Photochemical Properties of *cis*- and *trans*-1,2-Diphenylethenyltrimethyltin(IV) and *cis*-1,2-Diphenylpropenyltrimethyltin(IV): Organometallic Derivatives of Stilbene †

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Upon direct u.v. irradiation in cyclohexane, benzene, alcohol, or chloroform solution, [Sn(CPh=CHPh)Me$_3$] (1) undergoes *cis-trans* isomerization about the olefin double bond as the only efficient reaction. No evidence has been found for either homolytic or heterolytic photocleavage of the Sn–C bond as a primary process. Unusually for stilbenes the photostationary state reached on irradiation (313 nm) is rich in the *trans* isomer (the ratio *cis*:*trans* is 27:73 in cyclohexane), because of the higher absorption coefficient of the *cis* isomer at this wavelength. Isomerization may also be induced following energy transfer from organic sensitizers. Similar results have been observed for [Sn(CPh=CMePh)Me$_3$] (2).

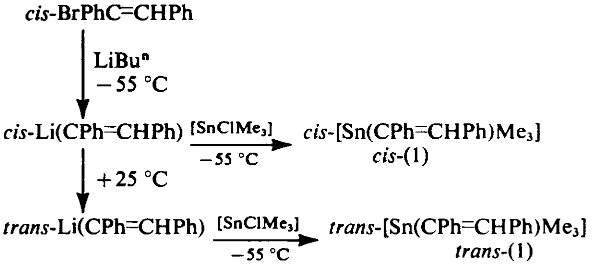
The predominant photochemical reaction of most organometallic compounds which contain a metal–carbon σ bond is homolytic cleavage of that bond.[1,2] Most such studies have been carried out on the photoreactions of metal alkyls and aryls, and much less is known about compounds containing metal–alkenyl σ bonds M–CR^1=CR^{2}R^3. In such compounds it is possible that reactions characteristic of the olefinic group may compete with those involving the M–C bond. Thus while it has been shown that the M–C bond is cleaved upon irradiation of transition metal alkenyl compounds such as [Zr(CPh=CMe$_2$)$_2$(η-C$_5$H$_5$)$_2$],[3] it is also known that alkenyl complexes of tin may undergo photoisomerization and cyclization.[4–6] In this paper we present details of a study of the photochemistry of *cis*- and *trans*-[Sn(CPh=CHPh)Me$_3$] and [Sn(CPh=CMePh)Me$_3$]. These compounds may be considered as organometallic derivatives of stilbene, a molecule which has been and continues to be of great interest to photochemists,[7–10] and the present study aims to show how the photochemical properties of stilbene are affected by a bulky, heavy-atom-containing substituent, namely trimethyltin.

Results

Synthesis and Spectroscopic Properties of cis- and trans-[Sn(CPh=CHPh)Me$_3$] (1) *and cis*-[Sn(CPh=CMePh)Me$_3$] (2).—The two isomers of (1) were prepared by reaction of 1). To obtain isomerically pure *cis*-(1) it is important that the [SnClMe$_3$] with either *cis*- or *trans*-Li(CPh=CHPh) (Scheme reaction is carried out at temperatures less than −50 °C as *cis*-Li(CPh=CHPh) isomerizes at temperatures greater than this.[11] Indeed *trans*-Li(CPh=CHPh) may be prepared in 100% yield by warming the *cis* isomer, and this was the preferred route to this material for our studies.

As the sharp signals of the SnMe$_3$ protons of each isomer are clearly separated, proton n.m.r. is a particularly useful technique for determining the isomeric purity of the complexes and for studying their isomerization (see below). The stereochemistry of the organotin compounds was confirmed by their reaction with HCl in CDCl$_3$[equation (i)]; it is known that cleavage of the Sn–C bond proceeds with retention of configuration under these conditions.[12]

$$\textit{trans}\text{-}[\mathrm{Sn(CPh{=}CHPh)Me_3}] + \mathrm{HCl} \longrightarrow \textit{trans}\text{-}\mathrm{PhHC{=}CHPh} + [\mathrm{SnClMe_3}] \quad \text{(i)}$$



Scheme 1. Preparation of *cis*-(1) and *trans*-(1)

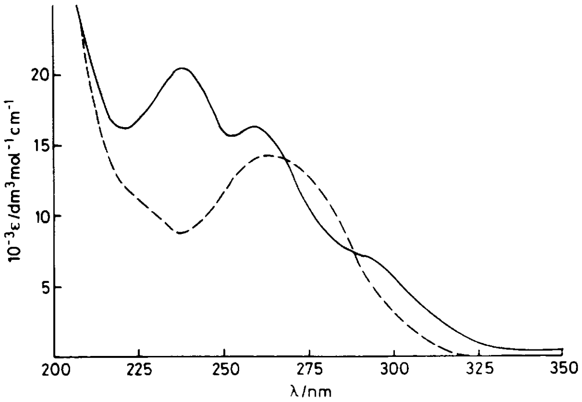


Figure 1. Absorption spectra of (——) *cis*-[Sn(CPh=CHPh)Me$_3$] and (— — —) *trans*-[Sn(CPh=CHPh)Me$_3$] in cyclohexane

The u.v. absorption spectra of the isomers are shown in Figure 1. Particular care was taken to ensure that the complexes were substantially free from traces of stilbenes and tetraphenylbutadienes, which were present in some crude samples and which gave rise to extra absorption, particularly at λ > 300 nm. The absorption spectra of the compounds are essentially similar in cyclohexane, alcohols, or chloroform. The isomers (1) emit only weakly at room temperature [Φ_f < 0.01], and it is probable that even this weak luminescence is due to traces of fluorescent impurities (*e.g.* *trans*-stilbene or tetraphenylbutadiene).

The u.v. absorption spectra of the organotin compounds may be compared with those of other substituted ' stilbenes '

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† *Non-S.I. unit employed*: 1 Torr = (101 325/760) Pa.

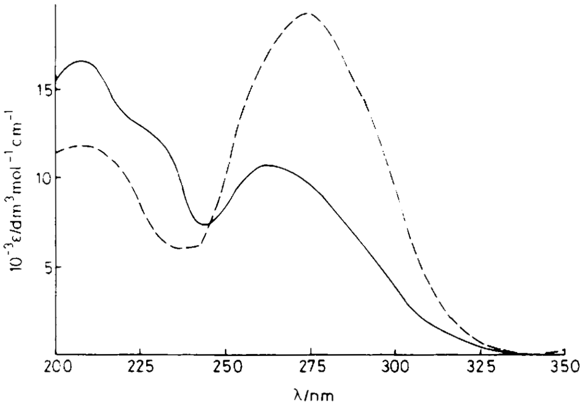


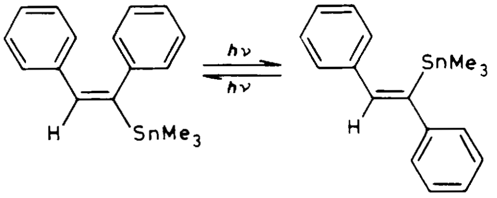
Figure 2. Absorption spectra of (——) *cis*-PhMeC=CHPh and (- - - -) *trans*-PhMeC=CHPh in cyclohexane

(*e.g.*, *cis*- and *trans*-1,2-diphenylpropene: Figure 2). The spectra of *trans*-(1) and *cis*- and *trans*-PhMeC=CHPh are typical of ' hindered stilbenes ', where steric interactions force the phenyl rings out of the plane of the double bond in the ground state and also induce non-planarity of the central double bond in the excited state.[13–15] It is predicted that the conjugation band should shift to shorter wavelength as the steric interaction increases, and our observation that $\lambda_{max.}$ for *trans*-(1) is at 264 nm, while those for *trans*-PhMeC=CHPh and *trans*-PhHC=CHPh are at 273 and 295 nm respectively, is consistent with this. The spectrum of *cis*-(1) departs somewhat from the established pattern. Thus although the band at 236 nm may be assigned to the phenyl-localised ($^1H^+ \leftarrow {}^1A$) transition and that at 255 nm to the conjugation band (at 260 nm in *cis*-PhMeC=CHPh), the band giving rise to a pronounced shoulder at *ca.* 295 nm has no counterpart in *cis*-PhMeC=CHPh. The possibility that this band is due to impurities has been carefully considered. Indeed crude samples did contain compounds absorbing at this wavelength but steps were taken to ensure that these were eliminated. Furthermore, as discussed below, the band at 295 nm both disappears upon photolysis of *cis*-(1) and appears upon irradiation of *trans*-(1) and the photostationary state obtained from either isomer is identical, observations that are difficult to explain in terms of an impurity. It is possible that the long-wavelength band may be the result of a transition involving the tin atom and possibly charge transfer in nature, but it is not clear why such a band would not be observed in *trans*-(1). Vanderlinden and Boué [5] have discussed such an assignment for the long-wavelength band in 2-trimethylstannylbuta-1,3-diene. It should be noted, however, that steric interactions in *cis*-(1) are expected to be large and it is possible that this long-wavelength band may be characteristic of such ' strongly hindered ' *cis*-stilbenes. For example, the spectrum of PhMeC=CMePh exhibits long-wavelength absorption.[13,15] A definitive assignment of this band in *cis*-(1) is therefore impossible at present, and further experimental studies including low-temperature spectra will be needed before this matter can be clarified. The presence of this band in *cis*-(1) but not in *trans*-(1) means that the *cis* compound absorbs more strongly than the *trans* at wavelengths greater than 300 nm, and this has important consequences for the photochemical studies reported in the next section.

The absorption spectrum of *cis*-[Sn(CPh=CMePh)Me$_3$] [*cis*-(2)] shows a maximum at 235 nm (probably the phenyl-localised transition) and a pronounced shoulder at *ca.* 285 nm [probably a band similar to that observed at *ca.* 295 nm for *cis*-(1)]. The conjugation band does not appear as a distinct peak but rather as a shoulder on the band at 235 nm, in agreement with the predicted shift to shorter wavelength of this type of band with increasing steric interaction. The *trans* isomer of (2) was not isolated but it is clear from the photochemical studies reported below that its absorbance at wavelengths greater than 280 nm is much less than that of *cis*-(2) (*e.g.* at 313 nm, $\varepsilon_{cis} : \varepsilon_{trans} = ca.\ 4$).

Photoisomerisation of cis- and trans-[Sn(CPh=CRPh)Me$_3$] (R = H *or* Me).—The photochemical reactions of (1) have been studied in cyclohexane, perdeuteriobenzene, deuteriochloroform, perdeuteriomethanol, and isopropyl alcohol using both u.v. spectrophotometry and n.m.r. spectroscopy to follow the reaction.

Irradiation (313 nm) of argon-flushed C_6D_6 solutions of *trans*-(1) (*ca.* 1×10^{-2} mol dm^{-3}) contained in n.m.r. tubes led to a reduction of the ^{1}H signal (δ 0.03 p.p.m.) of the SnMe$_3$ protons of *trans*-(1) and the appearance of signals (δ 0.18 p.p.m.) attributable to the SnMe$_3$ protons of *cis*-(1). Similarly, irradiation of C_6D_6 solutions of *cis*-(1) led to the formation of *trans*-(1). In neither case were other products observable so long as the solutions were carefully degassed. Changes in the u.v. spectrum following 313 nm irradiation of *cis*-(1) [9.16×10^{-5} mol dm^{-3}] in argon-flushed cyclohexane solution were monitored. Clean isosbestic points are present at 263.5 and 291.0 nm, indicating that secondary photoreactions or other side reactions are insignificant.* An identical final spectrum is obtained by irradiation of pure *trans*-(1) or of mixtures of the two isomers. These spectroscopic changes are entirely consistent with the hypothesis that irradiation is inducing *cis*–*trans* isomerization [equation (ii)]. Analysis of the optical density changes indicate that the final photostationary state occurs at *cis*-(1):*trans*-(1) of (27.3 ± 0.8) : (72.7 ± 0.8). The quantum yields of isomerization are listed in Table 1, along with those observed for stilbene and 1,2-diphenylpropene. The quantum yields found for the organotin compounds may be seen to be similar to those reported for the organic stilbenes. The substitution of a trimethyltin group, therefore, appears to result in no major change in the isomerization efficiency presumably indicating no major change in reaction pathways.



cis-(1) *trans*-(1)

(ii)

The course of the reaction induced by 313 nm irradiation of *trans*-(1) in CD$_3$OD was monitored by ^{1}H n.m.r. and that in Pr^{i}OH by u.v. spectrophotometry. In both cases isomerization was the only reaction noted and in Pr^{i}OH clean isosbestic points were recorded (Figure 3). In particular, no *trans*-stilbene was formed during the photoreaction in either solvent. Stilbene should be produced if free stilbenyl radicals are formed on photolysis as these would be expected to abstract hydrogen atoms from the alcohol solvent. It may therefore be deduced that the quantum yields for both light-induced homolytic

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* If the solutions are not purged free of oxygen, extra absorption is noted in the 240—260 nm region and clean isosbestic points are not recorded. This observation is probably due to the production of small amounts of phenanthrene derivatives by cyclisation and oxidation of *cis*-(1).

Table 1. Comparison of the quantum yields for isomerization by 313 nm irradiation of some substituted stilbenes

Compound	Solvent	$\Phi_{trans\rightarrow cis}$	$\Phi_{cis\rightarrow trans}$
[Sn(CPh=CHPh)Me$_3$] (1)	Cyclohexane	0.46 ± 0.04	0.52 ± 0.08
PhMeC=CHPh [a]	Cyclohexane	0.51	0.43
PhHC=CHPh [b]	Methylcyclohexane–2-methylpentane	0.50	0.35

[a] Ref. 24. [b] Ref. 23.

Table 2. Photostationary state (p.s.s.) reached on sensitized isomerization of [Sn(CPh=CHPh)Me$_3$] (1) and [Sn(CPh=CMePh)Me$_3$] (2)

Sensitizer	E_T/kJ mol^{-1}	[sens]/mol dm^{-3}	[(1), (2)]/mol dm^{-3}	% *cis* (p.s.s.)
(*a*) [Sn(CPh=CHPh)Me$_3$]				
Acetophenone	308	0.02—0.20	0.01—0.13	44
Benzophenone	287	0.05—0.11	0.011—0.015	43
Fluorene	285	0.05	0.015	52
Fluorenone	223	0.01—0.05	0.008—0.030	72
Benzil	224	0.05—0.15	0.015—0.034	44
Benzanthrone	193	0.013	0.015	62
(*b*) [Sn(CPh=CMePh)Me$_3$]				
Benzophenone	287	0.05	0.01	12
Fluorenone	223	0.04	0.01	42

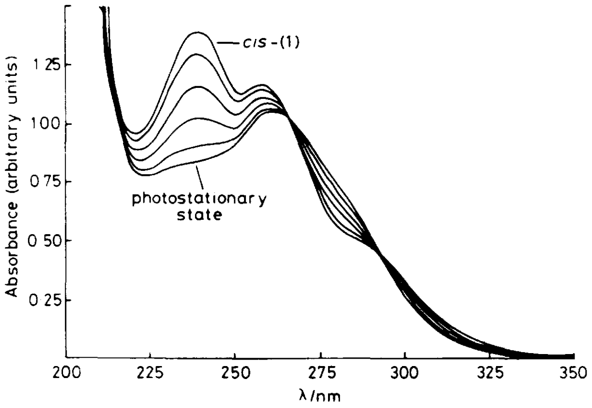

Figure 3. Changes in the absorption spectra of *cis*-[Sn(CPh=CHPh)Me$_3$] (6.95 × 10^{-5} mol dm^{-3}) in isopropyl alcohol upon irradiation with u.v. light (313 nm)

cleavage [reaction (iii)] and photosolvolysis [reaction (iv)] are negligible compared with those for isomerization.

$$[Sn(CPh{=}CHPh)Me_3] \xrightarrow{h\nu} Me_3Sn\cdot + \cdot CPh{=}CHPh \qquad (iii)$$

$$[Sn(CPh{=}CHPh)Me_3] + ROH \xrightarrow{h\nu} Sn(OR)Me_3 + PhHC{=}CHPh \qquad (iv)$$

A photostationary state of *cis* : *trans* of (27 ± 3) : (73 ± 3) was achieved upon 313 nm irradiation of *cis*- and *trans*-(1) in CDCl$_3$, the reaction being monitored by ^{1}H n.m.r. Less than 1% [SnClMe$_3$] or other Me$_3$Sn$^-$complexes are formed during the irradiation period required to reach this photostationary state.* This may also be taken as evidence for the low efficiency of homolytic cleavage reaction (iii) because the radical products formed by such a process would be scavenged by chloroform giving [SnClMe$_3$] and PhXC=CHPh [X = Cl, H, or D] as found with [M(CPh=CMe$_2$)$_2$(η^5-C$_5$H$_5$)$_2$] (M = Ti [16] or Zr [3]).

The isomerization of (1) may also be induced by transfer of energy from triplet state sensitizers. The reaction was most conveniently followed by ^{1}H n.m.r., as by this method the relative concentrations may be readily assayed in the presence of sensitizers, and the necessity to separate the isomers and the sensitizers is obviated. Reactions were carried out in argon-flushed C$_6$D$_6$ solution. Under the conditions employed (365 nm excitation) a negligible amount of light is absorbed by (1). As is well known for stilbene and its derivatives,[7,17] the ratio of isomers in the photostationary mixture is dependent on the triplet energy of the sensitizer (see Table 2). No evidence for dependence of the composition of the photostationary mixture on the concentrations of (1) or of the sensitizer was found. Approximate values for the quantum yield of isomerization sensitized by benzophenone were determined, by comparing the rate of isomerization of (1) with that of PhMeC=CHPh under identical conditions and monitoring the isomers by ^{1}H n.m.r. The approximate values obtained are $\Phi_{trans\rightarrow cis}$ = 0.46 ± 0.05 and $\Phi_{cis\rightarrow trans}$ = 0.61 ± 0.06, which may be compared with values for PhMeC=CHPh of $\Phi_{trans\rightarrow cis}$ = 0.54 and $\Phi_{cis\rightarrow trans}$ = 0.44.[17]

Although the photochemistry of [Sn(CPh=CMePh)Me$_3$] (2) has not been studied in the same detail as that of [Sn(CPh=CHPh)Me$_3$] our preliminary studies reveal that again photoisomerization is the only observable photoreaction. Thus irradiation (313 nm) of *cis*-(2) in C$_6$D$_6$ (*ca.* 1 × 10^{-2} mol dm^{-3}) results in a steady-state mixture, which was shown by ^{1}H n.m.r. integration to contain 5 ± 2% *cis*-(2) and 95 ± 2% *trans*-(2). This result was confirmed by demonstrating that decomposition of the photolysed solution by HCl gave a mixture of PhMe=CHPh isomers containing more than 90% of the *trans* species. Similarly, 313 nm irradiation of cyclohexane solutions of *cis*-(2) (6.97 × 10^{-5} mol dm^{-3}) gave a clean reaction in which the band at 235 nm decreased in intensity while sharp isosbestic points were observed at 229, 250, and 261 nm. Isomerization was also induced *via* energy transfer from organic sensitizers (benzophenone, fluorenone, and benzil), the reaction being monitored by ^{1}H n.m.r. The photostationary states found were *cis* : *trans* of 12 : 88 for benzophenone and 42 : 58 for fluorenone. [Sensitization with

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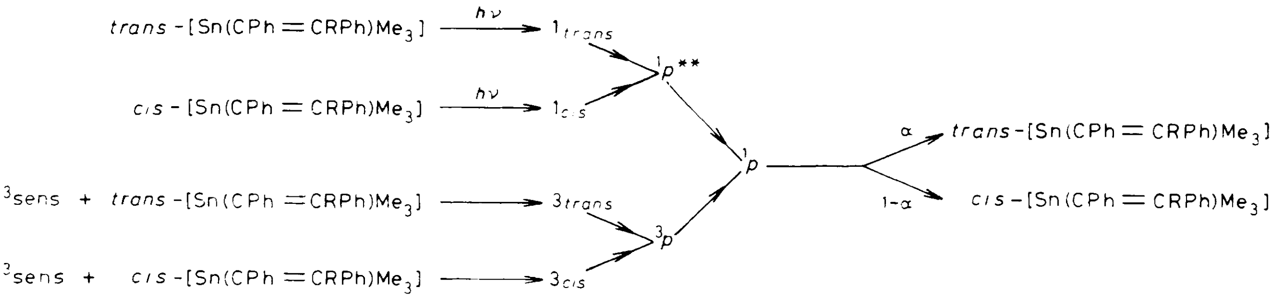
* In some samples, prolonged irradiation beyond the photostationary state led to the formation of some [SnClMe$_3$]. The mechanism for the formation of this material is not certain.



Scheme 2. Possible mechanism for photoinduced *cis–trans* isomerization of [Sn(CPh=CRPh)Me$_3$] (R = H or Me); sens = sensitizer

benzil led to the generation of secondary products as well as *trans*-(2).]

Discussion

The evidence presented here indicates that the predominant photoreaction of complexes (1) and (2) is *cis–trans* isomerization. No definite evidence for photoinduced homolysis or heterolysis of the Sn–C bond has been found, and the quantum yields for these processes are certainly low (<0.01). In this respect these complexes differ from simpler tin alkyls, aryls, and vinyls, where it is known that cleavage of the Sn–C bond occurs on irradiation.[18,19] It should be noted, however, that many of these reported reactions were carried out in the gas phase, and under these conditions the excited state will retain substantial amounts of vibrational energy for extended periods after excitation. It is also probable in these cases that the lowest-lying excited state is one in which the Sn–C bond is weaker than in the ground state (in some cases, indeed, that it is σ–σ^* Sn–C). For compounds (1), (2), and others [4–6] where the Sn–C bond remains intact on irradiation, it is probable that the excited state reached following excitation is essentially ligand localised, and therefore the weakening of the metal–carbon bond is slight. A possible exception to this generalisation is the photodestannylation of trimethyl(1-naphthyl)tin in methanol or cyclohexane–acetic acid, where the lowest excited state is apparently centred on the naphthyl group.[20] However, in this case also the quantum yield is rather low ($<0.5 \times 10^{-3}$).

The photoreactions of complexes (1) and (2) may therefore best be considered as those of α-substituted stilbenes. The SnMe$_3$ group might, however, be expected to influence the properties of the stilbene excited state both *via* steric interactions and by mixing of spin states *via* spin–orbit coupling due to the heavy tin atom. It is now generally accepted that the isomerization of *cis*- or *trans*-stilbene induced by direct u.v. irradiation takes place from the lowest singlet excited state of *cis*- or *trans*-stilbene, passing through a twisted excited state $^1p^{**}$, which appears to be the perpendicular form of a doubly excited state,[21] and then to the twisted form of the ground state (^1p).[8] Sensitized isomerization proceeds through the ^3p state. For some stilbenes substituted in the *para*-position of the phenyl ring it has been shown that the triplet state of the stilbene is the active species in the isomerization induced by direct irradiation.[22] The same general mechanism is proposed for a 1,2-diphenylpropene (α-methylstilbene) as for stilbene,[17,23,24] although to the best of our knowledge there is no definitive study on the spin multiplicity of the excited state responsible for the direct radiation-induced isomerization. We shall therefore consider the experimental results obtained with (1) and (2) assuming the mechanism shown in Scheme 2.

As the isomers of (1) are essentialy non-fluorescent and if it is assumed that there is no deactivation of the excited states which does not pass through ^1p we may derive that $\Phi_{cis\rightarrow trans} = \alpha$ and $\Phi_{trans\rightarrow cis} = 1 - \alpha$. The experimental values (0.52 and 0.46 respectively) sum, within experimental error, to unity as predicted, and allow a value of $\alpha = 0.53$ to be calculated. The concentration of *cis* and *trans* isomers present under photoequilibrium conditions is given by equation (v).

$$\frac{[\text{cis}]_\infty}{[\text{trans}]_\infty} = \left(\frac{\varepsilon_{trans}}{\varepsilon_{cis}}\right)\left(\frac{1-\alpha}{\alpha}\right) \qquad (v)$$

At 313 nm $\varepsilon_{trans}/\varepsilon_{cis} = 0.50$ giving a predicted *cis* : *trans* ratio of 30.6 : 69.4, within error of that calculated experimentally (27.3 : 72.7). Thus the experimental results are consistent with the mechanism presented in Scheme 2. It should be stressed, though, that no evidence has been obtained in our study which identifies the excited state responsible for the direct isomerization of (1). It might reasonably be argued that the increased spin–orbit coupling of the tin atom would increase the rate, and thus the efficiency, of the intersystem crossing, to the triplet manifold, and hence that the ^3p state rather than the $^1p^{**}$ state would be the species which forms ^1p. More detailed studies, including investigations of the effect of viscosity and low temperature on the quantum yields for isomerization would be required to clarify this point. Our preliminary studies with *cis*-[Sn(CPh=CMePh)Me$_3$] (2) show that direct irradiation produces a photostationary state containing 95% *trans*-(2). As the *trans* complex was not separately synthesised, no value for its absorption coefficient at 313 nm has been determined independently. However, it was observed that upon irradiation in cyclohexane the optical density at 313 nm of the photostationary state was only 30% of that of the starting *cis* compound, which would give a ratio of $\varepsilon_{cis}/\varepsilon_{trans}$ of *ca.* 4 if it is assumed that the absorbance is solely due to the isomers of (2). If this value of the absorption coefficient ratio is used in equation (v), a value for α of *ca.* 0.83 is obtained. Such a value would be quite unusually high for substituted stilbenes where most reported values are *ca.* 0.5. However, it is possible that ε_{trans} at 313 nm is less than that derived above as small amounts of strongly absorbing impurities would seriously distort the calculated value, and if this were the case, then the deduced value of α would be lower and more normal.

The sensitization experiments demonstrate that the triplet states of (1) and (2) undergo isomerization. As in the cases of stilbene and α-methylstilbene [17] a photostationary state is reached which depends on the energy of the sensitiser triplet state. With high-energy sensitisers such as benzophenone or acetophenone the photostationary state from (1) contains *ca.* 44% of the *cis* isomer. The quantum yield determined for benzophenone-sensitised conversion of *trans*-(1) to *cis*-(1) was 0.46 ± 0.05 and that for *cis*-(1) to *trans*-(1) was 0.61 ± 0.06. Within errors these sum to unity, and if the assumption is made that both isomerizations involve a common twisted triplet intermediate (^3p), then it may be calculated that 43% of these species yield *cis*-(1) while 57% give *trans*-(1). These values may be compared with the corresponding figures derived above for the twisted excited state assumed to be formed by direct irradiation [*i.e.* 47% giving *cis*-(1) and 53% giving *trans*-(1)]. The closeness of these derived quantities (certainly within experimental error) would be consistent with a common intermediate (*e.g.*, ^1p of Scheme 2) on both the direct and sensitised reaction routes. With lower-energy sensitisers (*e.g.*, fluorenone, E_T = 223 kJ mol^{-1}) the photostationary state is rich in the *cis* isomer, implying that the rate of energy transfer to *cis*-(1) is lower than that to *trans*-(1). This is presumably because E_T for *cis*-(1) is greater than that for fluorenone, and again this behaviour is very similar to that observed for stilbene and α-methylstilbene. The sensitization of *cis*-(2) with benzophenone or fluorenone gives results which are strikingly different from those of (1) or other stilbenes. In this case the high-energy sensitizer yields a photostationary state which contains 12% *cis*-(2) and 88% *trans*-(2). This result either implies that E_T for *trans*-(2) lies above that of benzophenone (E_T = 287 kJ mol^{-1}) or that the common triplet excited state of the isomers of (2) yields 88% *trans*-(2). This conclusion may be compared with that derived from the direct irradiation experiments, where by making the assumption of an absorption coefficient ratio of 4, it was calculated that the ^1p state gives 83% *trans*-(2). Such a partition would be quite unusual for stilbenes, and further experiments starting with pure *trans*-(2) should be made to test this hypothesis.

Experimental

Benzil, phenanthrene, fluorene, fluorenone, anthracene, and benzophenone were reagent grade materials and were twice recrystallized. Acetophenone (reagent grade) was distilled (10 Torr, 79 °C). Solvents for synthetic work were freshly distilled from sodium or potassium. [$^2H_6$]Benzene (Merck) was distilled from, and stored over, calcium hydride. Spectroscopic grade cyclohexane (B.D.H.) was used as received. Other materials were reagent grade and used as received. *cis*-1-Bromo-1,2-diphenylethene and *N*-bromopyridinium bromide were prepared following the method of Fieser.[25] ^{1}H N.m.r. spectra were recorded on JEOL JMX 60, Bruker WP60, or Bruker WP80 spectrometers. U.v.-visible spectra were recorded on either Perkin-Elmer 402 or Unicam SP8-200 spectrometers. I.r. spectra were recorded on Perkin-Elmer 599 or 298 spectrometers.

trans-1,2-*Diphenylpropene*.—Acetophenone (117 cm^3, 1.0 mol) in diethyl ether (400 cm^3) was added dropwise over 3 h to a solution of benzylmagnesium chloride prepared by addition of a solution of benzyl chloride (115 cm^3, 1.0 mol) in ether (300 cm^3) to magnesium turnings in ether (600 cm^3). After treatment with aqueous ammonium chloride (1 dm^3 of a 5 mol dm^{-3} solution) the ether layer was separated, and washed successively with aqueous ammonium chloride solution (5 mol dm^{-3}), 5% aqueous sodium bicarbonate solution, and water. After drying over magnesium sulphate, the ether was distilled off at atmospheric pressure. While still warm, a sulphuric acid–acetic solution (1 : 4, 200 cm^3) was added. The resulting solution was stirred for 1 h, although the reaction appeared to be almost instantaneous. The olefin was extracted with ether (600 cm^3) and then washed with water, 5% potassium bicarbonate solution, and again with water. After drying with magnesium sulphate the ether was removed under reduced pressure. The crude product was dissolved in ethanol (150 cm^3) and recrystallised at room temperature yielding *trans*-PhMeC=CHPh as white crystals (80 g, 0.41 mol), m.p. 77 °C. ^{1}H N.m.r. spectra agreed with published values.[26]

meso-1,2-*Dibromo*-1,2-*diphenylpropane*.—*N*-Bromopyridinium bromide (49.5 g, 0.21 mol) in acetic acid (150 cm^3) was added to *trans*-PhMeC=CHPh (20 g, 0.10 mol) dissolved in carbon tetrachloride (200 cm^3), and the mixture was stirred vigorously for 30 min. Upon standing the solution yielded white crystals of *meso*-BrPhCH–CMePhBr (17.9 g 0.050 mol), m.p. 128 °C. ^{1}H N.m.r. (CCl_4) : δ 2.33 (s, 3 H), 5.57 (s, 1 H), 7.1—7.5 (m, 10 H), in agreement with one of the isomers obtained by Friedrich *et al.*[26]

cis-1-*Bromo*-1,2-*diphenylpropene*.—*meso*-BrPhCH–CMePh-Br (17.0 g, 0.048 mol) was added to a solution of KOH (7.0 g, 0.123 mol) in ethanol (200 cm^3) and refluxed overnight. Filtration of the solution removed unreacted starting material. The filtrate was pumped to dryness and dissolved in hexane (20 cm^3). Cooling to −25 °C yielded white crystals of *cis*-PhMeC=CPhBr (8.8 g, 0.032 mol), m.p. 54—56 °C. The ^{1}H n.m.r. spectrum was in agreement with that in the literature.[26]

(cis-1,2-*Diphenylethenyl*)*trimethyltin*.—*cis*-1-Bromo-1,2-diphenylethene (6.05 g, 0.023 mol) in ether–benzene (3 : 1, 60 cm^3) was cooled to −55 °C. n-Butyl-lithium (13.3 cm^3 of a 1.74 mol dm^{-3} hexane solution, 0.023 mol) was quickly added and the solution stirred (5 min). A solution of chlorotrimethyltin (4.62 g, 0.023 mol) in ether–benzene (3 : 1, 60 cm^3) was added over 5 min, the temperature being maintained at −55 °C. The mixture was stirred at this temperature (2 h), and then poured into aqueous ammonium chloride (500 cm^3 of a 1 mol dm^{-3} solution). The organic layer was separated, washed with water until all chloride was removed, and dried over sodium sulphate. The ether was removed under vacuum, yielding *cis*-[Sn(CPh=CHPh)Me$_3$] (6.62 g, 0.20 mol) as a colourless oil. The crude product was purified on a Florisil column using hexane as eluant. This treatment removed all impurities present from the preparation but caused a slight (5%) decomposition to *cis*-stilbene. The material so obtained was then introduced into a sublimation apparatus and the *cis*-stilbene removed by pumping at 40 °C (0.001 Torr) (Found: C, 59.5; H, 6.0. $C_{17}H_{20}Sn$ requires C, 59.55; H, 5.85%). ^{1}H N.m.r. ($CDCl_3$): δ 0.17 [9 H, $J(^{119}Sn\text{–}H)$ = 54.3, $J(^{117}Sn\text{–}H)$ = 51.7 Hz], 7.07 (s, 1 H), 7.2—7.3 (m, 10 H). U.v. (cyclohexane): λ(log ε) 236 (4.31), 255 nm (4.20). I.r. (neat): 510m, 582vs, 698vs br, 765vs br, 931m, 1 030m, 1 070m, 1 335m, 1 445—1 450s, 1 490—1 495s, 1 600m cm^{-1}.

(trans-1,2-*Diphenylethenyl*)*trimethyltin*.—This was prepared in an analogous manner to the *cis* isomer, except that the Li(CPh=CHPh) was warmed to 25 °C (2 h) and then recooled to −55 °C before the chlorotrimethyltin was added, affording crude *trans*-[Sn(CPh=CHPh)Me$_3$] (83%). Recrystallisation from hexane at −20 °C failed to eliminate an impurity which absorbed at λ ⩾ 300 nm. However, sublimation yielded a sample whose u.v. spectrum indicated that this impurity had been removed (Found: C, 59.1; H, 6.0. $C_{17}H_{20}Sn$ requires C, 59.55; H, 5.85%). ^{1}H N.m.r. ($CDCl_3$): δ 0.015 [9 H, $J(^{119}Sn\text{–}H)$ = 54.6, $J(^{117}Sn\text{–}H)$ = 52.2 Hz], 7.29—7.34 (m, 10 H), 7.45 (s, 1 H). U.v. (cyclohexane): λ(log ε) 264 nm (4.16). I.r. (KBr): 425s, 488m, 525s br, 545s, 565s, 695s br, 760s vbr, 882s, 910s, 930s, 978m, 1 026s, 1 072s, 1 285—1 290s, 1 445m, 1 490m br, 1 575m, 1 595m cm^{-1}.

(cis-1,2-*Diphenylpropenyl*)*trimethyltin*.—n-Butyl-lithium (3 cm^3 of a 1.6 mol dm^{-3} hexane solution, 0.0048 mol) was added to *cis*-1-bromo-1,2-diphenylpropene (1.207 g, 0.0049 mol) in ether–benzene (3 : 1, 20 cm^3) at −55 °C. Chlorotrimethyltin (0.0908 g, 0.0046 mol) in ether–benzene (3 : 1, 10 cm^3) was added to the mixture (5 min). After stirring for a further 2 min the solution was poured into ammonium chloride (500 cm^3 of a 1 mol dm^{-3} solution), and worked-up as above. The crude material was dissolved in ether (3 cm^3) and methanol added (*ca.* 2 cm^3) until the solution went cloudy. Cooling to −80 °C yielded white crystals of [Sn(CPh=CMePh)Me_3] (0.70 g, 0.175 mol) (Found: C, 60.85; H, 6.40. $C_{18}H_{22}Sn$ requires C, 60.55; H, 6.20%). ^1H N.m.r. (C_6D_6): 0.21 [9 H, $J(^{119}Sn-H)$ = 53.1, $J(^{117}Sn-H)$ = 51.0], 2.23 [3 H, $J(^{119}Sn-H)$ = 11.4 Hz], 6.88—7.02 (m, 10 H). U.v. (cyclohexane): λ (log ε) 235 nm (4.29). I.r. (KBr): 508s, 522vs, 570m, 600m, 622br, 697vs, 745m, 862—875vs, 905m, 1 025m, 1 070m br, 1 190m, 1 262m, 1 375m, 1 450s, 1 488s, 1 570m, 1 600s cm^{-1}.

Photolysis Conditions.—The light source was either a Thorn MED 250 or a Phillips HPK 125 medium-pressure mercury lamp, and the 313 or 365 nm emissions were isolated using either chemical filters or an Applied Photophysics high-radiance monochromator, employing 5-nm slits.

Samples for the determination of quantum yields of (1) and (2) upon direct irradiation (*ca.* 1×10^{-4} mol dm^{-3} in cyclohexane) were outgassed with either nitrogen or argon for 30 min. Light intensity was measured using potassium ferrioxalate actinometry.[27,28] The samples absorbed *ca.* 20% at the excitation wavelength. On average, five measurements were made during each photolysis, during which time *ca.* 10% conversion occurred. The percentage conversion was calculated from the optical density change at 234 nm. No correction was made for the back reaction; however, the percentage light absorbed by the photoproduct was included. As a check of the above procedure the quantum yield for formation of *cis*-stilbene from *trans*-stilbene in cyclohexane was evaluated. This was determined as 0.50 ± 0.03, in agreement with the generally accepted values.[7,23] Benzophenone-sensitized quantum yields were determined for argon-outgassed C_6D_6 solutions that were 4.75×10^{-2} mol dm^{-3} in benzophenone, containing either *trans*-PhMeC=CHPh (4.74×10^{-2} mol dm^{-3}), *cis*-(1) (4.75×10^{-2} mol dm^{-3}), or *trans*-(1) (3.60×10^{-2} mol dm^{-3}). The samples were irradiated in a 'merry-go-round' photolysis apparatus (Applied Photophysics) at 365 nm, and the extent of isomerization was determined by measuring the relative integrated peak area [Me_3(Sn) resonance for the organotin compounds, Me for PhMeC=CHPh]. Light intensity was calculated by determining the moles of *cis*-PhMeC=CHPh produced, assuming $\Phi_{trans \rightarrow cis} = 0.54$.[17]

Photostationary states for (1) were estimated for 1×10^{-4} mol dm^{-3} solutions in cyclohexane, chloroform, or Pr^iOH. These were outgassed with either nitrogen or argon for 30 min and were irradiated at 313 nm. The ratio of isomers was calculated from the optical density at 234 nm. The photostationary state was achieved from both isomers and, in the case of cyclohexane solutions, from mixtures made up close to the apparent equilibrium concentrations. Photolyses were also monitored by n.m.r. using 1×10^{-2} mol dm^{-3} solutions in C_6D_6, $CDCl_3$, or CD_3OD. The ratio of isomers was calculated from the relative intensity of the Me_3(Sn) peaks. For [Sn(CPh=CMePh)Me_3] (2), both the Me_3(Sn) and MeC=C peaks were considered. Sensitised isomerisation in C_6D_6 was monitored by n.m.r. with concentrations of both the tin compound and the sensitiser being 1×10^{-2} mol dm^{-3}. After 30 min outgassing, the samples were irradiated at 365 nm and the extent of isomerisation measured as above.

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