limited by diffusion, the common rate constant is denoted by k_d.

Table 1. Rate constants for the self-quenching of xanthene-9-thione (**1**) in different solvents at 295 K

Solvent	k_s/dm^3 mol^{-1} s^{-1}
Benzene	11
Cyclohexene	9
Dichloromethane	12.1
Toluene	10.5
Acetonitrile	17

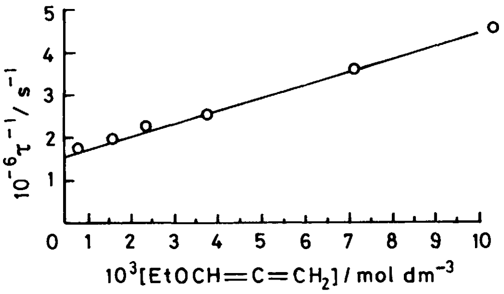


Figure 3. Stern–Volmer plot for the quenching of triplet state T_1 of xanthene-9-thione by $EtOCH=C=CH_2$

$$dC_T/dt = -k_d[C_T^2 + (C_0 - C_T)] - (1/\tau_T^0)C_T \qquad (2)$$

$$C_T(t) = C_T(0)\exp\{-[k_dC_0 + 1/\tau_T^0]t\} \qquad (3)$$

$$1/\tau_T = (1/\tau_T^0) + k_dC_0 \qquad (4)$$

If the triplet quantum yield Φ_T equals 1, Scheme 2 implies equation (2). The solution of equation (2) is (3) which leads to relationship (4). From equations (1) and (4) it is obvious that $k_s = k_d$. The slope of the line in Figure 2 (Table 1) yields k_s 1.05×10^{10} dm^3 mol^{-1} s^{-1}, which is to be interpreted as a diffusion-limited rate constant. The validity of equation (4) justifies the assumption $\Phi_T = 1$. A quantum yield $\Phi_T = 1$ resulting after exciting the second electronic singlet state S_2 means that both direct internal conversion from S_2 to S_0 and $S_2 \longrightarrow S_0$ fluorescence are negligible in the present context. The latter is in agreement with the quantum yield of 4×10^{-3} for the $S_2 \longrightarrow S_0$ fluorescence.[18,20]

No indication has been found for transient absorptions between 320 and 800 nm arising from products possibly formed due to self-quenching of the triplet state T_1 of xanthene-9-thione. However, this does not rule out the possibility that such products are formed.

Quenching of the lowest triplet state of the aromatic thiones by allenes, acetylenes, and a butatriene derivative follows normal Stern–Volmer behaviour (Figure 3). The rate constants k_a for quenching are given in Tables 2—5. The triplet-state quenching by allenes, acetylenes, and the butatriene derivative does not lead to new chemical species with optical absorptions between 320 and 800 nm, not even when their concentration C_Q is so high that the triplet lifetime τ_T is reduced by a factor of *ca.* 40 relative to its value at $C_Q = 0$, *e.g.* from 750 to 20 ns. In order to find out to what extent these quenchings of the triplet state T_1 of the thiones cause intersystem crossing to their ground state S_0, the repopulation of S_0 has been studied. The laser-induced reduction in the concentration of thione molecules in the S_0 state is observable as a decrease in the optical density of the solution at 430 nm, where only thione molecules in S_0 are absorbing. Figure 4 shows that the thione ground-state population recovers completely after the initial depletion, when the solution does not contain any of the mentioned triplet-state

Table 2. Rate constants for the quenching of triplet-state xanthene-9-thione by a butatriene, acetylenes, and allenes in dichloromethane and first ionization energy of the substrates

	Quencher	$10^{-8}\,k_a$/dm^3 mol^{-1} s^{-1}	$I_X(1)^a$/eV
(12)	$Me_2C{=}C{=}C{=}CHOMe$	36.4 ± 0.1	7.28[b]
(11a)	$MeSC{\equiv}CSMe$	4.17 ± 0.1	
(11b)	$Bu^tSC{\equiv}CSBu^t$	2.32 ± 0.006	
(2a)	$MeCH{=}C{=}CH_2$	0.177 ± 0.006	9.23[d]
(2b)	$Me_2C{=}C{=}CH_2$	1.25 ± 0.04	8.95[d]
(2c)	$Me_2C{=}C{=}CMe_2$	3.11 ± 0.1	8.47[d]
(2d)	$Bu^tCH{=}C{=}CH_2$	0.107 ± 0.003	9.32[d]
(2e)	$MeOCH{=}C{=}CH_2$	2.82 ± 0.09	8.73[d]
(2f)	$EtOCH{=}C{=}CH_2$	3.10 ± 0.09	8.47[c] (8.90 *trans*-isomer)
(2g)	$Bu^tOCH{=}C{=}CH_2$	5.59 ± 0.2	8.31[d]
(2h)	$MeSCH{=}C{=}CH_2$	6.06 ± 0.2	8.24[d]
(2i)	$EtSCH{=}C{=}CH_2$	7.58 ± 0.3	8.16[d]
(2j)	$Bu^tSCH{=}C{=}CH_2$	3.70 ± 0.1	8.32[d]
(2k)	$PhCH{=}C{=}CH_2$	2.02 ± 0.08	8.29[d]
(2l)	$PhCH{=}C{=}C(H)Ph$	6.66 ± 0.2	

[a] Adiabatic ionization energy ±0.03 eV. [b] ±3%. [c] R. G. Visser, Thesis, University of Utrecht, 1982. Value in parentheses = vertical ionization energy. [d] J. Kamphuis, C. W. Worrell, H. J. T. Bos, and W. Runge, to be published.

Table 3. Rate constants for the quenching of triplet-state thiones; xanthene-9-thione (**1**), thioxanthene-9-thione (**10**), and thiobenzophenone (**9a**) by phenylallene in dichloromethane at 295 K

Triplet excited state of	$10^{-8}\,k_a$/dm^3 mol^{-1} s^{-1}
(1)	2.03
(10)	0.402
(9a)	0.426

Table 4. Rate constants for the quenching of substituted thiobenzophenones $4\text{-}YC_6H_4CSC_6H_4Z\text{-}4$ (**9a—j**) by phenylallene in dichloromethane

	Substituent			
	Y	Z	$10^{-8}\,k_a$/dm^3 mol^{-1} s^{-1}	$10^9\tau_0{}^b$/s
a	H	H	0.426	1 021
b	Br	H	1.21	901
c	MeO	H	0.209	294
d	F	H	0.607	1 951
e	Cl	H	0.857	990
f	Ph	H	1.29	2 000
g	Me	H	0.324	886
h	MeO	MeO	0.415	364
i	NO_2	H	*a*	32
j	CN	H		73

[a] No quenching observed. [b] Calculated $1/\tau = 1/\tau_0 + k_s[\text{thione}]$.

Table 5. Rate constants for the quenching of triplet-state xanthene-9-thione (**1**) by ethoxyallene (**2f**) in five solvents

Solvent	$10^{-8}\,k_a$/dm^3 mol^{-1} s^{-1}
Iso-octane	10.4
Acetonitrile	9.09
Methanol	7.07
Benzene	5.13
Dichloromethane	3.10

quenchers (curve a) and that the recovery is only partial when the solution contains an allene (curve b). The rate constant for recovery of the S_0 population k_{rc} is equal to τ_T^{-1} in both cases. Curve b in Figure 4 rules out the possibility that quenching of the triplet state is followed by a slow reaction (*i.e.* with $k \ll \tau_T^{-1}$) of thione molecules in their ground state with some kind of species (*e.g.* allenic radicals) resulting from the quenching. If such a reaction occurs the recovered ground-state population must have a maximum as a function of time (curve c in Figure 4). The magnitude of the permanent bleaching $\text{O.D.}_{430}(\infty)$ of the optical density at 430 nm is a measure of the number of the triplet-state molecules which do not return to S_0. If the quenching reaction of quenchers Q like allenes (A) with thiones in their triplet state T_1 ($^3M_1$) prevents the latter completely from returning to their ground state M_0, Scheme 3 may be used to calculate the value of $\Delta\text{O.D.}_{430}(\infty)$. When calculated and observed values of $\Delta\text{O.D.}_{430}(\infty)$ are equal, Scheme 3 is to be considered valid. The calculation of $\Delta\text{O.D.}_{430}(\infty)$ requires two experimental steps. First the molar extinction coefficient $\varepsilon_T(\lambda)$ of the thione in state T_1 is determined at a suitable wavelength and this is used then to calculate $C_T(0)$ from observed values of $\text{O.D.}_\lambda(0)$. The full intensity of the laser was attenuated by a factor of 10 in the determination of $\varepsilon_T(\lambda)$, because then a region is reached where the $T_1 - T_n$ absorption varies linearly with laser intensity. The average concentration C_S of excited singlet molecules prepared by the laser pulse in the region traversed by the probe beam is

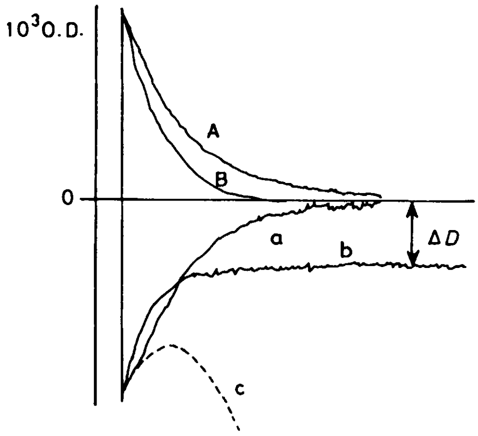


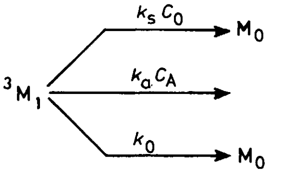
Figure 4. Decay of T_1—T_n absorption and recovery of ground-state absorption of xanthene-9-thione. Curves A and B show the decay of T_1, in the absence of an allene and in the presence of phenylallene, respectively. Curves a and b represent the recovery of the ground state in the absence and in the presence of phenylallene. Curve c shows an expected maximum in the ground-state absorption when products from the triplet quenching would react with triplet molecules. ΔD 0.08

Table 6. Rate constants for the quenching of triplet-state xanthene-9-thione by substituted phenylallenes in dichloromethane; first ionization energies of the arylallenes

Substituent	$10^{-8}k_a(X)$/dm^3 mol^{-1} s^{-1}	$I_X(1)$/eV
p-X		
OMe	4.90	7.93
Bu^t	2.39	8.25
Me	2.54	8.11
Cl	1.66	8.35
Br	1.40	8.50
H	2.02	8.32
m-X		
Me	2.29	8.19
Cl	1.28	8.43
CF$_3$	1.12	8.68
OMe	2.92	8.23

Table 7. Values for the bleaching ΔD and $\Delta D_{calc.}$ together with the phenylallene concentrations

10^3[Phenylallene]/mol dm^{-3}	$\Delta D_{calc.}$	$\Delta D_{exp.}$
8.16	0.154	0.168
4.08	0.130	0.131
2.46	0.101	0.109
1.64	0.085	0.080
0.82	0.066	0.062



Scheme 3.

calculated by using the measured input flux of laser photons and the optical density of the sample at 308 nm.

Since $\Phi_T = 1$, it follows that $C_T(0) = C_S$. Taking the 2.0 cm pathlength (d) of the probe beam into account, the value $\varepsilon_T(\lambda) = \text{O.D.}/2C_S$ is obtained. In this manner $\varepsilon_T(470)$ 2.85 × 10^3 dm^3 mol^{-1} cm^{-1} has been determined for the particular case of xanthene-9-thione. This value has been used to derive the value of $C_T(0)$ from O.D.$_{\cdot\lambda}(0)$ in the case when a high laser intensity is required to observe ground-state depletion.

Scheme 3 represents the decay of molecules $^3M_1$ in triplet state T_1 through monomolecular conversion into S_0, through self-quenching and quenching by for instance allenes. According to Scheme 3, the concentration ΔC_0 of thione molecules which reappear as ground-state molecules M_0, coming from $^3M_1$, is given by equation (5) where C_A is the concentration of

$$\Delta C_0 = C_T(0)[\tau_T(C_0, C_A)/\tau_T(C_0, 0)] \qquad (5)$$

allene and equation (6) holds. $\tau_T(C_0, 0)$ is obtained from

$$\tau_T(C_0, C_A) = (k_s C_0 + C_A + k_0)^{-1} \qquad (6)$$

equation (6) by setting $C_A = 0$.

The permanent ground-state bleaching is calculated finally as (7) where ε^0_{470} is the molar extinction coefficient of the thione

$$\Delta\text{O.D.}_{\cdot 430}(\infty) = \varepsilon^0_{470}\{C_0 - C_T(0) + \Delta C_0\}d \qquad (7)$$

in its ground state.

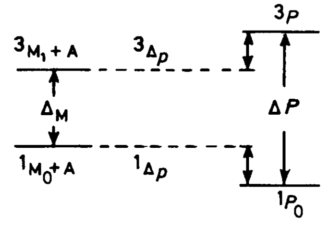


Figure 5. Diagram indicating energy gaps between singlet and triplet states of reactants M and A and of their photoproduct P

$$^3M_1 + A \xrightarrow{\Delta H > 0} {}^3P_1 \longrightarrow {}^1P_0$$

Scheme 4.

Table 7 shows the agreement between observed and calculated values of ΔO.D.$_{\cdot 430}(\infty)$ for the particular case of quenching of the lowest triplet state of xanthene-9-thione by phenylallene. The linear variation in Table 7 of ΔO.D.$_{\cdot 430}(\infty)$ with the concentration of phenylallene is consistent with an irreversible reaction of the quencher with the triplet-state thione. A question to be answered now is if the encounter of $^3M_1$ and A yields the several final products directly or *via* a sequence of steps. In each of the cases reported here, there are two or three different cycloaddition products P_i. If the products are formed directly, *i.e.* by formation of two bonds in a concerted fashion, they are born in an electronic triplet state. An initial triplet state of the products and therefore their direct formation from ^3M + A may be ruled out on the basis of the energy diagram in Figure 5.

It follows from the diagram that the separation $^3\Delta_P$ between the energy of the lowest triplet state ^3P of a product molecule and the energy of $^3M_1$ + A is given by equation (8). In the case

$$^3\Delta_P = \Delta P - {}^1\Delta_P + \Delta M \qquad (8)$$

of the photoreaction of xanthene-9-thione with phenylallene a calculation based on thermochemical data yields $^1\Delta_P$ *ca.* 79 kJ mol^{-1} and ΔM 176 kJ mol^{-1}.[18] The value of ΔP is approximately equal to or larger than the energy separation between the lowest electronic triplet state and the ground state of xanthene. From the observed highest frequency peak in the phosphorescense spectrum of xanthene in methylcyclohexane at 77 K it follows that $\Delta P \geqq 340$ kJ mol^{-1}. All this means that $^3\Delta_P > 85$ kJ mol^{-1} and that the concerted mechanism would imply thermal activation in the formation of P as in Scheme 4. However, the photochemical formation of P proceeds efficiently at temperatures as low as 193 K.[13] Apparently, the formation of $^1P_0$ does not require the thermal activation indicated in Scheme 4.

Having ruled out the direct formation of products P_i upon encounter of $^3M_1$ and A, it must be concluded that reaction intermediates are involved in the production of P_is. A conceivable mechanism is the formation of a triplet-state exciplex, yielding a vibrationally hot pair $^1M_0$ + A after intersystem crossing, which then leads with unit probability to the formation of two σ-bonds prior to vibrational relaxation. This mechanism therefore implies concerted cycloaddition upon intersystem crossing in the exciplex. An argument in favour of the formation of a triplet-state exciplex is that Figure 6 and Table 6 show that rate constant k_a satisfies a relation of the type (9) where k_a(H) and k_a(X) represent the rate constants k_a

$$\log\,[k_a(X)/k_a(H)] = \alpha + \beta I_X \qquad (9)$$

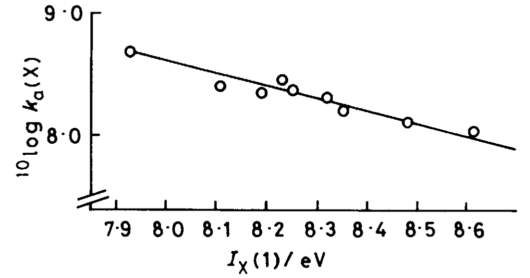


Figure 6. Linear relation between the rate constant $k_a(X)$ and the first ionization energy I_X of X-substituted phenylallenes in their photoreaction with xanthene-9-thione

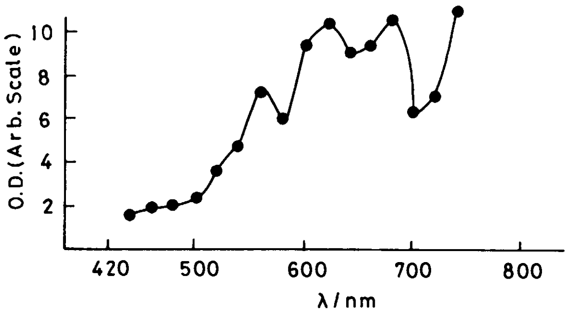


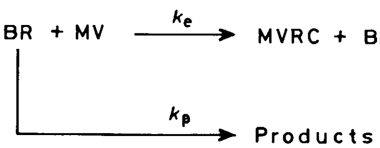
Figure 7. Transient spectrum attributed to the monopositive radical cation MVRC, arising after u.v. excitation of a solution containing xanthene-9-thione, phenylallene, and methyl viologen

respectively in the case of unsubstituted allene and in the case when the allene carries a substituent X on C(1) or on a *meta*- or *para*-position of phenylallene. The quantity I_X may be interpreted as the minimum energy needed to cause release of an electron from the π-system extending between C(1) and C(2) of the allene to which we refer as π-system 1. Its value is taken equal to the first ionization energy of the allene. Table 6 gives the values of $k_a(H)$ and $k_a(X)$. In equation (9) the value of the parameters are α 8.30 and β −1.01 (eV)$^{-1}$. The negative value of β implies the transfer of some electron charge from A to $^3M_1$ upon encounter.

The value of β is small compared with that encountered in the case of diffusion-controlled quenching reactions involving single-electron transfer, where β is equal to −17.0 (eV)$^{-1}$.[21] The validity of equation (9) could mean that the first reactive encounter of the triplet-state thione and the allene involves partial charge transfer from π-system 1 of the allene A to the thione and consequently the overlap of π-system 1 with certain molecular orbitals of M. Since the thione in state $^3M_1$ carries a hole in the *n* orbital on the sulphur atom, this would most likely be the MO orbital overlapping with π-system 1 in the reactive encounter. Based on the validity of equation (9) several authors[5,12] suggest that the reactive encounter leads to a triplet-state exciplex ^{3}(MA). In the present cases the exciplex would have the sulphur atom of the thione located somewhere in the space between C(1) and C(2) of the allene.

If the exciplex is not followed by other intermediates in the conversion to cycloaddition products, only a single product *viz.* (3) is to be expected, instead of the several products actually obtained. Therefore, other intermediates must be involved. Later on, other objections against the appearance of an exciplex in Scheme 1 will be encountered.

The nature of the cycloaddition products (Scheme 1) is such that they could have emerged from a 1,4-biradical as their



Scheme 5.

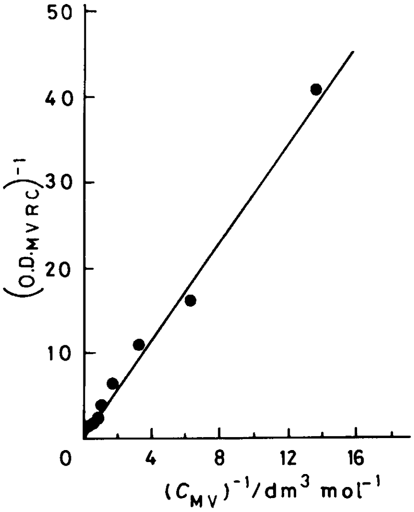


Figure 8. Inverse of the maximum height O.D.$_{\cdot MVRC}$ of the optical density due to MVRC, at a selected wavelength, plotted against the inverse of the concentration C_{MV} of methyl viologen

common precursor. The biradical should have the structure described in the Introduction. These types of 1,4-biradicals, but derived from the carbonyl analogues of the thiones, *e.g.* valerophenone, reveal efficient electron-transfer reactions with methyl viologen (MV).[6] The effect of methyl viologen in laser-irradiated solutions of xanthene-9-thione, of phenylallene, and of a mixture has been studied. A transient absorption band at *ca.* 603 nm due to the radical cation (MVRC) (Figure 7) can only be observed in solutions containing the reaction mixture and not in solutions containing either the thione or the allene alone. Obviously, MVRC is formed *via* electron transfer from a photoadduct of the thione and the allene to MV. It seems unlikely that an exciplex ^{3}(MA) could deliver the electrons to MV, since if it existed it would have a relatively minor charge-transfer character, meaning a small perturbation of its constituents ^{3}M and A, which are both unable to donate the electron. The photoadduct is therefore to be identified with a 1,4-biradical.

Note that no other transient absorptions of the reaction mixture other than those due to T_1—T_n transitions of the thione have been observed.

The 1,4-biradical may not have been observed either because it is not absorbing above 320 nm or because it is too short lived to be detected. The scavenging of the biradical BR by MV enables the determination of its lifetime τ_{BR}. This has been done by varying the concentration of MV in the reaction mixture and measuring the transient optical density O.D.$_{\cdot MVRC}$ due to MVRC, while the integrated laser pulse energy and the concentrations of the reagents are kept constant. According to Scheme 5 the quantum yield Φ_{MVRC} for formation of MVRC is given by equation (10) where Φ_{BR} is the quantum yield

$$\Phi_{MVRC} = \Phi_{BR}\tau_{BR}k_eC_{MV} \qquad (10)$$

of BR and τ_{BR} is given by equations (11). Equations (10) and (11)

$$\tau_{BR} = (k_p + k_e C_{MV})^{-1} \tag{11}$$

$$(OD)^{-1}_{MVRC} = \gamma(1 + k_p k_e^{-1} C_{MV}) \tag{12}$$

imply (12) where γ is constant as a function of C_{MV}.

Figure 6 shows that the maximum height of $O.D._{MVRC}$ at a selected wavelength satisfies equation (12). The ratio of the slope and the intercept of the straight line in Figure 6 is equal to k_p/k_e and amounts to k_p/k_e 2.2 mol dm^{-3}. A reasonable estimate of the magnitude of k_e here is to take it equal to its value obtained from the scavenging of BR derived from γ-methylvalerophenone, *i.e.* k_e 5×10^9 mol^{-1} dm^3 s^{-1}.[6] This leads to the estimated value k_p of 1.1×10^{10} s^{-1}. The lifetime τ^0_{BR} of BR in the absence of MV satisfies $\tau^0_{BR} = 1/k_p$ and therefore τ^0_{BR} is estimated to be 90 ps, which is about two and four orders of magnitude shorter than the lifetimes of respectively the oxygen analogue (**13**)[7] and the carbon analogue (**14**)[6] of BR.

Since biradical (**8**) does not lead back to the initial compounds, its lifetime τ^0_{BR} means that it leads unimolecularly to cyclization products with a total rate constant k_p of 1.1×10^{10} s^{-1}.

The differences in lifetimes of the biradicals (**8**), (**13**), and (**14**) may be a consequence of the difference in spin–orbit coupling, which drives the conversion of the triplet state of BR to a singlet state prior to or simultaneously with the ring closure.[22]

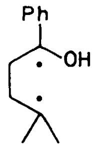
Apparently a large local spin–orbit coupling on the heavy sulphur atom must be effective. However, the heavy-atom effect is insufficient to explain the difference in lifetimes of (**8**) and its oxygen analogue. The spin density on the sulphur atom of the former has to be larger than on the oxygen atom of the latter. The required spin density on the sulphur atom has to be accumulated from both unpaired electrons, either during formation of BR or in its equilibrium conformation or during ring closure. In the first instance the formation may lead directly to a singlet state of BR, while in other instances intersystem crossing takes place respectively prior to and during ring closure.

Note that the rate at which ring closure occurs excludes the possibility of a dominant role of electron spin–nuclear spin hyperfine coupling in the required flipping of an electron spin.

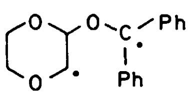
Further evidence for the participation of the biradical (**8**) in Scheme 1 is gained from the structure of the products obtained in the reaction of xanthene-9-thione with optically active (+)-1-phenylbuta-1,2-diene under continuous irradiation with light of 600 nm wavelength.[14] Using the butadiene in excess, non-optically active racemic mixtures of the cycloaddition products are obtained, while non-converted butadiene derivative shows no loss in rotatory power. This proves that the cycloaddition reaction involves a non-chiral intermediate such as the 1,4-biradical (**8**), and that the intermediate does not release the allene in a disproportionation reaction. The latter is consistent with the previous conclusion that a triplet state thione which encountered an allene never yields a ground-state thione molecule again.

Table 8. Rate constants for reaction of the triplet-state and ground-state thione (**1**) (k_a and k_t respectively)

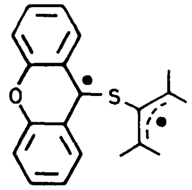
Allenes	$10^{-8}k_a$	$k_a(H)/k_a(D)$	$10^5 k_t$	$k_t(H)/k_t(D)$
$PhCH{=}C{=}CH_2$	2.02	0.90 ± 0.03	5.89	0.91 ± 0.03
$PhCD{=}C{=}CH_2$	2.24		6.49	
$H_3CC_6H_4CH{=}C{=}CH_2$	2.54	0.90 ± 0.03		
$H_3CC_6H_4CD{=}C{=}CH_2$	2.83			
$H_3COCH{=}C{=}CH_2$	2.82	1.20 ± 0.03	11.6	1.22 ± 0.04
$D_3COCH{=}C{=}CH_2$	2.35		9.5	
$Bu^tOCH{=}C{=}CH_2$	5.59	0.91 ± 0.02	29.8	0.90 ± 0.03
$Bu^tOCD{=}C{=}CH_2$	6.14		33.1	



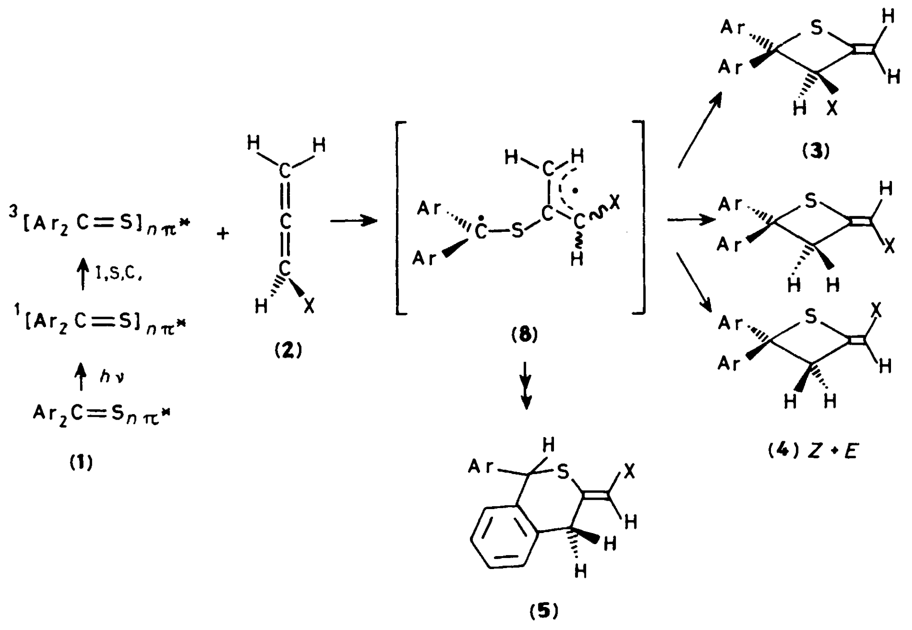
(**14**)
τ ≈ 100ns



(**13**)
τ≈6ns



(**8**)
τ ≈ 90ps



Scheme 6.

An effect of deuterium isotope substitution of the allene on the rate constant k_a for quenching of the triplet state of the thione has been found. Such an influence of deuterium labelling of triplet-state quenchers on the quenching rate constant has not been reported previously. The α-hydrogen of phenylallene ($PhCD{=}C{=}CH_2$) and of *p*-methylphenylallene ($H_3CC_6H_4CD{=}C{=}CH_2$) and the hydrogens of the methoxy group in methoxyallene ($D_3COCH{=}C{=}CH_2$) were substituted by deuterium. Table 8 presents the ratios of the rate constants $k_a(H)$ and $k_a(D)$ for quenching of triplet state xanthene-9-thione by the 'parent' and by the deuteriated allene respectively. The isotope effects in Table 8 are significant and reproducible. The magnitudes of the ratio $k_a(H)/k_a(D)$ indicate a secondary isotope effect associated with a change in hybridization of C(1) of the allenes (**2k** and **o**) and with a rotation of the OCH_3 group around the O–C(1) bond in (**2e**).[23] The observed isotope effect is difficult to fit within Scheme 1.

The major difficulty arises because an isotope effect on the rate of formation of the exciplex is not anticipated. There are two possibilities to get around the difficulty. Either a geometrical distortion of the allene in the exciplex is required or the biradical is formed directly upon encounter of the allene and the triplet-state thione. The first possibility may be rejected, because according to equation (9) exciplex formation will perturb the constituents only slightly and in contradiction to what is observed the transient T_1—T_n absorption band of the thione will not disappear entirely.

If the second possibility holds a new obstacle arises, namely to explain the validity of equation (9). However, the obstacle is removed by a comparison with the effect of deuteriation of the allene on the rate constant k_t for the disappearence of ground-state thione molecules in the thermal reaction with the allene.[24] For any particular kind of allene the ratio $k_t(H)/k_t(D)$ equals the ratio $k_a(H)/k_a(D)$, as indicated in Table 8. In addition a relation analogous to equation (9) holds also for the thermal reaction,[24] namely equation (13) with α_t 5.45 and β_t -0.65 $(eV)^{-1}$.

$$\log[k_t(X)/k_t(H)] = \alpha_t + \beta_t I_X \qquad (13)$$

Since no exciplex formation is involved in the thermal reactions BR must be formed directly in the photoreaction upon encounter of the allene with a triplet state thione. In other words Scheme 6 favoured.

Acknowledgements

This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO). We thank P. C. M. Weisenborn, P. J. M. van Kan, L. van Eijk, and P. A. Ruijter for assisting with the experiments, and Drs. C. J. Elsevier and P. Vermeer for providing the optically active allene.

References

1 D. R. Arnold, *Adv. Photochem.*, 1968, **6**, 301.
2 E. Paterno and G. Chieffy, *Gazz. Chim. Ital.*, 1909, **39**, 341.
3 G. Büchi, J. F. Kofron, E. Koller, and D. Rosenthal, *J. Am. Chem. Soc.*, 1956, **78**, 876.
4 R. A. Caldwell, G. W. Sovocool, and R. P. Gajewski, *J. Am. Chem. Soc.*, 1973, **95**, 2549.
5 I. E. Kochevar and P. J. Wagner, *J. Am. Chem. Soc.*, 1972, **94**, 3859.
6 J. C. Scaiano, *Acc. Chem. Res.*, 1982, **15**, 252.
7 S. C. Freilich and K. S. Peters, *J. Am. Chem. Soc.*, 1981, **103**, 6255.
8 P. de Mayo, *Acc. Chem. Res.*, 1976, **9**, 52.
9 A. Ohno, T. Koizumi, and Y. Ohnishi, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 2511.
10 A. C. Brouwer and H. J. T. Bos, *Recl. Trav. Chim. Pays-Bas*, 1984, **103**, 152.
11 A. C. Brouwer and H. J. T. Bos, *Recl. Trav. Chim. Pays-Bas*, 1983, **102**, 103.
12 N. J. Turro and V. Ramamurthy, *Tetrahedron Lett.*, 1976, 2423.
13 J. Kamphuis, J. G. Hupkes, R. G. Visser, and H. J. T. Bos, *Recl. Trav. Chim. Pays-Bas*, 1982, **101**, 114.
14 J. Kamphuis, P. D. J. Grootenhuis, A. P. Ruijter, R. G. Visser, and H. J. T. Bos, *Isr. J. Chem.*, 1985, **26**, 120.
15 J. Kamphuis, H. J. T. Bos, R. J. Visser, and C. A. G. O. Varma, Xth IUPAC Symposium on Photochemistry, Interlaken, 1984.
16 H. G. Heller and J. R. Langan, *J. Chem. Soc., Perkin Trans. 1*, 1981, 341.
17 C. A. G. O. Varma, F. L. Plantenga, A. H. Huizer, J. P. Zwart, Ph. Bergwerf, and J. P. M. van der Ploeg, *J. Photochem.*, 1984, **24**, 133.
18 R. P. Steer, *Rev. Chem. Intermed.*, 1981, **4**, 1.
19 N. J. Turro, V. Ramamurthy, W. Cherry, and F. Farneth, *Chem. Rev.*, 1978, **78**, 125.
20 M. Mahaney and J. R. Huber, *Chem. Phys. Lett.*, 1984, **105**, 395.
21 H. Knibbe, D. Rehm, and A. Weller, *Ber. Bunsenges. Phys. Chem.*, 1969, **73**, 839.
22 P. B. Dervan, 'Diradicals,' ed. W. C. T. Borden, Wiley, New York, 1982.
23 D. J. Pasto, P. F. Heid, and S. E. Warren, *J. Am. Chem. Soc.*, 1982, **104**, 3676.
24 J. Kamphuis, P. D. J. Grootenhuis, and H. J. T. Bos, *Tetrahedron Lett.*, 1983, **24**, 1101.

Received 20*th December* 1985; *Paper* 5/1381