

TRIPLET ENERGIES OF  $\alpha,\beta$ -UNSATURATED KETONES AND ESTERS

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## Summary

The triplet energies of ethyl *E*-2-methyl-2-butenolate (1a) and *E*-3-methyl-3-penten-2-one (1b) were determined by a competitive quenching technique in which a variety of sensitizers of known triplet energies were irradiated in the presence of *trans*-stilbene and either 1a or 1b. For sensitizers with triplet energies (as measured from the position of the 0-0 band in their phosphorescence spectra) less than 72 kcal mol<sup>-1</sup> both the unsaturated ester 1a and the ketone 1b became less competitive than *trans*-stilbene as a quencher. From measurements of the relative rates of quenching by 1a or 1b and *trans*-stilbene the triplet energies of ester 1a and ketone 1b were estimated to be 72.0 ± 0.5 kcal mol<sup>-1</sup>. The relationship between the singlet-triplet splitting in the unsaturated carbonyl compounds and their observed quantum efficiencies of *E-Z* isomerization is briefly discussed.

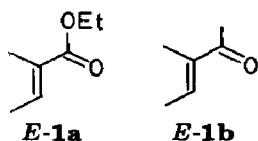
## 1. Introduction

The triplet excited states of simple acyclic  $\alpha,\beta$ -unsaturated ketones and esters decay rapidly to the ground state by a mechanism which is thought to involve twisting of the carbon-carbon double bond [1, 2]. The rates of decay of both the singlet and the triplet excited states of these compounds are sufficiently rapid that fluorescence and phosphorescence are not normally competitive. For example, weak emission has been observed [3] from 3-penten-2-one but was assigned to saturated ketone impurities, while at 77 K weak emission has been observed from propenal [4] and the quantum yields of emission were estimated as 0.007 ± 0.001 for fluorescence and 0.00004 ± 0.00002 for phosphorescence. The triplet energy of propenal determined from the position of the 0-0 transition in the phosphorescence spectrum was 69 kcal mol<sup>-1</sup> and is supported by the value indicated by the position of a band assigned to a singlet-triplet transition in the gas phase absorption spectrum [5]. In the case of cyclic ketones, where twisting of the double bond is inhibited by the ring, the excited states fluoresce and phosphoresce more strongly and this allows easy determination of their triplet energies from their phosphorescence spectra [6].

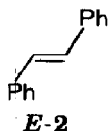
The failure of simple acyclic  $\alpha,\beta$ -unsaturated ketones and esters to show reliable phosphorescence has meant that the energies of their triplet excited states are not well characterized, possibly because the alternative methods for measurement of the triplet energies are tedious in comparison, require specialist apparatus or have been shown to give inaccurate values. These methods include the use of flash photolysis to measure the rate of quenching of a range of sensitizers of different triplet energies by the compound of unknown triplet energy [7, 8], measurement of the position of the  $S_0 \rightarrow T_1$  transition in heavy-atom-containing solvents and, for compounds capable of undergoing  $E-Z$  isomerization, measurement of the sensitized photo-stationary state composition of the compound of unknown triplet energy in the presence of a range of sensitizers of known triplet energy. The last procedure has been shown to give low values on occasions [8], while the use of the heavy atom effect is not always satisfactory because the solvent can give rise to new charge transfer absorption bands or may alter the triplet energy through a solvent effect. In addition, it is often difficult to assign the position of the weak  $S_0 \rightarrow T_1$  band as it appears as a tail on the much stronger  $S_0 \rightarrow S_1$  band.

Measurement of the quantum efficiency of a reaction derived from a triplet excited state of a compound of unknown triplet energy sensitized by a variety of sensitizers of known triplet energy can also allow an estimate of the triplet energy to be made since sensitizers of triplet energy close to or lower than that of the compound under study will not sensitize the reaction efficiently. However, this procedure requires accurate measurement of absorbed light intensities and also requires the concentration of the compound under study to be high enough that all of the sensitizer triplets can be quenched. Frequently, the requirement that all of the absorbed light must be absorbed by the sensitizer, and not by the quencher, is difficult to reconcile with the requirement that all of the sensitizer triplets must be quenched. This is because the absorption spectra and triplet lifetimes of the sensitizers are highly variable, and this creates problems in selecting suitable sensitizers and concentrations of sensitizer and quencher.

We have recently been engaged in synthetic and mechanistic studies of the photochemistry of acyclic  $\alpha,\beta$ -unsaturated esters [9] and ketones [10] with particular regard to the photoenolization reactions of these compounds; the photoenolization reaction has been shown to occur from the singlet excited state, but in order to confirm this and to exclude the possibility of simultaneous triplet reactivity we performed studies in which it was desirable to determine the triplet energies of these compounds. A simple procedure was developed which is derived from the method described in the preceding paragraph, but which does not suffer from the disadvantages mentioned; in particular quenching of all the sensitizer triplets is not necessary, nor is determination of the intensity of the absorbed light. The procedure involves the measurement of the relative efficiencies of  $E-Z$  isomerization of the unsaturated carbonyl compound, in this case ethyl  $E$ -2-methyl-2-butenoate (1a) and  $E$ -3-methyl-3-penten-2-one (1b)



and *trans*-stilbene (*E-2*)



present together in the same solution and sensitized by a variety of sensitizers of known triplet energy. The details are described here together with comments on the relevance of the triplet energies determined to the observed photochemistry of these compounds.

## 2. Results and discussion

In Fig. 1 is shown a scheme in which a sensitizer molecule, *S*, is irradiated and competitively quenched by two species, either the unsaturated carbonyl compound *E-1* or *trans*-stilbene, *E-2*, to give the triplet excited states  $^3\tilde{1}^*$  or  $^3\tilde{2}^*$  respectively. Each of the triplet states can then decay to either the *E* or the *Z* ground states of 1 and 2. Application of the steady state approximation to the kinetics scheme shown in Fig. 1 yields

$$\Phi_{Z-1} = \frac{k_1}{k_1 + k_2} \frac{k_q^1 [E-1]}{{}^3k_d + k_q^1 [E-1] + k_q^2 [E-2]} I_a \Phi_{isc} \quad (1)$$

$$\Phi_{Z-2} = \frac{k_3}{k_3 + k_4} \frac{k_q^2 [E-2]}{{}^3k_d + k_q^1 [E-1] + k_q^2 [E-2]} I_a \Phi_{isc} \quad (2)$$

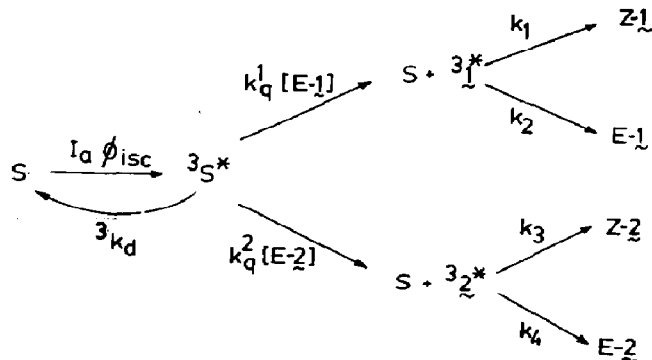


Fig. 1. Kinetics scheme for competitive quenching of a sensitizer by unsaturated carbonyl compound *E-1* and *trans*-stilbene 2.

which define the quantum yields of formation of the *Z* isomers of 1 and 2 in terms of the rate constants and concentrations of species shown in the scheme. The ratio of the quantum yields, which is equivalent to the ratio of the rates of formation of the *Z* isomers, is given by

$$\frac{\Phi_{Z-1}}{\Phi_{Z-2}} = \frac{k_3}{k_3 + k_4} \frac{k_1 + k_2}{k_1} \frac{k_q^1 [E-1]}{k_q^2 [E-2]} \quad (3)$$

which simplifies to

$$\frac{\Phi_{Z-1}}{\Phi_{Z-2}} = \frac{\alpha_2}{\alpha_1} \frac{k_q^1 [E-1]}{k_q^2 [E-2]} \quad (4)$$

if the partitioning ratios  $k_1/(k_1 + k_2)$  and  $k_3/(k_3 + k_4)$  for decay of the triplets of 1 and 2 to their *E* and *Z* isomers are denoted by  $\alpha_1$  and  $\alpha_2$  respectively. Equation (4) indicates that, for a given sensitizer, in a competitive quenching experiment the observed relative rates of isomerization of 1 and 2 reflect the relative rates at which they quench the sensitizer. If a sensitizer with a triplet energy substantially greater than those of 1 and 2 is used then both species should quench at close to diffusion-controlled rates, *i.e.*  $k_q^1$  and  $k_q^2$  are similar, and the observed rates of isomerization of *E*-1 and *E*-2 will reflect only their relative concentrations and partitioning factors. However, if a sensitizer of triplet energy which is similar to or lower than that of 1 but higher than that of 2 is used, then the rates of quenching will be very dissimilar because the rate of quenching by 1 will be slower than the rate of diffusion and the observed relative rates of isomerization will reflect this. Thus if a series of experiments is performed in which the sensitizer triplet energy is gradually lowered and the relative rates of isomerization of 1 and 2 are measured, a point will be reached where the isomerization of 1 will become inefficient relative to that of 2, and this point will correspond to the situation where the triplet energy of the sensitizer is similar to that of 1.

In this scheme the presence of other quenchers (*e.g.* impurities such as oxygen) is unimportant as long as the triplet excited states of 1 and 2 are not themselves quenched. Fulfilment of this condition makes stringent purification and oxygen removal unnecessary. The triplet excited states of 1 and 2 are sufficiently short lived to render quenching by saturation concentrations of oxygen (around  $10^{-3}$  M in ether) uncompetitive with relaxation by *E*-*Z* isomerization; for the same reason, quenching of the triplet excited state of 1 by 2 should not occur.

It should also be noted that in the scheme shown in Fig. 1 it is not necessary to know the intensity of the incident light, or that the sensitizer absorbs all of the incident light, only that the quenchers absorb none; nor is it necessary that all of the sensitizers are quenched by 1 and 2. All that need be known are the triplet energy of the sensitizer and the concentrations of 1 and 2, and all that need be measured are the relative rates of isomerization of *E*-1 and *E*-2 to their *Z* isomers. In addition, it is necessary to ensure that none of the *Z* isomers are isomerized back to the *E* isomers by sensitization; this means that conversions must be kept low.

In this work 2 was chosen as *trans*-stilbene because its triplet energy (49 kcal mol<sup>-1</sup>) is lower than the values anticipated for 1. Diethyl ether solutions containing both 1 and 2, in known concentrations, and various sensitizers were irradiated with light of wavelength 254 nm. The concentrations of the sensitizers were chosen so that only they absorbed light, and not 1 or 2. Inert non-light-absorbing internal standards were also present and the conversion of 1 and 2 to their *Z* isomers was monitored relative to the standard by gas chromatography. Conversions were kept below 5% to prevent sensitization of the *Z* isomers. Typical results are shown in Fig. 2 which is for the isomerization of 1b and 2 sensitized by 3-methoxyacetophenone. The ratio of the gradients of the lines divided by the ratio of the concentrations of 1 and 2 gives the ratio of quantum yields for isomerization of 1 and 2 and, indirectly, the ratio of the rate constants for quenching of the sensitizer by 1 and 2 according to eqn. (4). If desired, the internal standards may be omitted and the relative rates of isomerization determined from measurement of the ratio of the areas of the *Z* isomers being produced. However, for low energy sensitizers, where 1 is not being sensitized as efficiently, this can lead to large errors in the analysis.

The results obtained for 1a and 1b are given in Table 1 and displayed in Figs. 3 and 4 where the relative quantum yields of formation of the *Z* isomers of 1 and 2 are plotted against the triplet energies of the sensitizers which were determined from the positions of the 0-0 bands in their phosphorescence spectra measured in ether at 77 K. The triplet energies of the sensitizers were remeasured in this work because the values reported in the literature are for a variety of solvents [11]; the values determined were

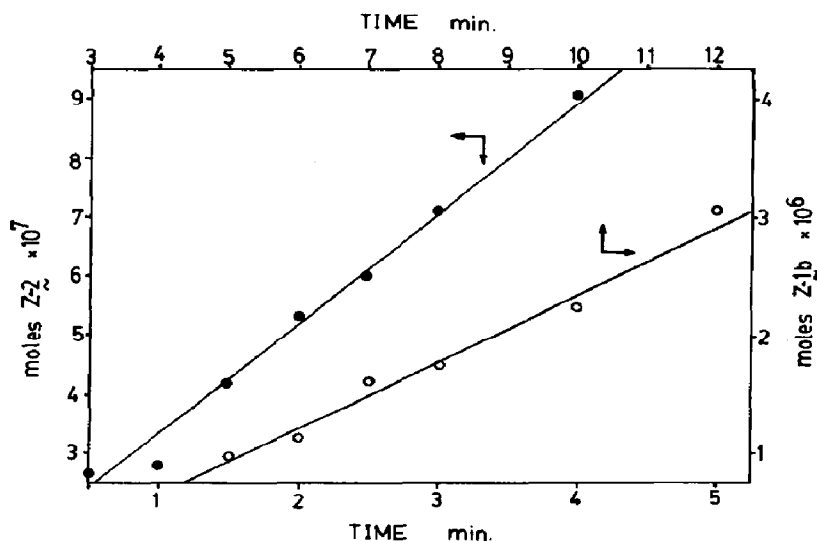


Fig. 2. Plot of time vs. amount of *Z*-1b and *Z*-2 formed in the competitive quenching of 3-methoxyacetophenone by *E*-1b and *E*-2 in diethyl ether: upper line, *Z*-2; lower line, *Z*-1b.

TABLE 1

Triplet energies of sensitizers and their relative rates of quenching by ester 1a, ketone 1b and stilbene<sup>a</sup>

Entry number <sup>b</sup>	Sensitizer	Triplet energy (kcal mol <sup>-1</sup> )	$\Phi_{Z-1b}/\Phi_{Z-2}$	$\Phi_{Z-1a}/\Phi_{Z-2}$
1	Phenanthrene	62.3 (61.9)	0.1577	— <sup>d</sup>
2	Biphenyl	65.7 (65.7)	0.1025	0.00249
3	Benzophenone	68.3 (68.6)	0.03589	0.01996
4	2-Methylbenzophenone	69.6 (69.2)	0.01174	— <sup>d</sup>
5	Benzaldehyde	72.2 (72.0)	0.0720	0.05196
6	3-Methoxyacetophenone	71.8 (72.4)	0.1321	0.06296
7	<i>p</i> -Anisaldehyde	70.3 (71.8)	0.2459	0.1369
8	4-Methylacetophenone	71.8 (72.9)	0.2602	0.2265
9	Propiophenone	72.2 (74.5)	0.2715	0.2249
10	Acetophenone	73.3 (73.7)	0.2943	0.2429
11	Methyl benzoate	78.3 (78.7)	0.2781	0.2757

<sup>a</sup> $\Phi_{Z-1a}/\Phi_{Z-2}$  is the relative quantum efficiency of sensitized *E* → *Z* isomerization of ester 1a and stilbene 2 as defined by eqn. (4);  $\Phi_{Z-1b}/\Phi_{Z-2}$  is the same function, but for ketone 1b.

<sup>b</sup>The entry number refers to the data points in Figs. 3 and 4.

<sup>c</sup>Triplet energies were determined from the position of the 0-0 band in the phosphorescence spectra recorded in diethyl ether at 77 K. The values in parentheses are taken from the literature summarized in ref. 11.

<sup>d</sup>Values not determined.

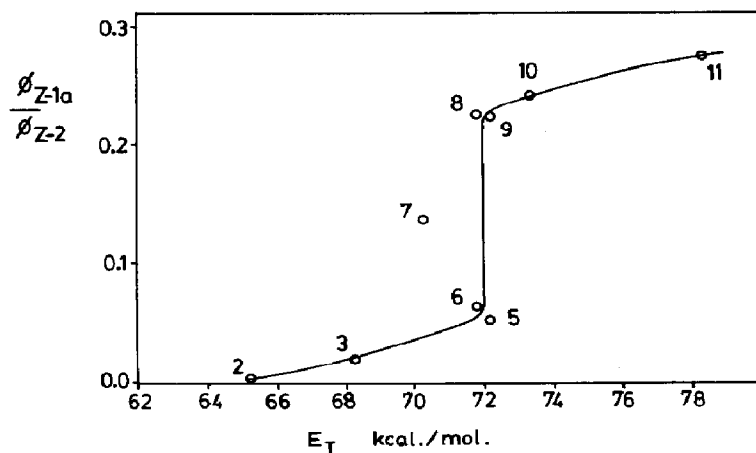


Fig. 3. Plot of relative quantum yield of sensitized formation of *cis* isomers of ester 1a and stilbene 2 against triplet energy of the sensitizer. The data point numbers refer to entries in Table 1.

mostly within 0.5 kcal mol<sup>-1</sup> of the reported values which are shown in parentheses in Table 1.

In Figs. 3 and 4 it can be seen that the efficiency of sensitization of both 1a and 1b relative to 2 diminishes at around 72 kcal mol<sup>-1</sup>, suggesting

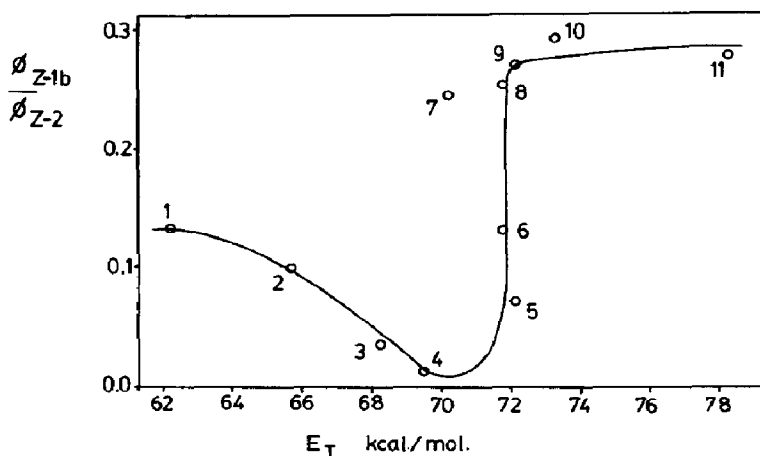


Fig. 4. Plot of relative quantum yields of formation of *cis* isomers of ketone 1b and stilbene 2 against triplet energy of the sensitizer. The data point numbers refer to entries in Table 1.

that the triplet energies of both compounds are in this vicinity. In both cases, if a deviant point corresponding to *p*-anisaldehyde (entry 7) is ignored, the triplet energies of 1a and 1b can be placed at  $72.0 \pm 0.5$  kcal mol<sup>-1</sup>.

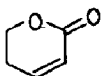
The anomalous entry 7 in Figs. 3 and 4 would appear to indicate that *p*-anisaldehyde acts as a sensitizer with a higher triplet energy than that determined by phosphorescence. Of the carbonyl-substituted aromatic sensitizers used in this work, *p*-anisaldehyde is the only one with a strongly electron-donating substituent directly conjugated with the carbonyl group and this might be expected to induce some charge transfer character into the excited state. If this is so, then it could explain the discrepancy evident in Figs. 3 and 4. The triplet energies of the sensitizers were determined from the position of the 0-0 band in the phosphorescence spectra recorded in ether at 77 K; at such a low temperature the dielectric constant of the solvent is increased substantially and this would stabilize a state possessing some degree of charge transfer relative to the ground state to which it is emitting and so lower the energy of the observed emission. In the case of *p*-anisaldehyde this would result in a triplet energy determined at 77 K which would be lower than the value at room temperature.

The anomalous result obtained with anisaldehyde as sensitizer could, in principle, also be explained by oxidation of the sensitizer during the irradiation, although anomalous results were not observed when benzaldehyde was used as the sensitizer. This explanation for the behaviour of anisaldehyde can be ruled out on several grounds. The irradiations were performed in sealed systems using solutions which had not been degassed. Thus the maximum concentration of oxygen initially present was around  $10^{-3}$  M compared with the sensitizer concentration of 0.16 M for both benzaldehyde and anisaldehyde. Even if all the oxygen present were consumed and resulted in oxidation of the anisaldehyde to form a species with a higher triplet energy capable of sensitization, this would be unlikely to yield sufficient material

to absorb light and to sensitize the reaction. This is supported by the observation of linear plots of the relative amounts of isomerization against time in all cases, including anisaldehyde, and by the fact that no products of oxidation of the aldehyde could be observed in the reaction mixture when it was examined for their presence by gas chromatography.

It can be seen in Fig. 4 for the ketone 1b that anomalous results are also obtained for the low energy sensitizers phenanthrene and biphenyl (entries 1 and 2 in Fig. 4). This is not seen for the ester 1a in Fig. 3. It appears that with these sensitizers the ketone is being sensitized quite efficiently, even though its triplet energy is concluded to be substantially higher than those of these sensitizers. This effect can be ascribed to singlet energy transfer from the sensitizer. Of the various mechanisms of singlet energy transfer which could be operating, the radiational ("trivial") mechanism appears to be the most probable here. Phenanthrene and biphenyl are the only sensitizers used in this work which fluoresce with any efficiency, and their emissions (346 nm for phenanthrene and 304 nm for biphenyl [12]) overlap at least partially with the absorption spectrum of the ketone ( $\lambda_{\max}$  of 294 nm tailing to 380 nm) but not at all with that of the ester ( $\lambda_{\max}$  of 220 nm tailing to around 260 nm). Förster or Dexter transfer would appear to be less likely since the singlet energies of phenanthrene and biphenyl (calculated as 83 kcal mol<sup>-1</sup> and 94 kcal mol<sup>-1</sup> respectively from the 0-0 band of their fluorescence emission) are lower than that of the ketone (97 kcal mol<sup>-1</sup>) determined from the position of the  $n \rightarrow \pi^*$  maximum in the absorption spectrum.

The value of the triplet energy determined for the ketone 1b is comparable with the values found from phosphorescence for cyclic enones such as cyclopentenone and cyclohexenone which are in the range 68 - 74 kcal mol<sup>-1</sup>, depending on substituents. Thus it would appear that the absence of the ring has little effect on the vertical excitation energy measured here, and that cyclic systems can be taken as models for the non-phosphorescing acyclic analogues for triplet energy estimation. For comparison, the phosphorescence spectrum of the cyclic ester 3



3

in ether at 77 K was also measured. This compound has a weak absorption at 242 nm (presumably  $n \rightarrow \pi^*$ ) together with strong absorption below 220 nm. Emission was seen at 410, 440 and 465 nm and, with the shortest wavelength band taken as the 0-0 transition, this ester therefore has a triplet energy of 70 kcal mol<sup>-1</sup> which is similar to that found for 1a.

The quantum yields of *E-Z* isomerization of  $\alpha,\beta$ -unsaturated ester and ketone 1a and 1b have been measured under sensitizing conditions and under conditions of direct irradiation [1, 2, 13]. It has been shown that the triplet excited states of these compounds decay almost exclusively by *E-Z* iso-



merization; under conditions of direct irradiation ketone 1b also decays exclusively by *E-Z* isomerization but in the case of ester 1a only about 50% of the excited states decay in this way [13]. It has been suggested that this could reflect the closer proximity of the  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  states in the ester compared with the ketone, which could enhance the rate of internal conversion, or that it could reflect a faster rate of intersystem crossing in the ketone compared with the ester [1, 2, 13]. The latter explanation is supported by the results obtained in this work which suggest that splitting between the singlet and triplet excited states for the ester 1a and ketone 1b are  $58 \text{ kcal mol}^{-1}$  and  $25 \text{ kcal mol}^{-1}$  respectively using values of the singlet excited state energy estimated from their absorption spectra of  $130 \text{ kcal mol}^{-1}$  for the ester and  $97 \text{ kcal mol}^{-1}$  for the ketone.

### 3. Conclusions

Using a simple competitive quenching technique in which the relative rates of sensitized isomerization of unsaturated carbonyl compound 1 and *trans*-stilbene 2 were measured, it has been shown that the ester 1a and the ketone 1b both have a triplet energy of  $72.0 \pm 0.5 \text{ kcal mol}^{-1}$ . Since the singlet energy of the ester is much higher than that of the ketone it is proposed that the lower efficiency of *E-Z* isomerization of the ester under direct irradiation can be attributed to a larger singlet-triplet splitting and hence slower intersystem crossing compared with the ketone.

### 4. Experimental details

#### 4.1. General details

Ester 1a was prepared by esterification of tiglic acid (Aldrich Chemical Co.) and purified by distillation followed by preparative gas chromatography (column, 6 ft  $\times$  1/4 in, of 5% SE30 on Chromosorb W at 68 °C). Ketone 1b (Aldrich Chemical Co.) was purified by distillation prior to use. Scintillation grade *trans*-stilbene (Eastman Kodak) was used as received. The triplet sensitizers were purified by distillation or recrystallization before use. The internal standards *n*-decane and *n*-octadecane (Aldrich) were used as received; *n*-hexyl acetate was prepared by Fischer esterification of acetic acid with hexanol and distilled prior to use.

The phosphorescence emission and excitation spectra of the sensitizers were recorded in diethyl ether solutions in Pyrex or quartz tubes (5 mm outside diameter) suspended in liquid nitrogen held in a quartz Dewar which was positioned in the sample chamber of a Perkin-Elmer MPF-4 emission spectrometer. The triplet energy of each sensitizer was determined from the position of the 0-0 band in the phosphorescence spectrum. The absorption spectra of the sensitizers and compounds 1a, 1b and 2 were recorded in diethyl ether using a Hewlett-Packard 8450 instrument.

#### 4.2. General irradiation procedure

A diethyl ether solution (12 ml) containing the ester **1a** or the ketone **1b** ( $2 \times 10^{-2}$  M), *trans*-stilbene ( $2 \times 10^{-3}$  M), accurately known amounts of internal standards octadecane, *n*-decane (in the case of the ester) or *n*-hexyl acetate (in the case of the ketone) and the sensitizer was irradiated until conversion of the ester or ketone and the stilbene had reached 5% - 6%. Irradiations were performed using a low pressure mercury lamp which emitted essentially all its light at 254 nm. The lamp was housed in a quartz tube and immersed in the solution to be irradiated in such a manner that all the emitted light entered the solution. The solution undergoing irradiation was housed in a vessel which was suspended in a thermostatted water bath maintained at a temperature of 21 °C. The solution undergoing irradiation was not degassed or purged to eliminate oxygen, but was sealed against the atmosphere to prevent solvent loss or uptake of extra oxygen. The progress of the isomerization of the ester **1a**, the ketone **1b** and *trans*-stilbene relative to the internal standards was followed by gas chromatography of very small aliquots of the irradiation mixtures removed using syringe techniques. *trans*-Stilbene was analysed on a 15 m Megabore DB-1 column (J&W Scientific Inc.) at 160 °C using octadecane as an internal standard. Ester **1a** was analysed on the same column, but at 70 °C, using decane as the internal standard. Ketone **1b** was analysed on a column of 20% diethylene glycol on Chromosorb W (8 ft  $\times$  1/8 in) at 110 °C using hexyl acetate as internal standard. Peak areas were measured using a Hewlett-Packard 3390A electronic integrator. Calibration curves were prepared for the internal standards and compounds *E*-**1a**, *E*-**1b** and *E*-**2**, and it was assumed that the response factors of the gas chromatograph flame ionization detector were the same for the *Z* isomers. The absorption spectra of the ester **1a**, the ketone **1b**, *trans*-stilbene and the sensitizer were recorded and used to determine the sensitizer concentrations necessary to ensure that all the incident light was absorbed by the sensitizer and none by the ester **1a**, or the ketone **1b**, or the *trans*-stilbene **2**.

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