SINGLET AND TRIPLET STATES IN CYCLOADDITION TO CONJUGATED DIENES

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INTRODUCTION

This paper is concerned with the mechanism of the addition of olefins to conjugated dienes initiated by light. *Table 1* lists some properties which serve to characterize several types of non-catalytic cycloadditions and to bring out their similarities and differences. Among thermal cycloadditions the concerted mechanism, typified by many Diels–Alder reactions, is most clearly recognizable by its unfailing stereospecificity. Considerations of orbital symmetry[1] have led to the accepted view that the concerted mechanism, favoured in six-electron systems, has a prohibitive energy of activation in the four-electron, cyclobutane-forming cycloadditions. In accord with this expectation, typical "1,2" cycloadditions are accompanied by stereoisomerization referable to free rotation in an intermediate biradical[2].

The same orbital symmetry considerations which rationalize these phenomena so successfully predict[1] that when one of the reactants is in an electronically excited state concerted cyclobutane formation will be favoured

*Table 1.* Characteristics of cycloadditions to dienes

	Mechanism				
	Thermal			Photochemical	
Observation	*Concerted*	*Biradical*	*Dipolar ion*	*Singlet*	*Triplet*
Forms 6-ring	+	When diene cis-fixed		+	When diene cis-fixed
Forms 4-ring	−	+	+	+	+
Stereospecific	+	−	(±)	(isom.)	−
Acceleration by ionizing solvents	(−)	−	+		
Head-to-head	±	+	(+)	±	+

while concerted cyclohexene formation will be forbidden. This prediction, however, applied only to reactants in the singlet state from which product can result without a multiplicity change. Authenticated examples of this photochemical reversal of the selection rules are very rare, probably the best being the "eight-electron" dimerization of anthracene across the 9,10 positions, which has been shown to involve the singlet state by its competition with fluorescence[3]. In a large number of *photosensitized* cycloadditions proceeding through the triplet state, including those to be discussed below,

prevalent stereoisomerization shows that concerted cyclobutane formation is absent.

THERMAL DIMERIZATION OF CYCLOPENTADIENE

A much-studied cycloaddition reaction is the thermal dimerization of cyclopentadiene, which proceeds by the concerted Diels–Alder pattern to give *endo*-dicyclopentadiene (I). The photosensitized dimerization of cyclopentadiene had been found by Turro and Hammond[4] to yield comparable amounts of this dimer, its exo isomer (II), and an *anti* head-to-head 1,2 dimer (III) which is one of the four possible dimerization products of

(I)   (II)   (III)
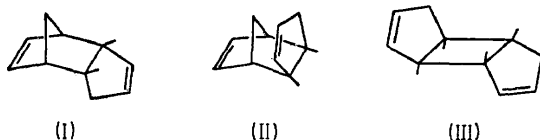
cyclopentadiene in the cyclobutane mode having *cis* ring fusions. These products, which we have also obtained in similar experiments, are consistent with a mechanism in which excited triplet cyclopentadiene attacks a ground state molecule with the formation of a head-to-head, doubly allylic biradical with the DL configuration of the biradical predominating over the *meso* by about 7 to 3.

In a search for a concerted cycloaddition from the singlet state we irradiated cyclopentadiene at 1°C with a 450-watt Hanovia quartz mercury vapour lamp. Again under these conditions about a third of the product was *endo*-dicyclopentadiene (I), but the principal product, comprising 69 per cent of the whole, was the isomeric dimer, tetracyclo[4.3.0.1^{2,5}.0^{7,9}]-dec-3-ene (IV), whose n.m.r. spectrum (*Figure 1*) clearly showed the presence
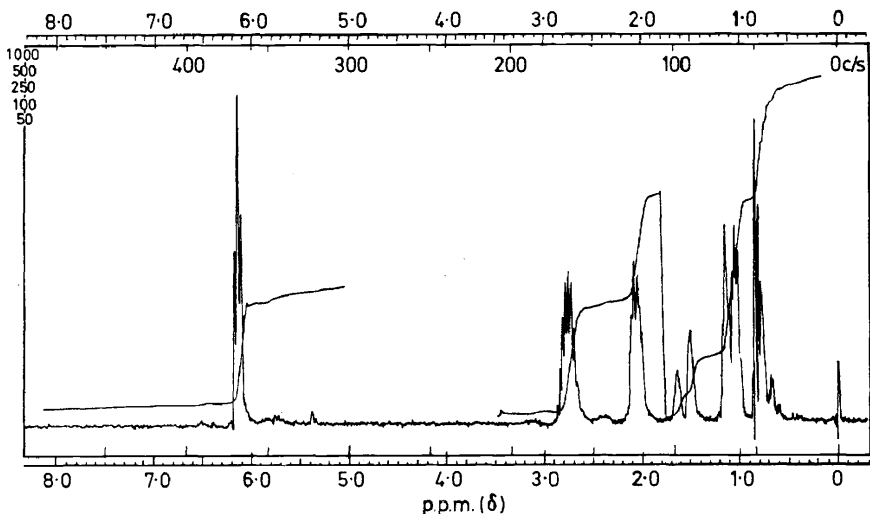

Figure 1. NMR spectrum of compound (IV)

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of the cyclopropane ring and which could be hydrogenated in two stages, yielding the same tetrahydrodicyclopentadiene as isomer (I). A paper by Brauman, Ellis, and van Tamelen[5] showed, however, that the first reaction of excited cyclopentadiene singlet was not a concerted dimerization but an intramolecular disrotatory isomerization to bicyclopentene (V), and we were able to show that the dimer (IV) results from the great reactivity of bicyclopentene as a dienophile toward cyclopentadiene, both reactants being in their ground states. *Table 2* compares the direct and sensitized

(IV)   (V)

photodimerizations of cyclopentadiene. It was subsequently possible to obtain photodimers with much smaller amounts of *endo*-dicyclopentadiene (I), and we are not yet sure how small the amount of this normal thermal dimer may be with completely dimer-free starting material and perfect temperature control.

Table 2. Direct and sensitized photodimerization of cyclopentadiene at 1°C

Product	Photodimerization	
	Direct (%)	Sensitized (%)
(I)	31	39·7
(II)	—	28·6
(III)	—	32·5
(IV)	69	—
Competing adducts of *trans*-dichloroethylene	2	68

The possible stereospecificity of singlet photocyclo-addition might be tested if light could be absorbed entirely by a diene in the presence of an olefin of *cis* or *trans* configuration to which concerted 1,2 cycloaddition might then occur. Cyclopentadiene was irradiated in five-fold excess of first *cis* and then *trans*-1,2-dichloroethylene. The dimer (IV) was obtained in 61 and 71 per cent yield, respectively, and only 1·64 and 2·58 per cent respectively, was obtained of a mixture of cross-cycloadducts. At the same

time the recovered dichloroethylene was isomerized to the extent of 4·4 and 4·7 per cent. While the amount of direct isomerization of dichloroethylene could probably have been controlled by a careful choice of the frequency of the irradiating light, yet it is clear from these results that the intramolecular isomerization of cyclopentadiene to bicyclopentene is so rapid as to take precedence over intermolecular processes. Under these circumstances the failure of the dimer to contain any (III) indicated that the occurrence of concerted cross-cycloaddition from excited singlet was even less to be expected.

Table 1 indicates a close correspondence between the properties observed in thermal cycloadditions by the biradical mechanism and those in photo-sensitized cycloadditions proceeding through an excited triplet. Cyclo-pentadiene and 1,2-dichloroethylene appeared to be a favourable case for a close study of photosensitized cycloaddition in order to learn whether its characteristics are only those of a biradical mechanism or whether its origin in an excited state gives it further distinguishing characteristics. The triplet energy of cyclopentadiene is about 53 kcal[6], and that of *trans*-dichloroethylene about 60–62[7]. Many available sensitizers with triplet energies between these limits should therefore be capable of exciting cyclo-pentadiene while leaving dichloroethylene unaffected. Any cross-cyclo-addition which occurs must then be between an excited cyclopentadiene triplet and ground state dichloroethylene.

By way of calibration, the well-known thermal cycloadditions of cyclo-pentadiene with *cis*- and *trans*-dichloroethylene were repeated at 200°C. The results were as shown in *Figure 2*. The dimerization of cyclopentadiene
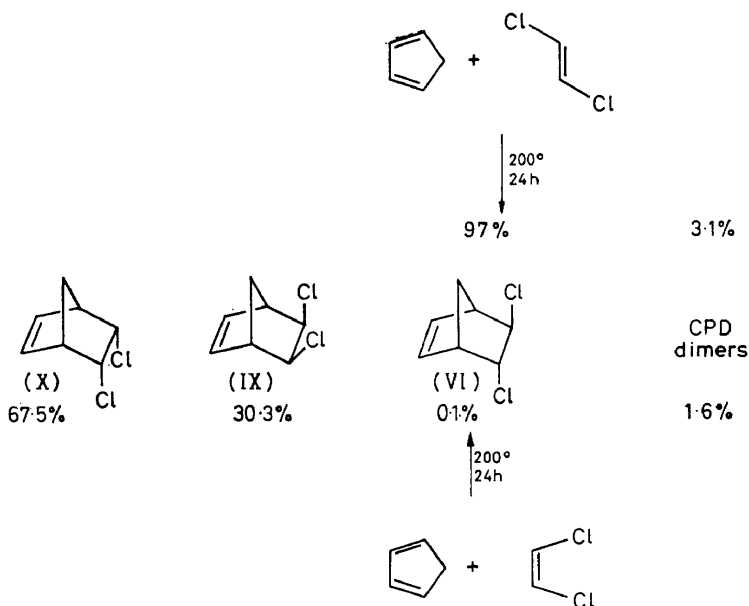

Figure 2. Thermal cycloadditions of cyclopentadiene with *cis*- and *trans*-dichloroethylene at 200°C

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is reversible at this temperature, and hence the dimer served only as a reservoir from which cyclopentadiene was regenerated. The thermal cyclo-addition of cyclopentadiene to both dichloroethylenes at 200° is completely 1,4 and stereospecific, there being at this temperature no appreciable isomerization of the dichloroethylenes under the conditions of the reaction.

There is only about a two-fold preference for forming *endo* product in the case of *cis*-1,2-dichloroethylene. This is quantitatively consistent with the even smaller preference seen in the thermal cycloaddition of vinyl chloride and trichloroethylene shown in *Figure 3*.
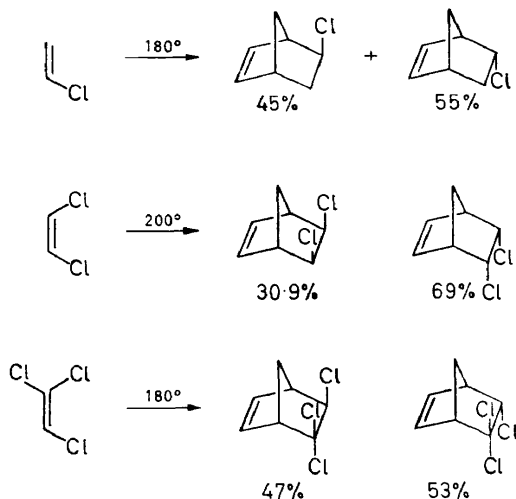

Figure 3. Orientation in thermal cycloaddition

The photosensitized cycloaddition of *cis*- and *trans*-1,2-dichloroethylenes to cyclopentadiene was carried out at 1 °C with three sensitizers: biacetyl (E_T 54·9 kcal), α-acetonaphthone (E_T 56·4 kcal), and β-acetonaphthone (E_T 59·3 kcal). Freshly distilled cyclopentadiene was dissolved in a ten-fold molar excess of either isomer of dichloroethylene (isomeric purity 99·9 per cent or better by vapour chromatography) together with about 0·2 molar equivalent of photosensitizer relative to cyclopentadiene. The reaction mixtures were degassed, sealed into Pyrex ampoules, and the samples were irradiated for 15 h with a 450-watt Hanovia high pressure mercury vapour lamp surrounded by a Pyrex cooling jacket through which tap water was circulated. The entire apparatus was cooled in ice. The product compositions were determined by vapour phase chromatography on an F and M Model 609 Gas Chromatograph with a flame ionization detector. The most useful column for separation was a 10 ft × 0·25 in. column packed with 20 per cent Carbowax 20M on 60/80 mesh Chromosorb P, the column temperature being 180°C. This column was capable of separating cyclopentadiene, *cis*-dichloroethylene, *trans*-dichloroethylene, a dicyclopentadiene fraction and each of the seven possible 1,2 and 1,4 addition products of dichloroethylene to cyclopentadiene, the retention times of the cross-cycloadducts running

from 23 min for (VI) to 82 min for (XI). Samples of the cycloadducts sufficient for n.m.r. examination were isolated by preparative vapour chromatography on an Aerograph Autoprep Model A700 with columns of γ-methyl-γ-nitropimelonitrile at 115° and Carbowax 20M at 170–200°.
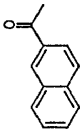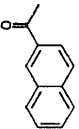
In all cases the products of photosensitized cycloaddition contain six of the seven possibilities, whether prepared from the *cis* or from the *trans* starting material. The missing isomer was the known *exo-cis*-dichloronorbornene (IX). As little as 0·3 per cent of this isomer could have been readily detected in the cycloadducts from *cis*-dichloroethylene and as little as 0·2 per cent in those from *trans*-dichloroethylene. The other two 1,4 addition products, (VI) and (X), were readily recognized by their n.m.r. spectra. Of the four possible 1,2 adducts, (VIII) and (XI) were readily distinguished from (VIIa) and (VIIb). The n.m.r. signals between 232 and 296 cycles, at next higher field above those of the ethylenic protons, must be due in each case to the hydrogen atoms on the same carbons as the chlorine atoms. These signals, spread by more than 33 cycles in (VIIa) and (VIIb), and by less than 3 cycles in (VIII) and (XI), show that the former two isomers have *trans*-chlorine atoms and the latter two, *cis*, as would also be expected from their elution times. These pairs show so much more shielding in (VIII) (by 32 cycles) as to establish it as the *cis-anti* isomer while (XI) is the *cis-syn*. The establishment of the individual configurations of (VIIa) and (VIIb) by n.m.r. is not unambiguous, and we shall leave them unassigned pending the chemical establishment of the structures which is now underway. In *Tables 3–5*, the uncertainty in the position of the double bond is represented by showing the compounds (VIIa) and (VIIb) as indeterminate hydrides of an allylic radical.

Table 3 shows that over the range of sensitizer energy used there is no significant difference in the composition of the cycloadduct mixture depending on the choice of sensitizer. This conclusion is in excellent accord with the interpretations previously given[8] of substantial sensitizer dependences in cyclodimerization of openchained dienes. The explanation in those cases rested upon different excitation energies of the diene in *cisoid* and *transoid* conformations. Since cyclopentadiene has only a *cisoid* conformation, the lack of dependence of the present results on the sensitizer constitutes additional support for the previous explanation.

Apart from the detailed product compositions, which will be discussed later, *Table 3* brings out several other facts of interest about the present system. Variable amounts of *cis,trans* isomerization of the recovered dichloroethylenes, never greater than 3 per cent, were observed. Comparison of the isomerization in the presence and absence of cyclopentadiene leads to the conclusion that no appreciable energy transfer occurs from excited cyclopentadiene to dichloroethylene and that the large amount of *cis,trans* isomerization involved in forming the products is not the result of a prior isomerization of the dichloroethylene but must be inherent in the reaction mechanism.

In this reaction cyclopentadiene and dichloroethylene compete for each excited cyclopentadiene triplet which is formed. Under the reaction conditions cyclopentadiene captures about twice as much triplet as does *cis*-dichloroethylene, which suggests that the relative reactivities of these ground

Table 3. Photosensitized cycloadditions—Variation of sensitizer

 + CHCl=CHCl, at 1° ± 0·5°

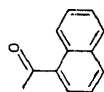| Sensitizer	Dienophile	Isomerized CHCl=CHCl in addition mixture (%)	CHCl=CHCl Isomerization in absence of diene (%)	Dimers	(VI)	(VIIa)	(VIIb)	(VIII)	(IX)	(X)	(XI)
2-acetonaphthone	cis-ClCH=CHCl	1	2·8	226	12·7	53·0	8·8	21·7	<0·3	1·0	2·8
1-acetonaphthone	cis-ClCH=CHCl	1	0·9	216	12·6	52·6	9·3	21·6	—	1·0	2·8
biacetyl	cis-ClCH=CHCl	<1	—	182	13·0	52·6	8·2	22·4	—	0·9	2·9
2-acetonaphthone	trans-ClCH=CHCl	2·1	1·7	47·2	53·5	18·9	11·1	10·0	<0·2	2·4	4·1
1-acetonaphthone	trans-ClCH=CHCl	1·7	1·1	46·4	54·0	18·5	10·8	10·0	—	2·5	4·2
biacetyl	trans-ClCH=CHCl	<3	—	36·9	54·2	18·5	11·7	9·4	—	2·4	3·8

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states toward triplet are in a ratio greater than 20:1. Under similar conditions *trans*-dichloroethylene captures more than twice as much triplet as does cyclopentadiene. Direct comparison of the two sets of experiments thus indicates that *trans*-dichloroethylene is about four times as reactive as *cis* toward the cyclopentadiene triplet.

In a number of cycloadditions brought about by light the course of the reaction is determined to an important extent by whether the light is absorbed by a single reactant molecule or by an absorbing complex of the two reactants[9]. No special absorption effects were noted in mixtures of cyclopentadiene and *cis*- or *trans*-dichloroethylene. A series of experiments with *a*-acetonaphthone as sensitizer at different degrees of dilution were carried out in order to see whether the degree of dilution affected the product distribution. *Table 4* shows that a 1:2 ratio of cyclopentadiene and dichloroethylene yields cross-adduct compositions similar to the 1:10 ratios in *Table 3* and that a further dilution of the 1:2 mixtures by the addition of 7·2 parts of 1,2-dichloroethane also produced no significant change in the product composition. This variation should have changed by a factor of 15 the fraction of the cyclopentadiene existing in any weak complex with dichloroethylene and should have affected the product had there been any competition between excitation of diene and of complex leading to different courses of reaction. There is indeed an approximate doubling in the proportion of cyclopentadiene dimers in the solutions containing proportionately less dichloroethylene. These facts all agree in indicating that the products observed result from transfer of triplet excitation energy from the sensitizer to the cyclopentadiene and that the dichloroethylene first enters the mechanism by being attacked by the cyclopentadiene triplet in the formation of a biradical.

If the biradical becomes rapidly thermally equilibrated with its surroundings, then the product composition depends upon a series of competitions between rotation around single bonds and radical coupling with ring closure. *Table 5* compares the product compositions from each dichloroethylene isomer at three temperatures over a range of about 50°. Only one isomer, (VIIb), changes its amount by a factor of more than 2 between the reaction products made at −25° and those at +25°. The amount of this isomer increases in the product from *cis*-dichloroethylene from 5·2 to 13·6 per cent over this temperature range, and in the product from *trans*-dichloroethylene from 6·8 to 17·4 per cent. In addition, the proportion of *cis-anti*-1,2-adduct (VIII) in the product from *trans*-dichloroethylene increases from 7·6 to 14·1 per cent, although in the product from the *cis*-dichloroethylene it decreases somewhat. We shall be in a better position to interpret these changes when the configuration of (VIIb) is finally established.

Table 6 shows overall characteristics of the product distributions from *cis* and *trans*-dichloroethylenes at the lowest and highest temperatures. In all cases there is more *trans* configuration than *cis* in the products. At −25° the *trans/cis* ratio is more than twice as great from *trans* starting material as from *cis* (6·2 *vs.* 2·8), but at +25° the *trans/cis* ratios from the two starting materials have approached each other so that *cis*-dichloroethylene yields a 3·1 *trans/cis* ratio and *trans*-dichloroethylene a ratio of 3·8. Thus it is evident that the

*Table 4.* Photosensitized cycloadditions—Concentration variations

Sensitizer: (1-acetylnaphthalene)   Temperature: $1° \pm 0.5°$

Reagents (mmoles)				Products							
(cyclopentadiene)	CHCl=CHCl	CH₂Cl–CH₂Cl (Diluent)	Dimers	(VI)	(VIIa)	(VIIb)	(VIII)	(IX)	(X)	(X)	(XI)
1·0	0·26 (cis, 2·0)	7·2	488	12·7	53·4	8·9	21·2	—	1·1	2·7
1·0	0·26 (cis, 2·0)	0	411	12·6	52·6	9·5	21·2	—	1·2	3·0
1·0	0·26 (trans, 2·0)	7·2	114	54·1	16·4	10·9	10·1	—	3·0	5·5
1·0	0·26 (trans, 2·0)	0	105	53·3	18·3	10·7	10·5	—	2·5	4·6

Table 5. Photosensitized cycloadditions—Variation of temperature
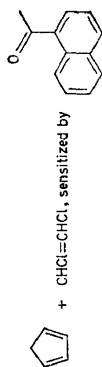
Temperature	*Dienophile*	*Isomerized* CHCl=CHCl (%)	Dimers	(VI)	(VIIa)	(VIIb)	(VIII)	(IX)	(X)	(XI)
$-24\cdot8° \pm 0\cdot2°$		$\sim0\cdot5$	229	11·8	56·8	5·2	22·3	—	1·2	2·7
$1° \pm 0\cdot5°$		1·0	216	12·6	52·6	9·3	21·6	—	1·0	2·8
$25\cdot0° \pm 0\cdot02°$		1	147	12·7	49·4	13·6	20·3	—	0·9	3·1
$-24\cdot8° \pm 0\cdot2°$		~1	44·7	62·0	17·3	6·8	7·6	—	2·2	4·1
$1° \pm 0\cdot5°$		1·7	46·4	54·0	18·5	10·8	10·0	—	2·5	4·2
$25\cdot0° \pm 0\cdot02°$		3	38·8	40·8	20·9	17·4	14·1	—	2·9	3·8

photosensitized cycloaddition involves an intermediate in which rotation of the two CHCl groups relative to each other is quite mobile compared to the rate of final ring closure.

However, there are other respects in which internal rotations in the intermediate are nowhere near so mobile, for the product distributions from the *cis* and *trans* olefins remain very different. This is seen in the second line of *Table 6* where the ratio of 1,2 to 1,4 addition products or of cyclobutane to cyclohexene ring closures is summarized. At $-25°$ this ratio is

Table 6. Trans/cis and 1,2/1,4 ratios in products of photosensitized cycloaddition of cyclopentadiene to cis- and trans-dichloroethylenes

Ratio	From cis		From trans	
	$-25°$	$+25°$	$-25°$	$+25°$
trans/cis	2·8	3·1	6·2	3·8
1,2/1,4	6·7	6·3	0·56	1·29

12 times as great from *cis* as from *trans*-dichloroethylene and it is still 4·9 times as great at $+25°$. Thus the most important and persistent difference in product composition between the isomers is that although the *cis-trans* distinction tends to disappear in the products, *cis*-dichloroethylene leads to a much greater relative amount of 1,2 cycloaddition compared to *trans*-dichloroethylene. It is clear that those internal rotations in the intermediate which determine the position at which the allylic portion of the biradical reacts to close the ring are far less mobile than those rotations which determine the *cis* or *trans* relation of the two chlorine atoms. Moreover, it is obvious that the biradical from *cis*-dichloroethylene is originally formed in a condition strongly predisposed toward 1,2 cycloadditions, while that from *trans*-dichloroethylene is relatively predisposed toward 1,4 cycloaddition. From the unequal effects of temperature upon the ratios in starting from the two isomers it appears that the activation energy of the critical rotation in the biradical from *cis*-dichloroethylene is equal to that for ring closure; in the biradical from *trans*-dichloroethylene the activation energy for the critical rotation is different from that for ring closure.

Perhaps the most remarkable feature of the product distributions is the undetectably small amount of product (IX) present. On vapour chromatography columns which will separate isomers (VIII), (IX), and (X), it is considered that amounts of (IX) as small as a few tenths of a per cent could be detected if present. The n.m.r. spectrum of (IX) has a strong narrow doublet at 4 p.p.m. of which there is no trace in the spectra of (VIII) and (X). It seems clear that in some of the product compositions from *trans*-dichloroethylene the isomeric norbornenes (VI) and (IX) are present in a *trans/cis* ratio of not less than 100. This presents a puzzling contrast to the near uniformity of *trans/cis* ratios in the products generally from these two isomeric olefins.

Large amounts of (VI) in the products from *trans*-dichloroethylene at least raise the question of whether it is possible for this olefin to undergo

some independent, concerted cycloaddition of the Diels–Alder type during photosensitized reaction (e.g. via "hot" ground state). From the experiments we can say that if this were possible, it is doubly remarkable that no such reaction whatever occurs with *cis*-dichloroethylene. We know that it does not, because the concerted Diels–Alder reaction of *cis*-dichloroethylene yields about 30 per cent of the totally missing isomer (IX). There is of course no possibility of ordinary thermal reaction being superposed upon the photosensitized, since the thermal reaction requires a temperature of about 200° and the photosensitized experiments were performed in the range of 25° to −25°. It seems then that we are forced to think of the present products as all being formed by branches of the same photosensitized mechanism. We must then consider in what possible ways the intermediate biradical may bear the stamp of the geometrical isomer from which it was formed when this stamp results not in any retention of geometric configuration but in a special control of product distribution in which the 1,2/1,4 ratio seems to be the most important variable.

At the moment of its formation the biradical from cyclopentadiene triplet and *cis*- or *trans*-dichloroethylene possesses three stereochemical characteristics: (i) the phase of rotation about the single bond joining the CHCl groups which corresponds initially to the configuration of the reactant olefin used but which, as *Table 6* shows, undergoes rapid equilibration; (ii) one of two permanent diastereomeric configurations with respect to the two new asymmetric carbon atoms joined by the newly formed bond; and (iii) the conformation or phase of rotation about the latter single bond. It is to these last two stereochemical characteristics, one permanent and one temporary, that we must look for an explanation of the differing product compositions from the two isomers of dichloromethylene.

Although the conformational history of the intermediates cannot be fully inferred until we have the full configurations of (VIIa) and (VIIb), we can determine the preference for *erythro* and *threo* biradical formation in the photocycloaddition of an analogue, trichloroethylene, to cyclopentadiene.

SENSITIZED CYCLOADDITION TO TRICHLOROETHYLENE

Because each chlorine atom in the α-position contributes about 4 kcal to the stabilization of a free radical[10], the initial bond formation from cyclopentadiene triplet to trichloroethylene should occur largely at the —CHCl group, and the product composition should show directly in what proportion *erythro*- and *threo*-biradicals are formed.

Table 7 shows the result of this experiment, again with a striking absence of any norbornene with two *exo* chlorine atoms, despite the abundance of this isomer in the product of *thermal* cycloaddition (*Figure 3*). The third compound to be eluted in v.p.c., (XIV), comprising 10 per cent of the product, proved to have the opposite orientation from the others, as evidenced by its hydrogenation to the same product as was had from (XIII). The adduct (XIV) must therefore have come from a biradical terminated by a —CHCl group. Of the 1,2-addition product, 18·5 per cent resulted from this "inverse" orientation and 81·5 per cent from the "normal" biradical involving a —CCl₂• radical component. This low orientational

Table 7. Photosensitized cycloaddition of cyclopentadiene
and trichloroethylene at 10°C

Compound	% in cycloadduct, sensitized by	
	β-*Acetonaphthone*	*Biacetyl*
(XII)	46	44
(XIII)	27	29
(XIV)	10	10
(XV)	17	17

selectivity is to be associated with the exothermic nature of the attack of cyclopentadiene triplet upon olefin, the transition state lying closer to the reactants than in thermal cycloaddition. From the ratio of (XIII) to (XV) in the product it would appear that the *threo* biradical is favoured; if the 1,4-addition product is formed from "normal" and "inverse" biradicals in the same proportion as the 1,2-product, then the *threo*/*erythro* ratio in the normal biradical is $(27 + 46 \times 0.815)/17 = 3.8$. The *endo*-1,4-addition product (XII) cannot, of course, come from an *erythro* biradical.

This experiment shows that there is a decided preference for formation of *threo* rather than *erythro* biradical in the attack of excited cyclopentadiene triplet on trichloroethylene. If this selectivity is very different for *cis* and *trans* dichloroethylenes, such a difference may make an important contribution to the different product compositions from the isomeric olefins. Such factors as the effect of olefin configuration on the preferred conformation, and on the rotational barriers, of the biradical, remain to be evaluated. So also does the role of orbital overlap, if any, in the *stepwise* cycloaddition, as it might influence the conformation and configuration of an intermediate biradical.

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