Photochemistry of Dienones. Part 7.[1] On the Photosensitized Isomerization of (*E*)-β-Ionone and its Isomeric α-Pyran. Evidence for Exciplex Formation between the α-Pyran and Fluoren-9-one

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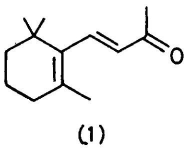
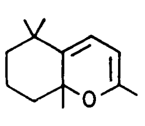
The photosensitized (*E*)-β-ionone (1)–α-pyran (2) isomerization in benzene as a solvent has been studied in some detail. For xanthone, benzophenone, and 1- and 2-acetonaphthone the (1) : (2) photostationary state (p.s.s.) ratio is 3.5 ± 0.2, whereas for the series of aromatic hydrocarbons studied and the ketones fluoren-9-one and benzanthrone it is 0.37 ± 0.07, both for a total substrate concentration of *ca.* 0.1M. The low {[(1)] : [(2)]} p.s.s. values observed with the second group of sensitizers are not the result of additional singlet sensitization. They are ascribed to a specific additional route of isomerization for the α-pyran *via* singlet exciplex formation which route is almost negligible for (*E*)-β-ionone. This explanation is in line with both the Stern–Volmer plots for the quenching of the fluorescence of fluoren-9-one by the α-pyran and by (*E*)-β-ionone [the quenching being far less with (*E*)-β-ionone than the α-pyran], and by the dependence of {[(1)]/[(2)]} p.s.s. on the total substrate concentration in the case of fluoren-9-one as a sensitizer. From the dependence of the photostationary state for the triplet photosensitized isomerization on the triplet energy of the sensitizer, it was concluded that the triplet energies of (*E*)-β-ionone and the isomeric α-pyran (2) are 54—56 and <54 kcal mol^{-1}, respectively.

In our effort to describe and understand the photochemistry of ionone-type compounds [1,2] we recently reported [2d] that (*E*)-β-ionone (1) upon direct 254 nm irradiation yields both the isomeric α-pyran (2) and (*Z*)-*retro*-γ-ionone (3), whereas the triplet-sensitized reaction only yields (2). It was suggested tentatively that the formation of (2) proceeds through the triplet state of (*E*)-β-ionone [*via* (*Z*)-β-ionone (4) as subsequent intermediate (*cf.* ref. 3)] and that (*Z*)-*retro*-γ-ionone is formed from the the excited singlet state. Direct irradiation of the α-pyran (2) yields (*Z*)-*retro*-γ-ionone (3) and (*E*)-β-ionone (1),[2d] whereas the sensitized reaction only yields (*E*)-β-ionone.[2d] Further, the photostationary ratios of (*E*)-β-ionone to α-pyran obtained using pyrene and 7*H*-benz[*de*]anthracen-7-one as sensitizers differed strongly from that obtained with benzophenone. The latter compound is known to be an efficient and specific triplet sensitizer and accordingly the sensitization with the former addenda may proceed differently.[4]



(1)



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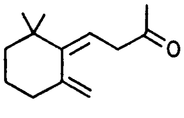

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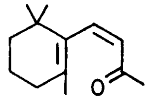
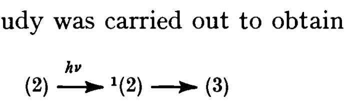


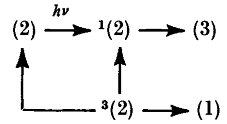
(4)

It was proposed [2d] that the photochemistry of (*E*)-β-ionone (1) and the isomeric α-pyran (2) proceeds by Schemes 1 and 2, respectively, in which the superscripts refer to the multiplicity of the excited states. It was not clear whether the conversion of triplet excited α-pyran [^{3}(2)] to its ground state proceeds *via* (*Z*)-β-ionone (4) or not. From the temperature dependence of the observed product formation upon irradiation of (*E*)-β-ionone, it appeared for the activation free energies that $\Delta G^\ddagger[^3(1) \rightarrow (2)] > \Delta G^\ddagger[^3(1) \rightarrow (1)]$, whereas as observed upon irradiation of the α-pyran, $\Delta G^\ddagger[^3(2) \rightarrow (2)] < \Delta G^\ddagger[^3(2) \rightarrow (1)]$.[2d] Thus the fate of ^{3}(1) differs from that of ^{3}(2). This infers that ^{3}(1) and ^{3}(2) are non-identical. Accordingly, the singlet excited states of (1) and (2) also have to be different.



Scheme 1

The present study was carried out to obtain more information on the mode of photosensitization in the (*E*)-β-ionone–α-pyran isomerization.



Scheme 2

RESULTS

Photosensitized Isomerization.—The results of the photosensitized (*E*)-β-ionone–α-pyran isomerization are shown in Table 1. The amount of (*Z*)-*retro*-γ-ionone formed is below the limit of detection which is 2% of the total amount of isomers. No photostationary (*E*)-β-ionone : α-pyran ratio could be obtained using biacetyl as sensitizer, since it photoreacts too rapidly with (*E*)-β-ionone.

The agreement between the photostationary ratios obtained upon starting with either isomer is satisfactory. They are further equal to the ratio of initial rates of disappearance of the two starting isomeric substrates under identical conditions.*

The photostationary ratio of (1) to (2) using fluoren-9-one as a sensitizer was found to vary with the sum of the concentrations of (1) and (2) (Table 2). Such a dependence could not be ascertained with the other sensitizers in view of the substantial light absorption by substrates (1) and (2) at concentrations >0.1.

TABLE 1

Photosensitized (*E*)-β-ionone–α-pyran isomerization in benzene [a]

Sensitizer	E_S (kcal mol^{-1})	E_T (kcal mol^{-1})	λ/nm	$[(E)$-β-ionone : α-pyran$]_{\text{p.s.s.}}$ [b]				$\dfrac{\{d[\alpha\text{-pyran}]/dt\}_{t=0}}{\{d[(E)\text{-}\beta\text{-ionone}/dt\}_{t=0}}$ [e]
				(*E*)-β-Ionone [c]	Time (h) [d]	α-Pyran [c]	Time (h) [d]	
Xanthone	77.6	74.2	366	4.2	8	3.6	12	3.7
Benzophenone	75.4	68.5	366	3.4	4	3.1	5	4.3
Fluorene	94.9	67.6	366	0.48	*f*			
Triphenylene	83.4	66.6	366	0.48	*f*			
Phenanthrene	82.8	62.2	366	0.30	*f*			
Naphthalene	92	60.9	366	0.39	*f*			
2-Acetonaphthone	77.7	59.3	366	3.1	*f*			
1-Acetonaphthone		56.4	366	3.7	5			
Fluoren-9-one	63.2	53.3	403	0.29	5			
(*E*)-Stilbene	94.2	50	366	0.31	*f*			
Pyrene	76.9	48.7	366	0.43	30	0.33	30	0.36
7*H*-Benz[*de*]anthracen-7-one		47	403	0.31	100	*g*		0.26

[a] The sensitizer and starting substrate concentrations were 1.0 and 0.10M, respectively. More than 90 and 94% of the irradiation was absorbed by the sensitizer upon starting with (*E*)-β-ionone and the α-pyran as substrate respectively. [b] The material balance, after the stationary ratio was reached, was >90%, but for those of xanthone [85% upon starting with (1)], pyrene [80% upon starting with (1)], and fluoren-9-one [70% upon starting with (1)]. [c] Starting material. [d] Irradiation time required to obtain the photostationary ratio. [e] Ratio of initial rates of disappearance of starting substrate. [f] Isomer ratio after 6 h of irradiation: probably, but not proven, to be the stationary state. [g] After 6 h of irradiation 4 ± 1% of (*E*)-β-ionone was found to be present.

TABLE 2

Variation of $\{[(1)]/[(2)]\}_{\text{p.s.s.}}$ for the fluoren-9-one sensitized λ 403 nm irradiation of (1) with the sum of the concentrations of (1) and (2) in benzene as solvent

$\{[1] + [2]\}_{\text{p.s.s.}}$	$\{[1]/[2]\}_{\text{p.s.s.}}$	Material balance at the initial stage of the p.s.s. (%)
0.98	4.31	98
0.73	3.05	97
0.46	2.23	95
0.21	1.37	84
0.095	0.73	76
0.071	0.29	71
0.06	0.12	69
0.03	0.03	60

Fluorescence Measurements.—The fluorescence of fluoren-9-one ($\lambda_{\text{excitation}}$ 430 nm) was found to be quenched by both the α-pyran and (*E*)-β-ionone, although only relatively weak by the latter.† The Stern–Volmer plots for the quenching of the fluorescence of fluoren-9-one by (2) and (1) (Figures 1 and 2, respectively) are linear. The quenching efficiency is strongly dependent on the solvent and increases in the order cyclohexane < benzene < dichloromethane < acetonitrile, *i.e.* in the order of increasing solvent polarity (*cf.* the values of the Dimroth solvent parameter in Table 3). A similar strong dependence on the solvent polarity was recently observed for the fluorescence quenching of fluoren-9-one by triethylamine.[6] The $k_q\tau$ values calculated from the Stern–Volmer plots of Figure 1 for the α-pyran (2) are almost the same as those for the fluorescence quenching of fluoren-9-one by triethylamine (Table 3). Therefore, it may well be that the α-pyran quenches singlet excited fluoren-9-one in the same way as triethylamine, *i.e.* by exciplex formation.

TABLE 3

Solvent dependence of $k_q\tau$ for the quenching of singlet excited fluoren-9-one by the α-pyran (2) and triethylamine

Solvent	$k_q\tau$		Dimroth solvent parameter [5a]
	α-Pyran (2)	Et_3N	
MeCN	162	141 [6a]	46.0
Me_2CO	96	93 [6b]	42.2
CH_2Cl_2	91		41.1
C_6H_6	24	22.4 [6a] 21 [6b]	34.5
cyclo-C_6H_{12}	10	6.0,[6a] 2.3 [6b]	31.2

Reduction and Ionisation Potentials.—In order to obtain more information on the probability of exciplex formation between fluoren-9-one on one hand and (2) and (1) on the other, the reduction ($E^{\frac{1}{2}}_{\text{red}}$) and ionisation (*I*) potentials of these compounds have been determined

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* Consider the triplet-photosensitized isomerization between A and B *via* the two different intermediates A* and B* each of which yields A and B in a given ratio, *viz.* ${}^{A*}k_A/{}^{A*}k_B$ and ${}^{B*}k_A/{}^{B*}k_B$, respectively; thus ${}^{A*}k_B$ is the rate constant of formation of B from A*. For the photostationary state (p.s.s.) it holds $d[A]/dt = 0$. Accordingly $-I_a\phi[A]_{\text{p.s.s.}} + I_a\phi[A]_{\text{p.s.s.}}{}^{A*}k_A/[{}^{A*}k_A + {}^{A*}k_B] + I_a\phi[B]_{\text{p.s.s.}}{}^{B*}k_A/[{}^{B*}k_A + {}^{B*}k_B] = 0$, in which *I* is the number of photons absorbed by the sensitizer and ϕ is the quantum yield for its intersystem crossing. It then follows for the stationary state ratio that $[A]_{\text{p.s.s.}}/[B]_{\text{p.s.s.}} = {}^{B*}k_A({}^{A*}k_A + {}^{A*}k_B)/{}^{A*}k_B({}^{A*}k_B + {}^{B*}k_B)$. The rates of initial substrate disappearance upon starting with A and B are ${}^{A*}v = I_a\phi{}^{A*}k_B/({}^{A*}k_A + {}^{A*}k_B)$ and ${}^{B*}v = I_a\phi{}^{B*}k_A/({}^{B*}k_A + {}^{B*}k_B)$. Thus ${}^{B*}v/{}^{A*}v = {}^{B*}k_A({}^{A*}k_A + {}^{A*}k_B)/{}^{A*}k_B({}^{B*}k_A + {}^{B*}k_B) = [A]_{\text{p.s.s.}}/[B]_{\text{p.s.s.}}$ (see before).

† No other emissions than the fluoren-9-one fluorescence were observed.

(Table 4). These data show that fluoren-9-one is a better electron acceptor than either (2) or (1), and that (2) is a better electron donor than (1). These orders thus explain both the quenching of singlet excited fluoren-9-one by (1) and (2) and their relative quenching ability. The rate constants k_q for quenching of singlet excited fluoren-9-one by (1) and (2) can be derived from the data of Table 4

$$\Delta G = E^{\frac{1}{2}}_{\mathrm{ox}}(\mathrm{donor}) - E^{\frac{1}{2}}_{\mathrm{red}}(\mathrm{acceptor}) - E_{\mathrm{singlet}}(\mathrm{acceptor}) - e_0^2/\varepsilon_a \quad (1)$$

in the following way. The ΔG for single electron transfer from a ground state donor to a photoexcited acceptor is given by equation (1).[7] The $E^{\frac{1}{2}}_{\mathrm{ox}}$(donor) has been calculated from the ionisation potential I using equation (2).[8] Taking E_{singlet} for fluoren-9-one to be 2.74 eV [5b] and e_0^2/ε_a for acetonitrile to be 0.06 eV [7] it follows that

$$I = 1.473\, E^{\frac{1}{2}}_{\mathrm{ox}} + 5.82\ \mathrm{eV} \quad (2)$$

the ΔG values for exciplex formation between singlet excited fluoren-9-one and the α-pyran and (*E*)-β-ionone are −11 and +4.8 kcal mol^{-1}, respectively. The k_q can now be calculated using equations (3) [7a] and (4),[9] where $\Delta G^{\ddagger}(0)$ (=2.4 kcal mol^{-1} [7a]) represents the free

$$\Delta G^{\ddagger} = \frac{\Delta G}{2} + \sqrt{\frac{(\Delta G)^2}{4} + [\Delta G^{\ddagger}(0)]} \quad (3)$$

$$1/k_q = 1/k_{\mathrm{diff}} + 10^{-11}\exp(\Delta G^{\ddagger}/RT) \quad (4)$$

enthalpy of activation for outersphere electron transfer when $\Delta G = 0$ (*e.g.* for electron exchange) and k_{diff} is the rate constant for a diffusion-controlled process. The latter was calculated from equation (5) (with p 2 500 and η 0.36 [5c]). The k_q values thus obtained for the α-pyran (2) and (*E*)-β-ionone with acetonitrile as a solvent are

$$k_{\mathrm{diff}} = 8RT/p\eta \quad (5)$$

1.44 × 10^{10} and 5.1 × 10^{6} l mol^{-1} s^{-1} respectively. The k_q values for acetonitrile as a solvent, obtained from our Stern–Volmer treatment by taking the singlet lifetime of fluoren-9-one in that solvent to be 18.5 ns,[10] are 0.92 × 10^{10} and 6.8 × 10^{8} l mol^{-1} respectively. The agreement is satisfactory for the α-pyran but poor for (*E*)-β-ionone. However, the large discrepancy between the k_q values for (*E*)-β-ionone obtained from the Stern–Volmer plot and from the reduction and oxidation potentials is of no importance for our evaluation of the photochemical data.

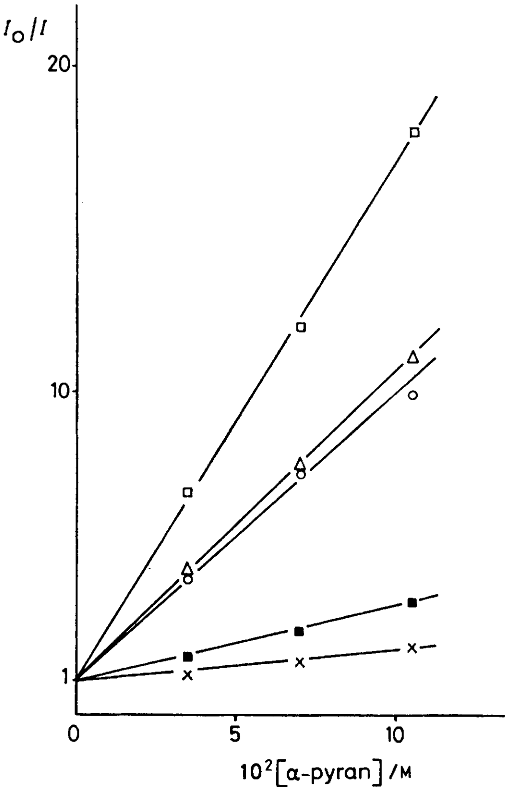


FIGURE 1 Stern–Volmer plots for the fluorescence quenching of fluoren-9-one by the α-pyran (2): □ solvent MeCN; △ Me$_2$CO; ○ CH$_2$Cl$_2$; ■ C$_6$H$_6$; × C$_6$H$_{12}$

TABLE 4

Reduction and oxidation potentials

Compound	$E^{\frac{1}{2}}_{\mathrm{red}}$/V	I/eV
Fluoren-9-one	−1.27	*a*
(*E*)-β-Ionone	−1.85	8.40
α-Pyran (2)	−1.75	7.39

[a] Not determined.

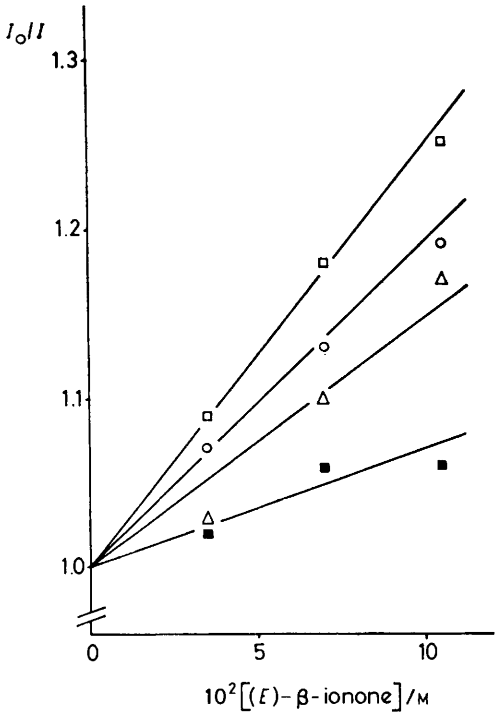


FIGURE 2 Stern–Volmer plots for the fluoren-9-one fluorescence quenching by (*E*)-β-ionone (1): □ solvent MeCN; △ Me$_2$CO; ○ CH$_2$Cl$_2$; ■ C$_6$H$_6$

DISCUSSION

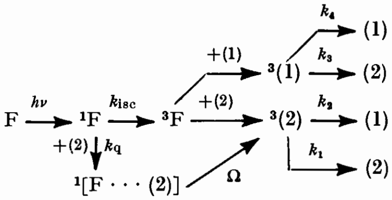
The $\{[(1)]/[(2)]\}_{\mathrm{p.s.s.}}$ data of Table 1 suggest that there are two types of photosensitizers. The first group, for which the p.s.s. ratios are 3.5 ± 0.2 comprises the ketones xanthone, benzophenone, and 1- and 2-acetonaphthone.

The other group, for which the p.s.s. ratios fall within the range 0.3—0.5, comprises the aromatic hydrocarbons and the ketones fluoren-9-one and 7*H*-benz[*de*]anthracen-7-one.

The triplet-sensitized isomerization of (*E*)-β-ionone to α-pyran proceeds *via* (*Z*)-β-ionone (4) as intermediate, which at room temperature rapidly converts to the α-pyran (2) (Scheme 2). This intermediate may also be excited by triplet-energy transfer. However, at room temperature the concentration of (*Z*)-β-ionone relative to that of α-pyran will be very small.[11] Further, considering that the energy transfer from the triplet sensitizers to (1), (2), and (4) will all be diffusion controlled, it follows that only a negligible small amount of triplet excited (*Z*)-β-ionone (4) will be involved in the triplet photosensitized (*E*)-β-ionone→α-pyran isomerization.

The low p.s.s. ratios observed on using sensitizers of the second group may be explained in terms of additional routes for sensitization,[12] *viz. via* singlet-energy transfer [13] and/or exciplex formation.[14] The first possibility, *i.e.* the singlet-energy transfer route, can be ruled out, as not even a trace of the singlet excited-state product, *viz.* (*Z*)-*retro*-γ-ionone, is formed in the photosensitized reactions. This leaves the exciplex mechanism as the possible explanation.

From our fluorescence measurements and data for the ionization and reduction potentials of fluoren-9-one, (1), and (2) (Table 4) it follows that the α-pyran may form an exciplex with singlet-excited fluoren-9-one and that this compound does it more readily than (*E*)-β-ionone. The dependence of the p.s.s. ratio on the (total) substrate concentration (Table 2) may be explained by considering that the singlet exciplex formation between fluoren-9-one (F) and (2) provides an additional route for formation of triplet-excited (2) (Scheme 3). The superscripts again denote the multiplicity of the excited state; Ω denotes the fraction of ^{1}[F · · · (2)] which yields ^{3}(2). The quenching of ^{1}F is over 50 times as fast by (2) than by (1), and the formation of ^{3}(1) *via* the exciplex of ^{1}F and (1) is therefore neglected.



SCHEME 3

The (1) : (2) p.s.s. ratio can now be calculated in the following way. The amount of (1) which disappears as a result of formation of ^{3}(1) is given by (6) on the assumption that the rate constants for energy transfer from ^{3}F to (1) and (2) are identical, where I_a is the number of photons absorbed by F. The amounts of (1) formed from ^{3}(1) and ^{3}(2) are given by (7) and (8), respectively. For the p.s.s. (6) = (7) + (8). Accordingly, $\{[(1)]/[(2)]\}_{\mathrm{p.s.s.}}$ is given by equation (9) [where $K = k_2(k_3 + k_4)/k_3(k_1 + k_2)$]. The plot of $\{[(1)]/[(2)]\}_{\mathrm{p.s.s.}}$ *versus* $\{[(1)] + [(2)]\}_{\mathrm{p.s.s.}}$ is shown in Figure 3. It is linear, as required by equation (9), but only at the high concentration side, where the material balance is satisfactory (see Table 2). At the lower concentrations the material balance becomes poor

$$I_a \frac{k_{\mathrm{isc}}}{k_{\mathrm{isc}} + k_q[2]} \times \frac{[(1)]}{[(1)] + [(2)]} \qquad (6)$$

$$I_a \frac{k_{\mathrm{isc}}}{k_{\mathrm{isc}} + k_q[2]} \times \frac{[(1)]}{[(1)] + [(2)]} \times \frac{k_4}{k_3 + k_4} \qquad (7)$$

$$I_a \left\{ \frac{k_{\mathrm{isc}}}{k_{\mathrm{isc}} + k_q[(2)]} \times \frac{[(2)]}{[(1)] + [(2)]} + \frac{k_q[(2)]\Omega}{k_{\mathrm{isc}} + k_q[(2)]} \right\} \frac{k_2}{k_1 + k_2} \qquad (8)$$

and the deviation from linearity is ascribed to side reactions, possibly as result of the interaction between photoexcited fluoren-9-one and oligomers formed from (1) and/or (2). Therefore only the five highest concentration points have been used for the determination of the regression line: intercept at zero concentration 0.44

$$\left(\frac{[(1)]}{[(2)]}\right)_{\mathrm{p.s.s.}} = K\left[1 + \frac{k_q}{k_{\mathrm{isc}}}\Omega\{[(1)] + [(2)]\}\right] \qquad (9)$$

(*s* 0.01); slope 3.8 (*s* 0.2); *r* 0.991.* The observed linearity is predicted by the mechanism presented in Scheme 3 [*cf.* equation (9)] in which the exciplex ^{1}[F · · · (2)] is intermediate in the photosensitized conversion of (2) into (1) with the sensitizers of the second group (see first paragraph of the discussion). Applying equation (9) Ω was calculated to be 0.3 ± 0.1, using the intercept at zero concentration (*K* 0.44 ± 0.01) and the slope (3.8 ± 0.2) of the linear graph of Figure 3, and taking k_q (8 ± 2) × 10^9 s^{-1} [from $k_q\tau$ 24 (obtained from Figure 1) and τ 3 ± 1 ns [6b] for benzene as solvent] and k_{isc} 0.31 s^{-1}.[15] This value of Ω suggests that the exciplex ^{1}[F · · · (2)] yields ^{3}(2) with <100% efficiency.

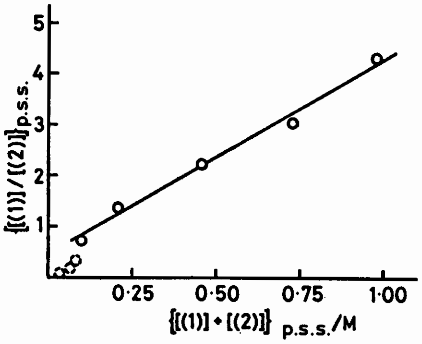


FIGURE 3 Dependence of $\{[(1)]/[(2)]\}_{\mathrm{p.s.s.}}$ on $\{[(1)] + [(2)]\}_{\mathrm{p.s.s.}}$ for the fluoren-9-one sensitized λ 403 nm irradiation of (1) at various concentrations of (1) in benzene as a solvent. The dotted circles were not used for the calculation of the regression line (see text)

The free enthalpy changes for the single electron transfer from some of the singlet-excited sensitizers of Table 1 to (2) have been calculated using equations (1)

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* For the three and four highest concentration points these data are 0.35 (0.26); 3.9 (0.3); 0.978, and 0.52 (0.13); 3.7 (0.2); 0.987, respectively.

and (2), and are given in Table 5. For fluorene, phenanthrene, and naphthalene the ΔG values do not differ very much from that of fluoren-9-one. Further their singlet lifetimes are equal to or even larger than that of fluoren-9-one. Accordingly, the formation of ^{3}(2) *via* an additional exciplex route is also feasible with these sensitizers. The ketones xanthone, benzophenone, and 1- and 2-acetonaphthone, contrary to fluoren-9-one, do not or only very weakly fluoresce. Accordingly, their singlet lifetimes will be much smaller than that of fluoren-9-one (*cf.* Table 5). Therefore, on using these sensitizers the formation of ^{3}(2) *via* an exciplex route will be negligible relative to the triplet-energy transfer. For the ketone group of sensitizers, except fluoren-9-one, the (1) $\rightleftarrows$ (2) photoisomerization is thus obtained *via* triplet-energy transfer only. The $\{[(1)]/[(2)]\}_{\text{p.s.s.}}$ ratio for xanthone, benzophenone, and 2- and 1-acetonaphthone (*i.e.* over the triplet-energy range of 74.2—56.4 kcal mol^{-1}) is constant with a value of 3.5 ± 0.3 (see Table 1); for the *triplet* photosensitization by fluoren-9-one (E_T 53.3 kcal mol^{-1}) it is 0.44, *i.e.* the value of the intercept of the linear graph of Figure 3 with the vertical axis. From the dependence of the $\{[(1)]/[(2)]\}_{\text{p.s.s.}}$ ratio on the E_T for the triplet photosensitization (Figure 4), it follows [1,17] that the triplet energy of (2) is 54—56 kcal mol^{-1} and that of (1) <54 kcal mol^{-1}. These values are somewhat higher than the values of 47—50 and <47 kcal mol^{-1} tentatively suggested previously.[2d]

TABLE 5

The free enthalpy change (ΔG) for the electron transfer from the excited singlet state of various sensitizers to the α-pyran (2) and the lifetimes of the excited singlet states (τ_s) of these sensitizers

Sensitizer	$E^{\frac{1}{2}}_{\text{red}}$/V [16]	E_s/eV [5b]	ΔG/ kcal mol^{-1}	τ_s/ns [5b]
Xanthone		3.37		
Benzophenone		3.25		0.005
Fluorene	−2.77 [a]	4.12	−8	10
Triphenylene		3.62		37
Phenanthrene	−2.46 [b]	3.59	−3	60
Naphthalene	−2.63 [a]	3.99	−8	100
2-Acetonaphthone		3.37		
1-Acetonaphthone	−1.44 [c]			
Fluoren-9-one	−1.27 [a]	2.74	−11	3; [6b] 18.5 [10]
(*E*)-Stilbene		4.08		
Pyrene	−2.19 [a]	3.38	−4.5	450

[a] Solvent system: MeCN–Et_4NClO_4; reference electrode: saturated calomel. [b] Solvent system: 75% dioxan–Bu^n_4NI; reference electrode: saturated calomel. [c] Solvent system: phosphate–citric acid buffer–KCl, pH 6.5; reference electrode: Ag–AgCl.

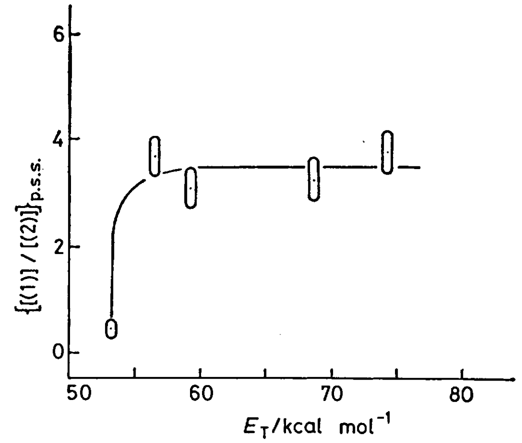

FIGURE 4 Dependence of $\{[(1)]/[(2)]\}_{\text{p.s.s.}}$ on the triplet energy of the sensitizer for the *triplet* photosensitized interconversion of (*E*)-β-ionone (1) and the α-pyran (2)

Finally, it may be recalled that a complicated triplet-energy transfer mechanism was proposed by Chapman to explain the dependence of the efficiency of the energy transfer on the sensitizer concentration, observed in the triplet-photosensitized addition of cyclohex-2-enones to alkenes using $^3(\pi-\pi^*)$ aromatic ketones as sensitizers.[18]

EXPERIMENTAL

Materials.—(*E*)-β-Ionone was obtained from Naarden International, Holland. The isomeric α-pyran (2) was obtained by λ 254 nm irradiation of (*E*)-β-ionone.[2d] Purification of the α-pyran was achieved by silica gel column chromatography using a 9 : 1 (v/v) mixture of hexane and ethyl acetate as eluant. The photosensitizers were purchased from Baker Chemical Corp. and used as such, except for fluoren-9-one which was recrystallized from ethanol.

Procedures.—The photosensitization experiments and the product analysis were performed as described before.[2d]

Fluorescence Measurements.—These were performed with a Zeiss ZFM 4c spectrofluorometer. The excitation wavelength was selected from the emission of a high-pressure Xenon arc (Osram XBO 450W, operated at 25 A direct current) by a Zeiss M4Q III monochromator. The fluorescence was detected at right angles by an EMI 9785 photomultiplier *via* a second motor-driven M4Q III monochromator. The signal was amplified by a Zeiss PMQ II amplifier and recorded on a Philips PM 8100 multirange recorder.

Reduction Potentials.—They were determined with a Radiometer PO4 instrument by direct-current polarography at the dropping-mercury electrode relative to the saturated calomel electrode in acetonitrile as a solvent containing tetraethylammonium perchlorate (0.1M) as supporting electrolyte at 20 °C.

Photoelectron Spectra.—These were recorded on a Perkin-Elmer PS-18 photoelectron spectrometer modified with a Helectros He$^{\text{I}}$–He$^{\text{II}}$ source. The spectra were calibrated with respect to Ar and Xe as internal calibrants.

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