215

STUDY OF THE PHOTOCHEMICAL BEHAVIOUR OF SUNSCREENS — BENZYLIDENE CAMPHOR AND DERIVATIVES
II: PHOTOSENSITIZED ISOMERIZATION BY AROMATIC KETONES AND DEACTIVATION OF THE 8-METHOXYPSORALEN TRIPLET STATE

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Summary

The benzophenone- and acetophenone-photosensitized E–Z isomerization of benzylidene camphor (BC) and *p*-trimethylammoniobenzylidene camphor methylsulphate was studied quantitatively. Initial sensitized quantum yields and concentrations of both isomers in the photostationary state were measured in CCl_4 for the systems (BC + benzophenone) and (BC + acetophenone). Simultaneously, the rate constants of the quenching process of the phosphorescent triplet state of the two sensitizers were determined in CCl_4. A diffusion-controlled energy transfer between acetophenone and BC accounts for the results, the energy transfer between benzophenone and BC being somewhat slower. In the sensitized isomerization of the trimethylammonio derivative in $CHCl_3$, phosphorescence quenching experiments and the determination of the photostationary states show that the quaternized derivative is as efficient as BC in quenching the triplet state of ketones. A well-known skin photosensitizer 8-methoxypsoralen (8-MOP) is observed to be an efficient sensitizer for the isomerization of the quaternized derivative of BC. The latter compound quenches the photocycloaddition of 8-MOP on *N*-methylmaleimide. It is concluded that BC and the trimethylammonio derivative show deactivating properties in addition to the usual filter effect.

1. Introduction

Benzylidene camphor (BC) and its derivatives have been used for many years in sunscreen preparations [1]. These compounds are UV filters and their photostability is extremely good [2]. They are tolerated very well by

the skin as they do not provoke any allergy or cutaneous photosensitization. The literature includes many articles concerned with the E–Z photo-isomerization of α,β unsaturated ketones [3 - 7] but there are few studies concerning benzylidene camphor. Several publications [8 - 10] in the general field of the isomerization of benzylidene cyclanones only can be mentioned. The only quantitative data reported are the ratios of the concentrations of the E and Z isomers at the photostationary equilibrium under polychromatic excitation: $[Z]_\infty/[E]_\infty = 0.18$. As this ratio is wavelength dependent, it must not be considered as an intrinsic value.

In our previous work on BC and its derivatives, quantum yields of direct photoisomerization and efficient E–Z isomerization have been reported, especially for dimethylaminobenzylidene camphor (quantum yields close to 0.30) [11]. In this paper, photosensitized isomerizations of these compounds are reported with the emphasis on obtaining quantitative data. Aromatic ketones were initially used since they are conventional sensitizers well adapted to a quantitative approach. In Section 3 the ability of BC to deactivate 8-methoxypsoralen (8-MOP), a well-known skin photosensitizer [12 - 14], is evaluated.

In the field of sunscreens, the work of Morrison et al. [15] on the photosensitized E–Z isomerization of urocanic acid should be pointed out. However, in their work, only photostationary states were examined and the ratio of the direct isomerization quantum yields under various mono-chromatic excitations determined. More recently, Morlière et al. [16] published a study of the direct isomerization of the p-methoxycinnamates during continuous excitation. These authors also describe the deactivation of 8-MOP and of the 5-methoxypsoralen by the p-methoxycinnamates.

2. Materials and methods

The synthesis of the four compounds under investigation (I - IV) has been previously described [12]. In this paper, the results are limited to compounds I and III.
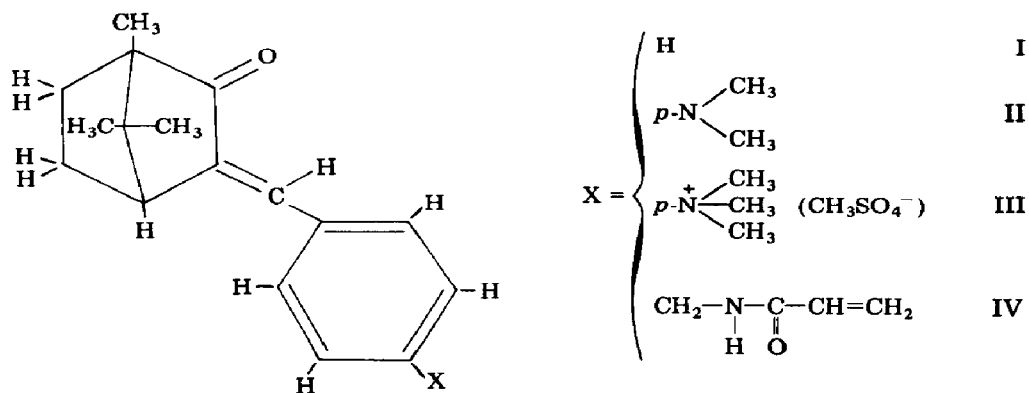
I is 1,7,7-trimethyl-3-benzylidene-*bicyclo*[2.2.1]hept-2-one (BC); II is 1,7,7-trimethyl-(4,4-dimethylamino-3-benzylidene)-*bicyclo*[2.2.1]hept-2-one (*p*-dimethylaminobenzylidene camphor); III is 4-(2-oxo-3-bornylidene)methyltrimethylammonium methylsulphate (*p*-trimethylammoniobenzylidene camphor methylsulphate); IV is 3-(acrylamidomethyl-4-benzylidene)camphor and its polymer.

The light source used was a 2500 W xenon lamp fitted with a water filter and a Schoeffel G.M. 250 monochromator. A low-pressure mercury vapour lamp (Philips TUV 15 W) was used to produce 253.7 nm irradiation. The reaction kinetics were monitored by means of Cary 118C and 219 spectrophotometers. The fluorescence emission spectra and the phosphorescence extinction were recorded using a Perkin–Elmer MPF 444 spectrofluorometer. The actinometric method used was based on the photo-oxidoreduction of potassium ferrioxalate [17].

All experiments described in the following sections were carried out in deoxygenated solutions. The solutions were thoroughly degassed by means of successive freeze–pump–thaw cycles. The vacuum was obtained using an Edwards pump unit (model BRV 10).

The acetophenone (Fluka), benzophenone (Koch–Light) and 8-MOP (Fluka) were of purissimum grade. The first two sensitizers were used in CCl_4, $CHCl_3$ or a binary mixture of water and acetonitrile. The $CHCl_3$ used in the phosphorescence extinction studies was purified by eliminating any traces of ethyl alcohol.

3. Experimental results

3.1. Photosensitized isomerization of benzylidene camphor and its derivatives by aromatic ketones

Although acetophenone and benzophenone are widely used as sensitizers in solution and solid state photochemistry, many data about the properties of their triplet state are unknown. In 1979 the lifetime at infinite dilution and the self-quenching rate constant for benzophenone and acetophenone triplet states were determined in CCl_4 (see Table 1).

TABLE 1

Main characteristics of the lowest triplet of acetophenone and benzophenone

Sensitizer	Solvent	E_T (kJ mol^{-1})	τ_T (s)	ϕ_{ISC}	k_{sq} (mol^{-1} l s^{-1})
Benzophenone	CCl_4	282 ± 4[a]	$(2 \pm 0.2) \times 10^{-4}$ [a]	1[b]	$(7.5 \pm 0.7) \times 10^3$ [a]
Acetophenone	CCl_4	301 ± 4[a]	$(5 \pm 1) \times 10^{-6}$ [a]	1[b]	$(1.1 \pm 0.2) \times 10^6$ [a]

E_T, energy of the lowest triplet state.
τ_T, lifetime of the lowest triplet state at infinite dilution.
ϕ_{ISC}, quantum yield of the intersystem crossing $S_1 \rightarrow T_1$.
k_{sq}, self-quenching rate constant of the triplet state.
[a]From Jeandrau *et al.* [18].
[b]From Murov [19].

This affords a means of defining quantitatively the features of the isomerization of BC and its derivatives photosensitized by such donors in CCl$_4$.

3.1.1. Photosensitized isomerization of benzylidene camphor (I)

The initial quantum yields ϕ_S^0 of the E–Z isomerization of I photosensitized with benzophenone or acetophenone have been measured and are reported in Tables 2 and 3. Since the self-quenching rate constants of both sensitizers were known, high concentrations of the donor could be used and no correction for direct excitation of the acceptor was needed. The rate of disappearance of the initial isomer was determined from the variations in the absorbance at 315 nm (with both sensitizers). The ratio of E and Z isomer concentrations at the photostationary state $[Z]_\infty/[E]_\infty$ was found to be 1.02 ± 0.04 and 1.0 ± 0.02 with benzophenone and acetophenone respectively.

It is well known that phosphorescence is observed when benzophenone and acetophenone are excited in non-hydrogenated solvents and especially in

TABLE 2

E–Z isomerization of benzylidene camphor photosensitized at 365 nm with benzophenone (1.5×10^{-2} mol l^{-1}) in CCl$_4$

Compound	Concentration (mol l^{-1})	I_0 (einstein cm^{-3} s^{-1})	ϕ_S^0
I$_E$	2.0×10^{-5}	8.93×10^{-10}	0.31 ± 0.03
I$_E$	1.3×10^{-5}	3.66×10^{-10}	0.25 ± 0.03
I$_E$	1.16×10^{-5}	8.62×10^{-10}	0.29 ± 0.03
I$_E$	2.66×10^{-5}	8.56×10^{-10}	0.36 ± 0.04
I$_E$	6.06×10^{-5}	7.94×10^{-10}	0.40 ± 0.04
I$_Z$	1.01×10^{-5}	7.94×10^{-10}	0.22 ± 0.02
I$_Z$	1.64×10^{-5}	7.94×10^{-10}	0.26 ± 0.03
I$_Z$	4.09×10^{-5}	7.94×10^{-10}	0.42 ± 0.04

TABLE 3

E–Z isomerization of benzylidene camphor photosensitized at 334 nm with acetophenone (1.5×10^{-2} mol l^{-1}) in CCl$_4$

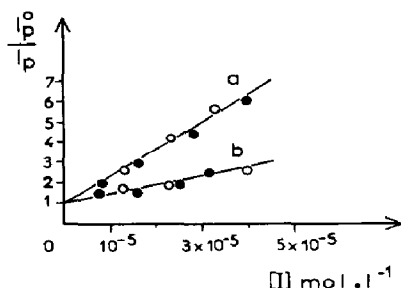| Compound	Concentration of I (mol l^{-1})	I_0 (einstein cm^{-3} s^{-1})	ϕ_S^0
I$_E$	2.5×10^{-5}	5.97×10^{-10}	0.24 ± 0.02
I$_E$	3.0×10^{-5}	5.93×10^{-10}	0.25 ± 0.02
I$_E$	1.3×10^{-5}	9.9×10^{-10}	0.19 ± 0.02
I$_E$	6.66×10^{-5}	9.9×10^{-10}	0.38 ± 0.04
I$_E$	1.3×10^{-5}	6.0×10^{-10}	0.18 ± 0.02
I$_Z$	1.0×10^{-6}	5.9×10^{-10}	0.15 ± 0.02
I$_Z$	8.59×10^{-6}	6.33×10^{-10}	0.14 ± 0.02
I$_Z$	4.55×10^{-5}	6.33×10^{-10}	0.35 ± 0.04

Fig. 1. Quenching of the benzophenone and acetophenone phosphorescence in CCl_4 solution at various concentrations of I in the E ($\bullet$) or Z form ($\circ$): curve a, benzophenone (2.5×10^{-3} mol l^{-1}); curve b, acetophenone (6×10^{-3} mol l^{-1}). I_p^0, intensity of the phosphorescence in the absence of I (arbitrary unit); I_p, intensity of the phosphorescence in the presence of I.

CCl_4 [18, 20, 21]. Phosphorescence spectra show two maxima at 421 and 541 nm. At low concentrations, BC and its derivatives are efficient quenchers of this phosphorescence (it was checked that no significant amounts of incident light were absorbed neither at 350 nm (benzophenone) nor at 330 nm (acetophenone)). Variations of the ratio of the phosphorescence intensity I_p or I_p^0 in the presence or absence of I respectively as a function of the initial concentration of I (E or Z) have been represented as Stern–Volmer plots (Fig. 1).

$$\frac{I_p^0}{I_p} = 1 + k_q \tau [I]$$

The rate constant k_q of the quenching process of the triplet state of the donor can be derived from the slope of the Stern–Volmer plots, using the known values of the triplet state lifetimes τ in the solutions used.

$$k_q^F \tau = k_q^Z \tau = (1.40 \pm 0.14) \times 10^5 \text{ mol}^{-1} \text{ l} \qquad \text{(benzophenone)}$$

$$k_q^E \tau = k_q^Z \tau = (4.4 \pm 0.4) \times 10^4 \text{ mol}^{-1} \text{ l} \qquad \text{(acetophenone)}$$

Therefore the rate constants of the quenching process in CCl_4 have been found to be

$$k_q^E = k_q^Z = (6.8 \pm 1.4) \times 10^8 \text{ mol}^{-1} \text{ l s}^{-1} \qquad \text{(benzophenone)}$$

$$k_q^E = k_q^Z = (8.9 \pm 2.7) \times 10^9 \text{ mol}^{-1} \text{ l s}^{-1} \qquad \text{(acetophenone)}$$

3.1.2. Photosensitized isomerization of trimethylammoniobenzylidene camphor (III)

Similar measurements have been carried out in $CHCl_3$ (in CCl_4, the solubility of III is lower than 10^{-5} mol l^{-1}) or in water containing 5% - 10% CH_3CN. Monochromatic light at 335 nm was used for excitation, and analysis of the isomerization was carried out at 357 nm. It was found that direct measurement of the initial photosensitized isomerization quantum

yields was difficult even under these experimental conditions. Only photo-stationary states were determined using benzophenone (2.5×10^{-3} - 10^{-2} mol l^{-1}) or acetophenone (2.5×10^{-3} - 4×10^{-2} mol l^{-1}). As the concentrations of compounds III_E or III_Z were varied from 1.34×10^{-4} mol l^{-1} (in 95%water–5%CH_3CN) to 3.75×10^{-4} mol l^{-1} (in 50%water–50%CH_3CN), the ratio $[Z]_\infty/[E]_\infty$ was found to be 0.99 ± 0.03 (from 19 measurements).

Extinction of phosphorescence of donors in $CHCl_3$ by various concentrations of III in the E or Z forms yields (Fig. 2)

$$(k_q{}^E \tau)_{CHCl_3} = (k_q{}^Z \tau)_{CHCl_3} = (2.4 \pm 0.2) \times 10^3 \, mol^{-1} \, l \qquad \text{(benzophenone)}$$

$$(k_q{}^E \tau)_{CHCl_3} = (k_q{}^Z \tau)_{CHCl_3} = (4.1 \pm 0.4) \times 10^3 \, mol^{-1} \, l \qquad \text{(acetophenone)}$$

The observed values were therefore 10 - 50 times lower than the corresponding values of $k_q \tau$ in CCl_4 determined using compound I. Therefore, experiments on the extinction of phosphorescence of both donors in $CHCl_3$ by I in the E form have been carried out. From Stern–Volmer plots, the following were derived:

$$(k_q{}^E \tau)_{CHCl_3} = (4.0 \pm 0.4) \times 10^3 \, mol^{-1} \, l \qquad \text{(benzophenone)}$$

$$(k_q{}^E \tau)_{CHCl_3} = (4.5 \pm 0.4) \times 10^3 \, mol^{-1} \, l \qquad \text{(acetophenone)}$$

It can be concluded that the quaternized derivative of BC (III) is an efficient quencher of the triplet state of aromatic ketones (as efficient as BC (I)). This result is not unexpected. It is well known that conversion of dimethylamino into trimethylammonio substituents annihilates the inductive effect of the amino group — as checked, for example, from the UV spectra and from the direct isomerization quantum yield [11].

3.2. Interaction of the triplet state of 8-methoxypsoralen with trimethyl-ammoniobenzylidene camphor (III)

No interaction was observed between 8-MOP and III_E or III_Z (each in the ground state). For example, the addition of 8×10^{-4} mol l^{-1} of compound III_E did not modify the absorption spectrum of a 4.4×10^{-5} mol l^{-1} solution of 8-MOP in 96%water–4%methanol.
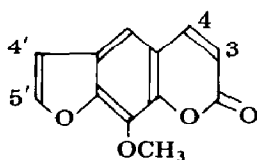
8-MOP

Photosensitization of the E–Z isomerization of III_E was observed in degassed solution using 8-MOP (2×10^{-4} mol l^{-1}) excited with 298 nm monochromatic light. Low initial quantum yields $\phi_S{}^0$ were measured and found to obey a Stern–Volmer law (see Fig. 3). Direct excitation of III_E was avoided by the use of 8-MOP at high absorbance; the Stern–Volmer plot was
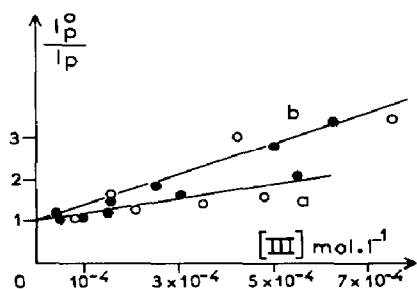
Fig. 2. Quenching of the benzophenone and acetophenone phosphorescence in $CHCl_3$ solution at various concentrations of III in the E (●) or Z form (○): curve a, benzophenone (2.5×10^{-3} mol l^{-1}); curve b, acetophenone (10^{-2} mol l^{-1}). I_p^0, intensity of the phosphorescence in the absence of III (arbitrary unit); I_p, intensity of the phosphorescence in the presence of III.
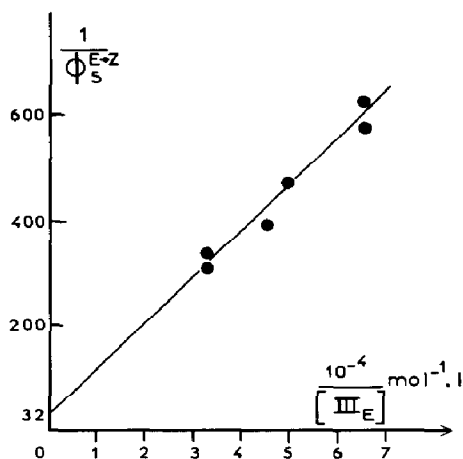
Fig. 3. Variations in the reciprocal quantum yield of isomerization of compound III in the E form photosensitized by 8-MOP (2×10^{-4} mol l^{-1}) in degassed aqueous solution containing 12% methanol as a function of the reciprocal concentration of III.

only obtained in a limited range of the acceptor concentration $((1.5 - 3) \times 10^{-5}$ mol $l^{-1})$. The slope of the plot yielded $k_q\tau = 3700$ mol l^{-1}. Using the previously reported data on the 8-MOP triplet state [22], in our experimental conditions the triplet lifetime is $\tau = (9.9 \pm 1.0) \times 10^{-7}$ s. The rate constant k_q can be calculated as $(3.7 \pm 0.9) \times 10^9$ l mol^{-1} s^{-1}.

In water, the quantum yield of the intersystem crossing process $S_1 \rightarrow T_1$ has been found to be 0.06 in 8-MOP [22]. The maximum value for ϕ_S^0, obtained by extrapolation from Fig. 3 (*i.e.* 1/32 = 0.03), is accounted for by a quasi-complete energy transfer followed by deactivation of the III_E triplet state into both isomers, E and Z, with equal probabilities.

The sensitization of the isomerization of III_E should also result in the quenching of the photocycloaddition reactions of 8-MOP. In a previous work, we showed that furocoumarins give rise to photocycloaddition reactions with N-methylmaleimide; we have proposed this model for DNA in the study of furocoumarin photoreactivity with DNA bases [23, 24]. To check the ability of III_E to quench the triplet state of 8-MOP, the influence of III_E on the reactions of 8-MOP with N-methylmaleimide was examined. The disappearance of 8-MOP excited at 350 nm in dilute aqueous solution (1.3×10^{-4} mol l^{-1}) is very slow ($\phi = 4 \times 10^{-4}$). In the presence of N-methylmaleimide, even in aerated solutions, 8-MOP undergoes photocycloaddition on the 3,4 and 4',5' bonds. The 4',5' adduct is highly fluorescent and can therefore be detected at very low concentrations. For example, such a formation is observed in an aerated solution of 8-MOP (5×10^{-5} mol l^{-1}) and of N-methylmaleimide (5×10^{-4} mol l^{-1}) in water—methanol (24%). A

monochromatic irradiation at 350 nm was used and the fluorescent compound was analysed at 460 nm (under the same excitation at 350 nm). An inhibition of the formation of this fluorescent adduct was observed in the presence of III_E. The ratio of the photocycloaddition rates V and V_0 in the presence and in the absence of III_E respectively was again found to obey a Stern–Volmer law.

$$\frac{V_0}{V} = 1 + k_q\tau'[III_E]$$

with $k_q\tau' = 1250 \; mol^{-1} \, l$.

Using the lifetime τ' of the 8-MOP triplet state in the presence of $5 \times 10^{-4} \; mol \; l^{-1}$ of N-methylmaleimide which has been previously determined [25],

$$\tau' = (2.0 \pm 0.2) \times 10^{-7} \, s$$

$$k_q = (6.3 \pm 1) \times 10^9 \, s$$

The quenching process is almost diffusion controlled.

4. Discussion and conclusions

The initial quantum yields of direct photoisomerization of BC and its derivatives do not depend on the concentration, the presence of dissolved oxygen or on the solvent used [2]. The isomerization quantum yield of BC was wavelength dependent; no wavelength dependence was observed in the other derivatives (see Table 4). When BC was grafted onto a polymer and irradiated in the solid state, the quantum yield of isomerization remained unchanged as shown in Table 4.

TABLE 4

Initial quantum yields of direct isomerization (mean value of at least three determinations) (from ref. 11)

Compound	$\phi_{E \to Z}$ in $S_1(n,\pi^*)$	$\phi_{Z \to E}$ in $S_1(n,\pi^*)$	$\phi_{E \to Z}$ in $S_2(\pi,\pi^*)$	$\phi_{Z \to E}$ in $S_2(\pi,\pi^*)$
I	0.31 ± 0.03 at 370 nm	0.29 ± 0.03 at 370 nm	0.13 ± 0.01 between 254 and 290 nm	0.15 ± 0.02 between 254 and 300 nm
II	0.30 ± 0.03 at 350 nm	0.32 ± 0.03 between 350 and 415 nm	0.30 ± 0.03 at 350 nm	0.32 ± 0.03 between 350 and 415 nm
III	0.11 ± 0.01 at 370 nm	0.10 ± 0.01 at 357 nm	0.10 ± 0.01 between 254 and 290 nm	0.10 ± 0.01 between 254 and 290 nm
IV	—	—	0.14 ± 0.01 at 293 nm	—

The quantum yields of the irreversible disappearance of BC and its derivatives have been found to be close to 10^{-4}. No photochemical process can therefore account for the differences between unity and the sums $(\phi_{E \to Z} + \phi_{Z \to E})$.

Interactions between excited aromatic ketones and BC or its trimethylammonio derivatives can be accounted for by the conventional "vertical" energy transfer mechanism[†].

This mechanism is schematically represented in the diagram below.
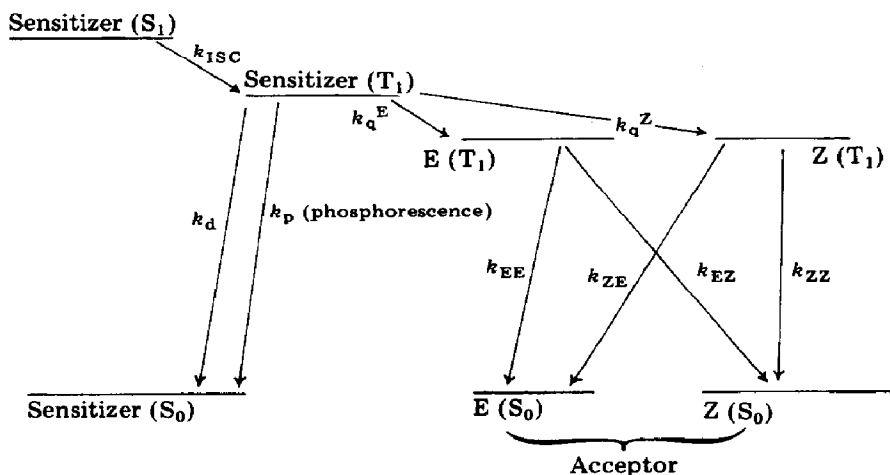
The following expression for the initial quantum yield of sensitized isomerization is easily derived (assuming quasi-stationarity)

$$\frac{1}{\phi_{S_{E \to Z}}^{0}} = \frac{k_{EZ} + k_{EE}}{k_{EZ}} \frac{1}{\phi_{ISC}} \left(1 + \frac{1}{k_q^{E} \tau [E(S_0)]}\right)$$

This relationship has been checked by plotting the variations in the reciprocal quantum yields of both isomers of compound I as a function of the reciprocal concentration of the corresponding acceptor (see Fig. 4). $k_q^{E}\tau$ and $k_q^{Z}\tau$ are defined as the quotient of the ordinate intercept and the slope of the Stern–Volmer plot. From the ordinate intercept, the ratios $(k_{EZ} + k_{EE})/k_{EZ}$ (or $(k_{ZE} + k_{ZZ})/k_{ZE}$) can be obtained since ϕ_{ISC} is known.

At photostationary equilibria, the ratio $[Z]_\infty/[E]_\infty$ was calculated as

$$\frac{[Z]_\infty}{[E]_\infty} = \frac{k_q^{E}}{k_q^{Z}} \frac{k_{EZ}(k_{ZE} + k_{ZZ})}{k_{ZE}(k_{EZ} + k_{EE})}$$

The data obtained from initial quantum yield measurements from photostationary states and from phosphorescence quenching experiments appear in Table 5.

[†]As a referee suggested, an addition–elimination mechanism, such as that proposed by N. J. Turro [26], might also account for the sensitized isomerization.
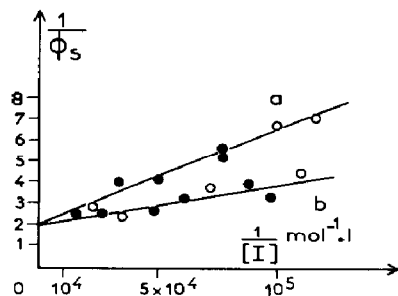
Fig. 4. Variations in the reciprocal quantum yields ϕ_S of isomerization of compound I photosensitized by benzophenone (10^{-2} mol l^{-1}, curve a) by acetophenone (1.5×10^{-2} mol l^{-1}, curve b) in degassed CCl_4 solution as a function of the reciprocal concentration of compound I in the E (●) or Z form (○).

A satisfactory fit between the values of $k_q\tau$ and $(k_q{}^E/k_q{}^Z) \times k_{EZ}(k_{ZE} + k_{ZZ})/k_{ZE}(k_{EZ} + k_{EE})$ was obtained in the two independent series of experiments. The following conclusions can be drawn.

(i) The quantitative population of the triplet level of BC in its E and Z forms, through an energy transfer, stimulates an E $\rightleftarrows$ Z isomerization with a probability of 50%.

(ii) The sum of the two limiting quantum yields of isomerization is unity. No deactivation of the triplet states through non-radiative processes occurs other than isomerization. Each triplet state deactivates into the E or Z forms with equal probability (50%).

(iii) The energy transfer probability, expressed by $k_q\tau$, is equal for both isomers using benzophenone or acetophenone as donors (in CCl_4 as well as in $CHCl_3$). A "non-vertical" energy transfer would account for the results equally well as a "vertical" energy transfer.

(iv) BC and its quaternized derivative have very similar acceptor properties in the same solvent.

(v) Quenching of the acetophenone triplet state by compound I occurs through a process which is diffusion controlled. Energy transfer from benzophenone appears to be slower.

When the lowest triplet state of BC is quantitatively populated through energy transfer, the isomerization quantum yield is maximum (i.e. 0.50) for both isomers. Lower quantum yields are observed in direct excitation. Hence the isomerizable triplet state is not quantitatively populated under direct excitation and there are radiationless transitions $S_1(n,\pi^*$ or $\pi,\pi^*) \rightarrow S_0$. Although isomerization occurs from the singlet state, the corresponding process is less probable than that from the triplet state. The irreversible disappearance, which is very slight ($10^{-5} < \phi_{disp} < 9 \times 10^{-5}$) during direct excitation in water, is not detected in sensitization experiments, even during long irradiation (1 - 3 h). The absence of irreversible photochemical processes from triplet or singlet states explains the remarkable stability of BC and its derivatives and their excellent tolerance by the skin.

8-MOP appeared to be an efficient sensitizer for the isomerization of the quaternized derivative of BC (III). The energy transfer process revealed

TABLE 5

Comparison of the data obtained from various experiments

Type of experiment	Compounds	Benzophenone	Acetophenone
Initial sensitized isomerization quantum yields	Benzylidene camphor (I)	$k_q^Z \tau = k_q^E \tau$ $= (1 \pm 0.1) \times 10^5$ mol^{-1} $\dfrac{k_{EZ} + k_{EE}}{k_{EZ}} = 2$ $\dfrac{k_{ZE} + k_{ZZ}}{k_{ZE}} = 2$	$k_q^Z \tau = k_q^E \tau$ $= (4.4 \pm 0.4) \times 10^4$ mol^{-1} $\dfrac{k_{EZ} + k_{EE}}{k_{EZ}} = 2$ $\dfrac{k_{ZE} + k_{ZZ}}{k_{ZE}} = 2$
Photostationary states	I	$\dfrac{k_q^E}{k_q^Z} \dfrac{k_{EZ}(k_{ZE} + k_{ZZ})}{k_{ZE}(k_{EZ} + k_{EE})} = 1.02 \pm 0.04$	$\dfrac{k_q^E}{k_q^Z} \dfrac{k_{EZ}(k_{ZE} + k_{ZZ})}{k_{ZE}(k_{EZ} + k_{EE})} = 1 \pm 0.02$
Phosphorescence quenching in CCl$_4$	I	$k_q^Z \tau = k_q^E \tau$ $= (1.4 \pm 0.14) \times 10^5$ mol^{-1}	$k_q^Z \tau = k_q^E \tau$ $= (4.4 \pm 0.4) \times 10^4$ mol^{-1}
Phosphorescence quenching in CHCl$_3$	I	$k_q^Z \tau = k_q^E \tau$ $= (4 \pm 0.4) \times 10^3$ mol^{-1}	$k_q^Z \tau = k_q^E \tau$ $= (4.5 \pm 0.4) \times 10^3$ mol^{-1}

TABLE 5 (continued)

Type of experiment	Compounds	Benzophenone	Acetophenone
Photostationary states	Trimethylbenzylidene camphor (III)	$\dfrac{k_q^E}{k_q^Z}\dfrac{k_{EZ}(k_{ZE}+k_{ZZ})}{k_{ZE}(k_{EZ}+k_{EE})}=0.98\pm0.02$	$\dfrac{k_q^E}{k_q^Z}\dfrac{k_{EZ}(k_{ZE}+k_{ZZ})}{k_{ZE}(k_{EZ}+k_{EE})}=0.99\pm0.03$
Phosphorescence quenching in CHCl$_3$	III	$k_q^Z\tau=k_q^E\tau$ $=(2.4\pm0.2)\times10^3\,\text{mol}^{-1}]$	$k_q^Z\tau=k_q^E\tau$ $=(4.1\pm0.4)\times10^3\,\text{mol}^{-1}]$

through isomerization is fast though not diffusion controlled ($k_q \approx 1.1 \times 10^9$ $1 \ mol^{-1} \ s^{-1}$). The same process observed through the quenching of photocycloaddition of 8-MOP with N-methylmaleimide is diffusion controlled ($k_q \approx 6 \times 10^9 \ 1 \ mol^{-1} \ s^{-1}$). This discrepancy may arise from an uncertainty in the lifetime of the triplet state of 8-MOP in the absence or in the presence of N-methylmaleimide.

The BC derivatives (III) therefore present deactivating qualities in addition to the usual filter effect. Furthermore, it should be recalled that the excess of energy transferred to the quaternized derivative of BC is dissipated through the isomerization process alone.

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