PART ONE

PHOTODIMERIZATIONS OF COUMARIN

PART TWO

ASYMMETRIC INDUCTION DURING ENERGY TRANSFER

Thesis by

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ABSTRACT

PART I

Studies on the mechanism of the photodimerizations of coumarin are reported. Trans coumarin photodimers are shown to result from excited triplet coumarin. It seems likely that an intermediate triplet-ground state complex precedes a biradical intermediate which closes to trans-dicoumarin. This dimer, formed by benzophenone sensitization is also produced by direct irradiation in benzene. Here coumarin has a low intersystem crossing yield of 2.2×10^{-2}. We account for 98% of the absorbed quanta by a photocleavage of coumarin singlets, competing with the other modes of unimolecular decay. No evidence supporting singlet self quenching was found. Singlet energy transfer from benzophenone to coumarin occurs by emission-reabsorption. The low efficiency of the latter process makes it insignificant compared to competing mechanisms.

ABSTRACT

PART II

Studies on the detailed mechanism of an energy transfer are reported. Optically active photosensitizers induce optical activity into *trans*-1,2-diphenylcyclopropane, II, while effecting the *trans* → *cis* isomerization. The asymmetric induction is shown to result from differing rates of energy transfer to the two optical isomer of *trans*-II. A rather large steric effect operative during energy transfer is thus demonstrated. Quenching studies indicate that the reaction occurs by a singlet mechanism resulting in production of 1,3-diphenyltrimethylene. The intermediate apparently has the same decays paths as that generated by triplet energy transfer to II. The asymmetric induction results from a number of sensitizers are useful in constructing a probable transition state for this energy transfer reaction.

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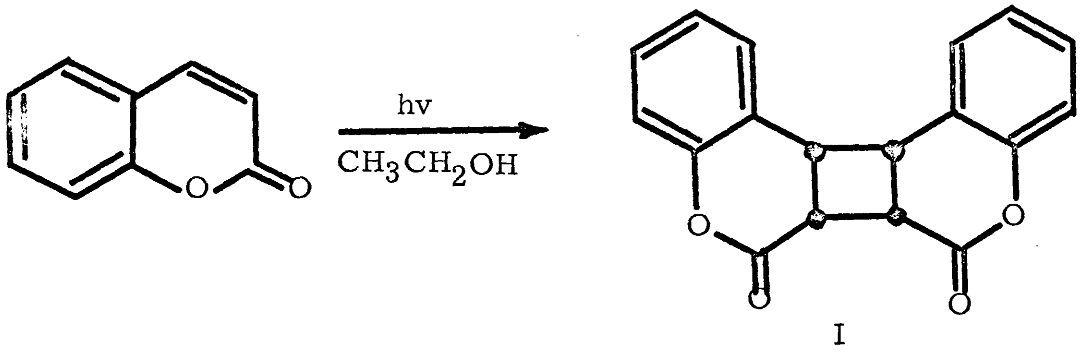
PART I

PHOTODIMERIZATION OF COUMARIN

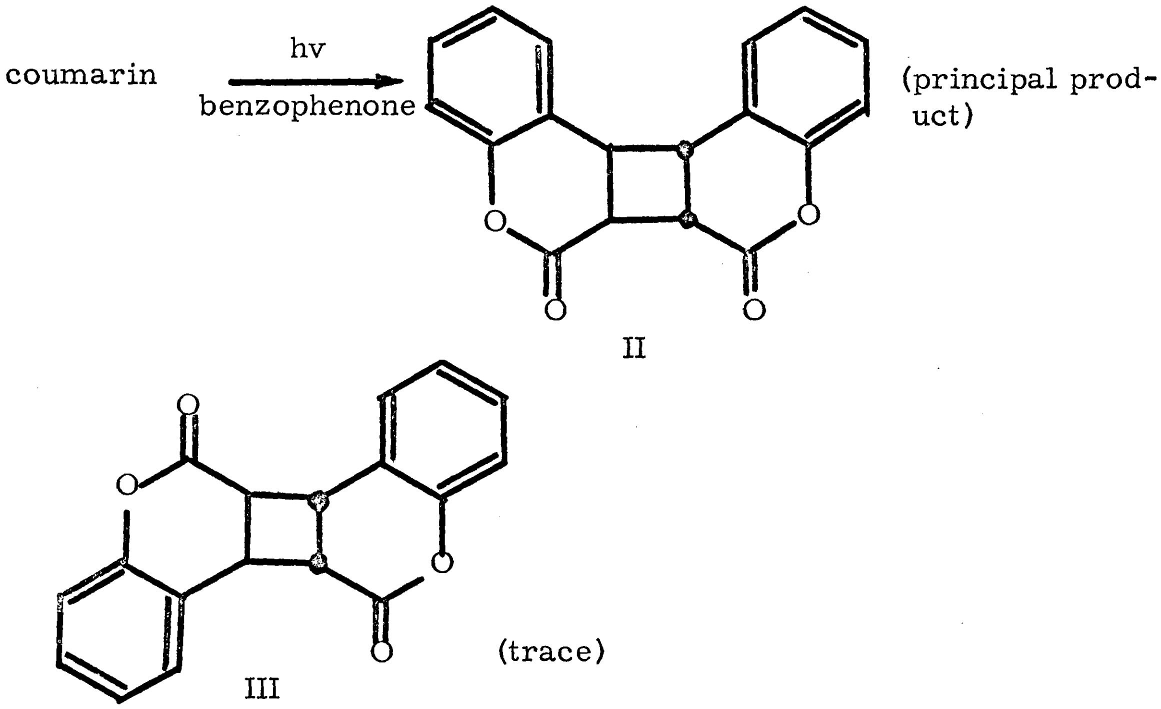
INTRODUCTION

The photochemical behavior of coumarin has been studied by a number of investigators. Despite a substantial amount of work, the intimate details of this rather complex photochemical system are not well resolved.

The photodimerization of coumarin in ethanol has been known for 65 years (1). Anet (2) in her studies on this system demonstrated a <u>cis</u> head-to-head structure for this dimer (I).



A sensitized photodimerization of coumarin producing the trans head-to-head dimer (II) (together with a trace of III) was next reported by Schenck and co-workers (3). They also noted



II

III

that irradiation of a benzene solution of coumarin in the absence of a sensitizer yields no dimeric product.

Using spectroscopic techniques to supplement their photochemical study, Hammond, Stout and Lamola (4) proposed a rather interesting and complex mechanism for the coumarin photodimerizations, accounting well for their results and those of previous workers. They found that the presence of benzophenone completely controls the course of the reaction, even when coumarin is the primary absorber of excitation. In their postulated mechanism shown below,[a] they suggest that excited singlet coumarin leads to I, while excited triplet coumarin gives II and III.

$$C + h\nu \longrightarrow {}^{1}C^{*} \qquad (1)$$

$${}^{1}C^{*} \longrightarrow C + h\nu \qquad (2)$$

$${}^{1}C^{*} + C \longrightarrow 2\,C + \text{energy} \qquad (3)$$

$${}^{1}C^{*} + C \xrightarrow[\text{solvents}]{\text{polar}} \text{I} \qquad (4)$$

$${}^{1}C^{*} \longrightarrow {}^{3}C^{*} \qquad (5)$$

$${}^{3}C^{*} + C \longrightarrow \text{II and III} \qquad (6)$$

for the direct irradiation, and

$$B + h\nu \longrightarrow {}^{1}B \longrightarrow {}^{3}B^{*} \qquad (7)$$

$${}^{3}B^{*} + C \longrightarrow B + {}^{3}C^{*} \qquad (8)$$

$${}^{3}C^{*} + C \longrightarrow \text{II and III} \qquad (6)$$

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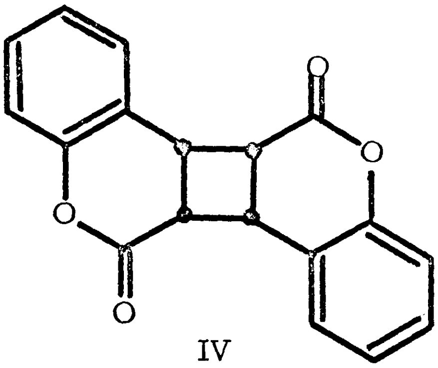
[a] Throughout this thesis we have used an asterisk (*) at the upper right of a chemical symbol to designate that this species is in an excited state. The number at the upper left refers to the spin multiplicity of this species.

for the benzophenone (B) sensitized dimerization. A singlet energy transfer from coumarin to benzophenone,

$$^{1}C^{*} + B \longrightarrow C + {}^{1}B^{*}, \qquad (9)$$

was also reported and Schenck's observation that no dimeric product is formed by direct irradiation of coumarin benzene (3) was confirmed for the case of high coumarin concentrations. However, at low coumarin concentrations (ca. 10^{-2} M) the production of II was noted. Under these conditions step 5 should compete with step 3, providing a formation of triplet species leading to II.

On further investigation Schenck (5) isolated the <u>cis</u> head-to-tail dimer (IV) from photolysis of coumarin in ethanol. Contrary to previous work, he found that I, II, III, and IV were indeed formed in benzene and other non-polar solvents. The relative proportion of



IV

dimers II : I seems to be a function of the dielectric constant of the solvent, decreasing from 20 in benzene to 0.23 in formic acid.

Schenck also discovered that all of the dimers are converted back to monomeric coumarin by irradiation with 2800 Å light.[a]

About the same time Morrison, Curtis and McDowell, also detecting dimers in non-polar system, reported the absence of a heavy atom affect on the unsensitized photolysis. (6)

The results of previous workers may be summarized as follows: (a) I is probably formed by reaction of an excited singlet with ground state coumarin, perhaps through an intermediate excimer; (b) II results from reaction of triplet with ground state coumarin; (c) all dimers can be formed by unsensitized photolysis in a variety of solvents, the distribution of products being a function of the dielectric constant of the solvent.

The objectives of our investigations are: (a) identification of the intermediates involved in the sensitized and direct photolysis of coumarin; (b) determination of the nature of the singlet energy transfer from coumarin to benzophenone; and (c) measurement of the quantum

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[a] This photo-cleavage probably accounts for the failure by previous workers to isolate dimers from non-polar, unsensitized systems, since they likely used unfiltered light. A high cleavage quantum (eg., 2) yield competing with the 3×10^{-3} dimerization yield will result in coumarin being the major product in a photostationary system.

efficiency of the dimerizations. With this information we should be able to construct a more comprehensive and knowledgeable picture of the coumarin photodimerization system.

RESULTS AND DISCUSSIONS

Coumarin - Benzophenone Singlet Energy Transfer

The singlet energy transfer of step 9 can take place by three recognized modes. The Forster mechanism (15), which can occur even when donor and acceptor are separated by distances of up to 100 Å, depends upon dipole-dipole coupling between donor and acceptor states. Collisional transfer (23), which is also non-radiative, requires intimate contact between the transfer pair. The third mechanism, "trivial" energy transfer occurs by acceptor absorption of donor fluorescence.

The detailed mechanism for reaction 9 appears to be that of emission-reabsorption, or trivial energy transfer. We infer this by comparison of the coumarin fluorescence spectra observed in the absence and presence of benzophenone. These emission spectra are shown with the benzophenone absorption spectrum in Figure 1. Addition of benzophenone shifts the position of the maximum fluorescent emission away from the benzophenone absorption. A non-radiative transfer would be accompanied by a decrease in intensity at wave lengths where benzophenone does not absorb. The small difference observed is within experimental error. There is, however, some question as to the identity of the emitting species (8).

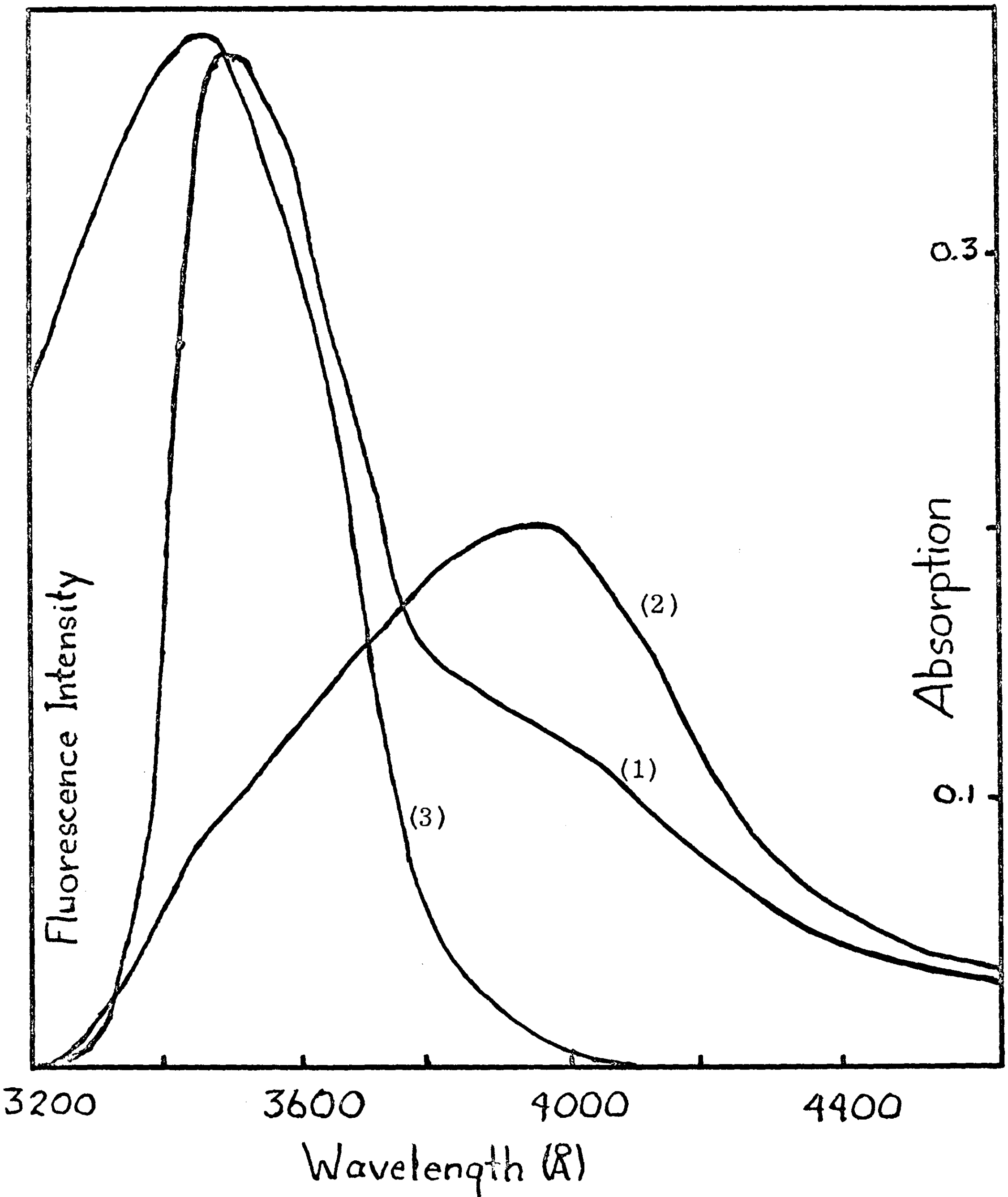

Figure I.

(1) Total emission from 2.5 x 10^{-4}M coumarin; (2) Total emission from 2.5 x 10^{-4}M coumarin and 5 x 10^{-3}M benzophenone; (3) Absorption spectra of 5 x 10^{-3}M benzophenone. All spectra in benzene at 25°C. Spectrometer sensitivity of (2) is greater than that of (1).

The emission is quite weak and the maximum is located near the 3660 line of the excitation source, making measurements experimentally difficult. It has been suggested that the weak fluorescence is due to an impurity (8). We were unable to detect this emission when using carefully purified and dry ethanol as a solvent.

The singlet energy transfer does not contribute significantly to the dimer formation quantum yield, which we measured to be about 5×10^{-3}, when coumarin absorbs 99% of the light. The quantum yield in the corresponding system without benzophenone is 3×10^{-3}. Since the quantum yield for the sensitized dimerization is 0.15 (discussed later in the quantum yield sections of this thesis), the slight increase from 3×10^{-3} to 5×10^{-3} by the addition of benzophenone (coumarin absorbing most of the light) can be accounted for by benzophenone absorbing 1.3% of the incident quanta, either directly or by emission-reabsorption. Under the experimental conditions used, benzophenone directly absorbs about 1% of the light. Evidently, the singlet energy transfer, if it occurs at all, does not measurably contribute to the dimerization quantum yield or alter other paths.

Chemical Spectroscopy on the Sensitized Coumarin Photodimerization System

"Chemical spectroscopy" (11) derives from the photochemical behavior of certain compounds which permits them to be used as probes to "count" indirectly the number of excited species produced in a system, and to distinguish these species by means of their triplet energy. For instance, an energy acceptor such as stilbene can be added to a photochemical system under study. This acceptor will intercept triplet excitation from the various triplet species produced upon irradiation. Since the distribution of products derived from the acceptor is a function of the triplet energy of the donor, the identity of the donor can be inferred if its triplet energy is known. The following equations show the expected consequences of addition of a monitoring cosubstrate to a mixture of coumarin and benzophenone.

$$B + h\nu \longrightarrow {}^1B^* \longrightarrow {}^3B^* \qquad (7)$$

$${}^3B^* + A \longrightarrow B + {}^3A^* \qquad (10)$$

$${}^3B^* + C \longrightarrow B + {}^3C^* \qquad (8)$$

$${}^3C^* + A \longrightarrow C + {}^3A^* \qquad (11)$$

$${}^3C^* + C \longrightarrow II \qquad (6)$$

In the above scheme with benzophenone and coumarin, A represents a *cis-trans* isomeric pair of acceptors. A is chosen so that the *cis-trans* photostationary state is different, depending on whether the energy is transferred from B to A or from C to A. When A is present in high concentrations, it will preferentially intercept the excitation from B, giving a photostationary state characteristic of the triplet energy of B. At lower A concentrations the energy will be preferentially transferred through C before it is transferred to A. This should lead to a photostationary state characteristic of C. Thus A can be effectively used to infer the presence of the excited benzophenone and coumarin triplet species. Quantum yield measurements on this system facilitate determination of the rates of the various processes in the above scheme.

Acceptors chosen to probe the coumarin system were 1,2-diphenylbutene-2, (V) and 1,2-dichloroethylene. In all experiments of this type, where it is known that only coumarin absorbs the incident light, little or no dimerization of coumarin or isomerization of the acceptor is noted. This is consistent with the inefficient or inoperative singlet energy transfer step.

Coumarin in 0.1 M. concentration decreases the benzophenone sensitized cis → trans isomerization rate of 0.1 M cis-1,2-dichloroethylene by a factor of about 12 (See Table I). Thus coumarin efficiently intercepts benzophenone triplets, verifying reaction 8. The resultant photostationary state both in the absence and presence of coumarin is cis/trans = 6.1. Evidently coumarin triplet species

TABLE I

Benzophenone sensitized isomerization of cis-1,2-dichloroethylene in presence of coumarin

Irradiation time (min.)[a]	Coumarin conc.[b]	% *trans*-dichloroethylene formed[c, d]
5	0.0	0.1
20	0.0	1.2
40	0.0	1.8
120	0.0	4.8
420	0.0	10.7
5	0.1	0.0
20	0.1	0.1
40	0.1	0.2
120	0.1	0.4
420	0.1	0.8

[a] Uranium glass filter

[b] Initial coumarin concentration

[c] Corrected for 1.1% *trans* isomer at t = 0; ± 0.1%.

[d] Initial *cis*-dichloroethylene conc. = 0.1 M.

relax and/or react much faster than they transfer energy to dichloroethylene.

Results using 1,2-diphenylbutene-2, (V) as an acceptor verify the presence of the coumarin triplet as precursor to trans-dicoumarin. The isomers of V can be brought to photostationary states (p.s.s.) using either benzophenone or coumarin as the sensitizer; the values of the V photostationary ratios are 3.5 and 6.4 (trans/cis) respectively. The latter was determined by irradiation of benzene solution containing trans-V (0.1M) and coumarin (0.02 M).

The benzophenone sensitized trans → cis isomerization rate of V (0.1M) in the presence of coumarin (0.1 M) is one-half that of a similar system without the coumarin. The difference can be attributed mainly to the amount of light absorbed by the benzophenone in the two cases. This was calculated on the basis of the spectral distribution of the light source and the extinction coefficients of the absorbing species. These systems proceeded to the photostationary states of coumarin and benzophenone respectively. This result was at first rather surprising. We expected the p.s.s. of V for the ternary system to be intermediate between those of coumarin and benzophenone. Examination of the Saltiel plot for V provides an explanation. The benzophenone triplet energy is below the high energy region (13) where the rate of energy transfer to both isomers of V is near that of a diffusion controlled process. In addition,

TABLE II

Sensitized isomerization of *trans*-V by benzophenone in the presence of coumarin.

Irradiation[b] time (hrs.)	Coumarin Concentration	*trans*-V/*cis*-V[d]	% *cis*-V[d]	% Coumarin[a] remaining
1	0.0	14	6.7	--------
6 1/4	0.0	12	7.7	--------
16	0.0	4.6	17.9	--------
2 days[c]	0.0	3.4	22.7	--------
1	0.1 M.	27	3.6	100
6 1/4	0.1 M.	27	3.6	100
16	0.1 M.	10	9.1	72
7 days	0.1 M.	6.4	13.2	39

[a] Calculated from relative areas of V.P.C. traces of photolysis mixtures.

[b] $NiSO_4$ - $CoSO_4$ filter solution described in experimental diluted to 1/2 original conc.

[c] Uranium glass filter.

[d] Conc. V = 0.10 M.

transfer to the cis isomer is preferred. The ratio of coumarin to cis-V is about three near the p.s.s.. Triplet energy transfer from benzophenone to coumarin should be diffusion controlled. Thus, triplet excitation can be preferentially transferred to coumarin which then relays it to cis- and trans-V, giving a resultant p.s.s. near that observed for coumarin. At lower coumarin concentrations, the V cis/trans ratios are intermediate between those of coumarin and benzophenone.

The results from V contrast with those obtained using dichloroethylenes as acceptors. When coumarin is present, systems containing V reach the coumarin photostationary state. When dichloroethylene is used as an acceptor, the benzophenone p.s.s. is approached. Coumarin competitively inhibits the isomerization of cis-dichloroethylene, but does not seem to appreciably affect trans-V isomerization rate, except by partial absorption of light. These observations apparently reflect the natural lifetimes of coumarin and benzophenone triplets compared to their rate of transfer to the two acceptors. The combined results from these two acceptors are consistent with the presumed mechanism for formation of trans-dicoumarin (4).

Quantum Yield for the Sensitized Dimerization

The "chemical spectroscopic" measurements provided valuable information as to the identity of the various species formed during irradiation. Quantum yield measurements can now be effectively used to infer much about the kinetic parameters of the various processes.

The quantum yields vs. coumarin concentration are shown in Table III.

Two rather interesting observations are immediately apparent. First, the quantum yield is far from its maximum of unity. Second, there is no variation in Φ in the 1.0 M. to 4×10^{-3} M. concentration range. The latter result suggests that coumarin triplets do not undergo unimolecular decay before they encounter and react with ground state coumarin species, even at 4×10^{-3} M. coumarin concentrations. Surprisingly, 85% of the absorbed quanta do not show up in the formation of dimer, although the constancy of the quantum yield suggests that the excited triplet coumarin is destroyed exclusively by bimolecular interaction with ground state. A modification of the previous mechanism can account for this.

Reaction 7, the intersystem crossing of benzophenone occurs with unit efficiency (16). Exothermic triplet energy transfer from benzophenone to coumarin should be diffusion controlled, and also

TABLE III

Dimer formation Quantum yields vs. Coumarin Concentration

Coumarin Conc.[b]	Quantum Yield ($\Phi \pm 0.02$)	$\Phi_{ave.} \pm 0.02$
1.0 M.	0.15	0.15
0.5 M.	0.15	0.15
0.2 M.	0.17	0.17
0.1 M.	0.17 0.19 0.14 0.18	0.17
0.04 M.	0.16 0.17 0.16 0.16	0.16
0.008 M.	0.15 0.16 0.13	0.15[a]
0.004 M.	0.16 0.15 0.13	0.15[a]

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[a] These values are corrected for the fraction of light not absorbed.

[b] Also equal to benzophenone sensitizer concentration.

occur with near unit efficiency at coumarin concentrations above 5×10^{-3}M. (3). This leaves reaction 6, the interaction of triplet and ground state coumarin as the most reasonable candidate for loss of absorbed quanta. The data suggest formation of a coumarin triplet ground state complex (triplet excimer) decaying to ground state molecules and II in a ratio of 5.3.

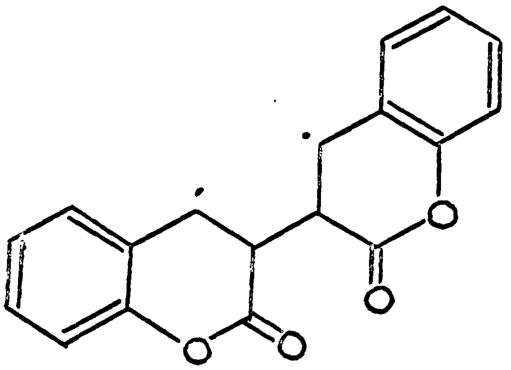
$$^{3}C^{*} + {}^{1}C \longrightarrow \text{complex} \qquad (12)$$

$$\text{Complex} \longrightarrow 2C \qquad (13)$$

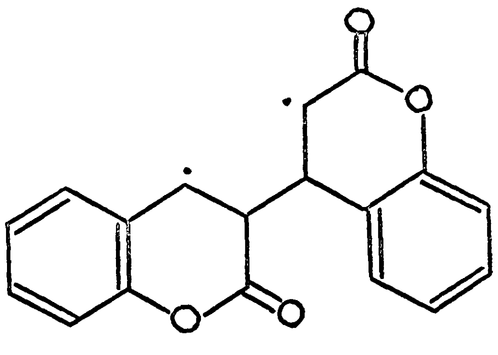
$$\text{Complex} \longrightarrow \text{IIa} \longrightarrow \text{II} \qquad (14)$$

$$^{3}C^{*} \longrightarrow C \qquad (15)$$

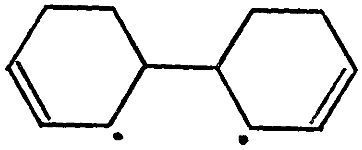
This triplet complex cannot be a biradical such as IIa. The latter should close to II with unit efficiency. The activation energy for cleavage into monomeric coumarin should be similar to that for the separation of IX into 1,3-cyclohexadiene. The latter reaction does not compete with closure to product (12).



IIa

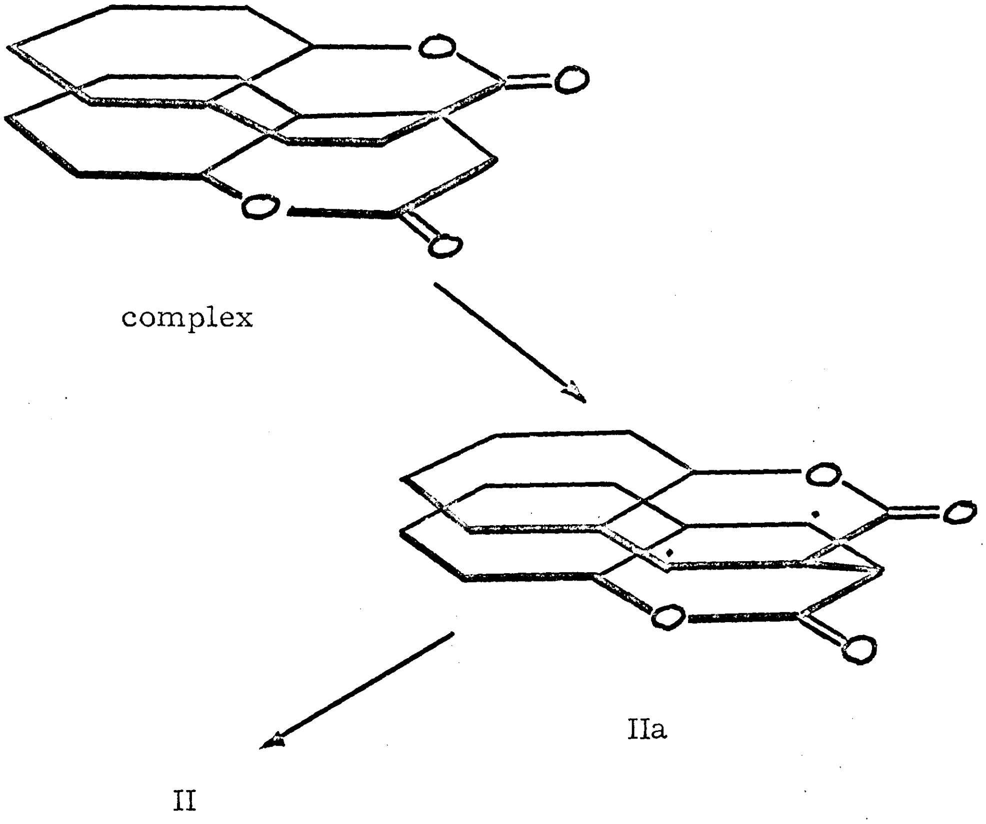


IIIa



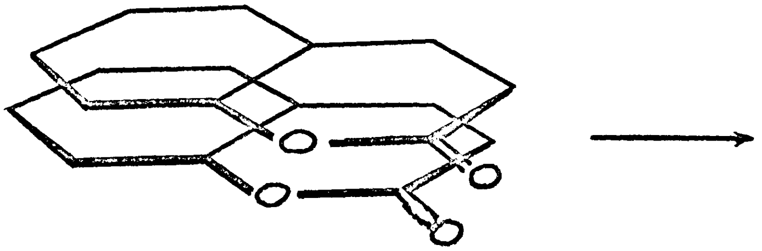
IX

Structures such as IIa and IIIa are likely precursors to II and III respectively. IIa might readily be derived from a sandwiched triplet complex or excimer as shown below:



(19)

IIa differs from the proposed singlet excimer (6), Ia, leading to I, in that the reactive



I

Ia

double bonds are adjacent in Ia, facilitating decay directly to I. IIa is set up for bond formation between the positions shown in the above figure. Scale molecular models indicate a perfect fit in position and bond angles, proceeding from the complex to sandwiched IIa. Interconversion and rotation around the newly formed bond are necessary for closure to II. IIIa can not easily be formed from this complex. If it were formed by another mechanism, it could not attain a "sandwiched" structure similar to IIa. This probably accounts for III being only a minor product of the sensitized photodimerization.

The quantum yield expression for our sensitized mechanism, including the terms for quenching of dimerization by added triplet acceptors is:

$$\Phi_{sens.} = \Phi_{ic.}\left(\frac{k_8[C]}{k_{10}[A] + k_d + k_8[C]}\right)\left(\frac{k_{12}[C]}{k_{12}[C] + k_{15} + k_{11}[C]}\right)\left(\frac{k_{19}}{k_{19} + k_{13}}\right)$$

Φ_{ic} and k_d are respectively the quantum yield of triplets and the first order decay constant for benzophenone, and their magnitudes are unity (16) and 10^5 sec^{-1} (21). Reaction 8, transfer from benzophenone to coumarin is exothermic by 6 k cal. and should be diffusion controlled. The first expression in parenthesis, the efficiency of energy transfer to coumarin should then be near unity at coumarin concentrations above 5 x 10^{-3} M. The constancy of $\Phi_{sens.}$ indicates that the second factor is also near unity in the concentration range studied. The last factor, the decay of triplet complex to II is 0.15. In a later section of this thesis we show how the variation in Φ_{sens} by addition of a triplet quencher, A, is used to calculate $k_{12} = 3 \times 10^8$ l. mole^{-1} sec.$^{-1}$.

Quantum Yield for Coumarin Dimer Formation by Direct Irradiation

Direct irradiation of coumarin in benzene produces mainly II (5), presumably by a similar triplet mechanism (4). Quantum yields (Φ) for this reaction vs. coumarin concentration are tabulated in Table IV and plotted in Figure II.

These quantum yields were also surprising. We expected $\Phi_{\text{unsen.}}$ to have a maximum around 10^{-3} - 10^{-4}M. coumarin concentration, the low concentration decrease being due to unimolecular decay of coumarin triplets and the high concentration decrease a result of self quenching of excited singlets by coumarin, as had been suggested (4).

$$^{1}C + hv \longrightarrow {}^{1}C^{*} \qquad (1)$$

$$^{1}C + C \longrightarrow 2C \qquad (3)$$

$$^{1}C^{*} \longrightarrow {}^{3}C^{*} \qquad (5)$$

$$^{3}C^{*} + C \longrightarrow II \qquad (6)$$

$$^{3}C^{*} \longrightarrow C \qquad (15)$$

Examination of the data in Table IV shows that $\Phi_{\text{unsen.}}$ is essentially constant down to about 5×10^{-3}M., the same range in which $\Phi_{\text{sen.}}$ is constant for the sensitized dimerization.

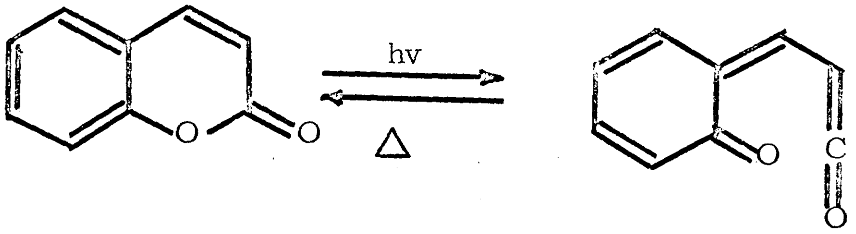
Apparently, singlet self quenching is not the mechanism by which coumarin rids itself of excitation. The data suggest that most of the absorbed quanta are degraded by a unimolecular path.

It seems easiest for us to account for this loss of energy by a reversible photocleavage of excited singlet coumarin. A possibility might be:

TABLE IV

Direct irradiation quantum yields for dimer formation at various coumarin concentrations.

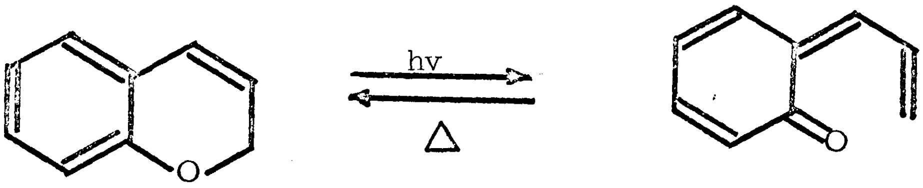
Initial coumarin conc. (M.)	Average conc. (M.)	$\Phi_{\text{unsen.}} \times 10^3$
0.1	9.6×10^{-2}	3.2
	9.5×10^{-2}	3.3
5.0×10^{-2}	4.8×10^{-2}	3.0
	4.7×10^{-2}	2.7
1.7×10^{-2}	1.42×10^{-2}	2.6
1.0×10^{-2}	9.7×10^{-3}	2.7
	9.1×10^{-3}	2.7
	8.3×10^{-3}	2.1
	8.4×10^{-3}	2.0
5.0×10^{-3}	4.8×10^{-3}	2.3
	4.4×10^{-3}	2.8
	4.2×10^{-3}	1.8
	4.1×10^{-3}	1.4
1.0×10^{-3}	8.5×10^{-4}	1.2
	9.4×10^{-4}	0.94
	8.1×10^{-4}	0.95
	8.2×10^{-4}	0.88
5.0×10^{-4}	2.9×10^{-4}	0.88
	4.5×10^{-4}	0.66
	2.9×10^{-4}	0.49
	3.9×10^{-4}	0.44
1.0×10^{-4}	9.4×10^{-5}	0.23



(18)

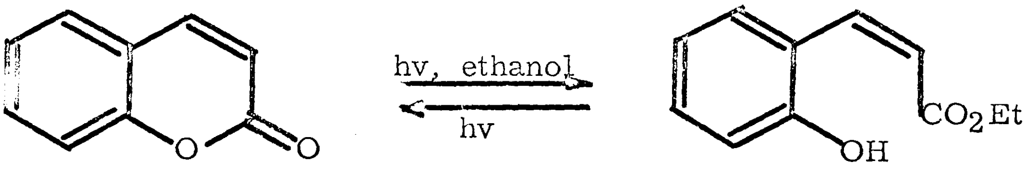
VI

This type of reaction is reported for 2-4-chromene (VII), a molecule quite similar to coumarin.



VII

Support for the presence of VI comes from Stout's (9) and Lamola's (8) observation that ethyl coumarate (VIII) is produced by irradiation of coumarin in ethanol. Addition of ethanol to the ketene, VI, would provide a mechanism for formation of the ester VIII. The reaction is readily photoreversible (9).



VIII

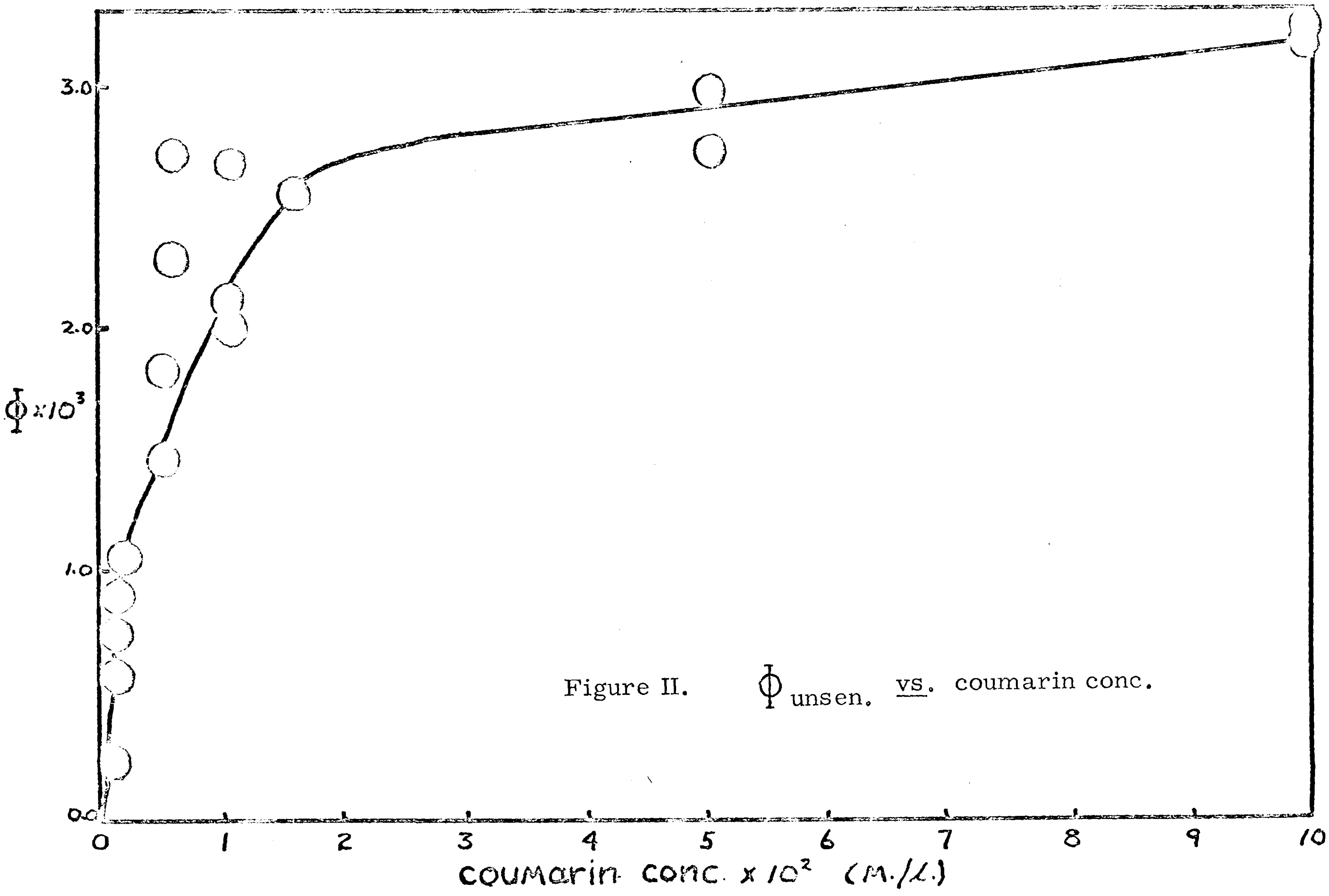


Figure II. $\Phi_{\text{unsen.}}$ vs. coumarin conc.

Whenever triplet quenchers are present during the direct excitation of coumarin, side products imparting a bright yellow color to the solution are formed. They are not observed in the sensitized dimerization. The color is produced in the presence of 2,5-dimethyl 2,4-hexadiene, cis-dichloroethylene and trans-diphenylbutene indicating that reaction between excited coumarin and quencher is not the source. This colored product, undoubtedly an excellent triplet quencher, is probably responsible for the erratic quantum yields. It may even contribute to the formation of dimer, but more important it gives a clue to the fate of the absorbed quanta.

VI is sufficiently conjugated to have an absorption in the visable spectrum. We tested for the presence of VI in yellow benzene solutions of coumarin irradiated in the presence of 2,5-dimethyl-2,4-hexadiene. Addition of ethanol and acetic acid did fade the color. The permanent yellow color is clearly not VI. However, a compound like VI, with its assortment of functional groups and photochemically active sites, undoubtedly has a variety of possible photochemical reactions. We would be greatly surprised if some of the products of these reactions were not highly colored.

In the next section we show that II formed by direct excitation results primarily from excited triplet coumarin reacting with ground state species. Thus, the unsensitized dimer formation quantum yields at higher concentrations indicate an inherent intersystem crossing yield of only 2.2×10^{-2}, the remaining 98% of the absorbed quanta being degraded by a competing unimolecular path. Coumarin fluorescence in solution is very weak (7, 8, 14), comprising less than 1% of the absorbed quanta, even at low concentrations (ca. 1×10^{-4}M). Self quenching has been suggested (4) as the dominant mode of energy wastage at higher coumarin concentrations since several substituted coumarins display marked fluorescence intensity dependence upon concentration (7). There is, however, no spectroscopic evidence of singlet self quenching for the parent compound in solution at 25°C (7, 14). The constancy of the quantum yields at higher concentrations is contrary to singlet self quenching. Lamola (8) has made an interesting and significant observation of coumarin emissions. In ethanol glass at 77°K coumarin displays only a green phosphorescent emission with the 0-0 band located at 4950 Å (62.5 K cal/mole). Coumarin in an isopentane glass has only a short lived blue emission band centered at 4000 Å. The latter is not that reported as being coumarin fluorescence, having a maximum of 3575 Å (4) in ethanol and 3500 Å in benzene. Lamola suggests that the blue emission comes from coumarin singlet excimers, whose formation should be more favored in hydrocarbon rather than ethanol glasses.

One might rationalize this apparent contradiction by suggesting that <u>trans</u> coumarin dimers are formed inefficiently from an intermediate leading to self quenching (reaction 16). Alternatively, an excited singlet mechanism forming II might compete with self quenching (reaction 17).

$$\begin{tikzcd} {}^{1}C^{*} + C \arrow[r] & \text{excimer} \arrow[r] \arrow[dr] & \text{II} \\ & & 2C \end{tikzcd} \tag{16}$$

$$\begin{tikzcd} {}^{1}C^{*} + C \arrow[r] \arrow[dr] & 2C \\ & \text{II} \end{tikzcd} \tag{17}$$

These two possibilities can be eliminated on the basis of the results of quenching experiments. These results, discussed in the next section, demonstrate that the same intermediates leading to II are encountered in both the sensitzed and direct excitation. One can get around this dilemma by allowing the excimer to intersystem cross and cleave into triplet and ground state coumarin. There is, however, no precedent for this and it tends to make the above mechanism unreasonably cumbersome. The consistency of the quantum yields above 5 x 10^{-3} M. does not rule out singlet excimer formation and decay as an energy wastage step, but the necessary inclusions in this mechanism give it an awkward and improbable appearance. We feel that cleavage to VI followed by closure to coumarin affords a much more direct and plausible explanation accounting for the energy wastage.

According to our preferred mechanism, the unsensitized dimerization quantum yield expression may be written as

$$\Phi = \left(\frac{k_5}{k_5 + k_{18} + k_4[C]}\right)\left(\frac{k_{12}[C]}{k_{12}[C] + k_{15}}\right)\left(\frac{k_{19}}{k_{19} + k_{13}}\right)$$

The first parenthetic expression, coumarin's intersystem crossing yield is apparently nearly constant at 2.2×10^{-2}. In non-polar solvents, even at high coumarin concentrations, k_4 [C] is much smaller than the other terms (5). The last factor is also a constant, 0.15. The quantum yield expression is now written as

$$\Phi^{-1} = 3.02 \times 10^2 \left(1 + \frac{k_{15}}{k_{12}[C]}\right)$$

Quenching of the Sensitized and Unsensitized Dimerization by 2,5-dimethyl-2,4-hexadiene.

Quantum yields for the formation of II by the sensitized and direct photolysis of coumarin in the presence and absence of 2,5-dimethyl-2,4-hexadiene (X) are tabulated in Table V. We note that both $\Phi_{\text{sens.}}$ and $\Phi_{\text{unsen.}}$ are strongly quenched by X, implicating the presence of quenchable triplet species leading to II.

In spite of the unfortunate scatter of the quenching data, a rather interesting correlation is noted. The ratios of Φ to Φ_{quenched} are 33 and 16.5 for the sensitized and unsensitized systems respectively at these concentrations. This is exactly what we would expect if the formation of dimer goes completely by interaction of a triplet and ground state coumarin.

We can see this from inspection of the quantum yield expressions on page 20. $\Phi_{sens} : \Phi_{s.-q.}$ is the ratio of the sensitized quantum yields in the respective absence and presence of a triplet quencher, A.

$$\frac{\Phi_{sens.}}{\Phi_{s.-q.}} = \left(\frac{k_8[C] + k_d + k_{10}[A]}{k_8\,[C] + k_d}\right)\left(\frac{k_{12}[C] + k_{15} + k_{11}[A]}{k_{12}[C] + k_{15}}\right) \quad (20)$$

The rate of triplet energy transfer from benzophenone or coumarin to X should be near that of a diffusion controlled process. The lowest triplet levels of both donors are at least 5 k cal. above that of X. With [C] and $[A] = 5 \times 10^{-3}$M., $k_8[C]$, $k_{10}[A]$, $k_{12}[C]$, and $k_{11}[A] >> k_d$, k_{15}. This is supported by the constancy of Φ above this concentration. We chose $[C]_o = [A] = 0.02$M. for the quenching experiments. Expression 20, with these stipulations reduces to

$$\frac{\Phi_{sens.}}{\Phi_{s.-q.}} = \left(\frac{k_8 + k_{10}}{k_8}\right)\left(\frac{k_{12} + k_{11}}{k_{12}}\right) \quad (21)$$

TABLE V

Quenching of Dimerization by 2,5-Dimethylhexadiene

Diene Concentration	Φ	
	Sensitized Photolysis[a,b]	
0.00 M.	0.15	
0.02 M.	0.0027	
0.02 M.	0.0055	
0.02 M.	0.0031	ave. $= 4.5 \times 10^{-3}$
0.02 M.	0.0032	
0.02 M.	0.0078	
	Direct Photolysis[b]	
0.00 M.	2.7×10^{-3}	
0.02 M.	0.105×10^{-3}	ave. =
0.02 M.	0.225×10^{-3}	1.65×10^{-4}

[a] Benzophenone conc. = 0.04 M.

[b] Initial coumarin conc. = 0.02 M.

Reactions 8, 10 and 11, being diffusion controlled processes, should have essentially equal rate constants of about 5 x 10^9 sec^{-1} reducing 21 to

$$\frac{\Phi_{sens.}}{\Phi_{s.-q.}} = 2 \left(1 + \frac{5 \times 10^9}{k_{12}} \right)$$

Experimentally the above ratio is 33. Thus $k_{12} = 3.2 \times 10^8$ l. $mole^{-1}$ sec^{-1}.

Similarily, this ratio for the unsensitized mechanism is written as follows:

$$\frac{\Phi_{unsens.}}{\Phi_{unsens.-q.}} = \left(\frac{k_{12}\,[C] + k_{11}\,[A]}{k_{12}\,[C]} \right)$$

Here the ratio of quantum yields is 16.5, using the same [C] and [A] as employed for the sensitized reaction. Again we calculate $k_{12} = 3.2 \times 10^8$ l. $mole^{-1}$ sec^{-1}.

Lifetime of the Coumarin Triplet

The measured decay time of the coumarin phosphorescence is 0.30 ± 0.02 sec. at 77° K in an ethanol glass. Assuming a reasonable emission quantum yield of 0.1 to 0.01, the radiative lifetime is somewhere between 3 and 30 sec. A lifetime of this duration is indicative

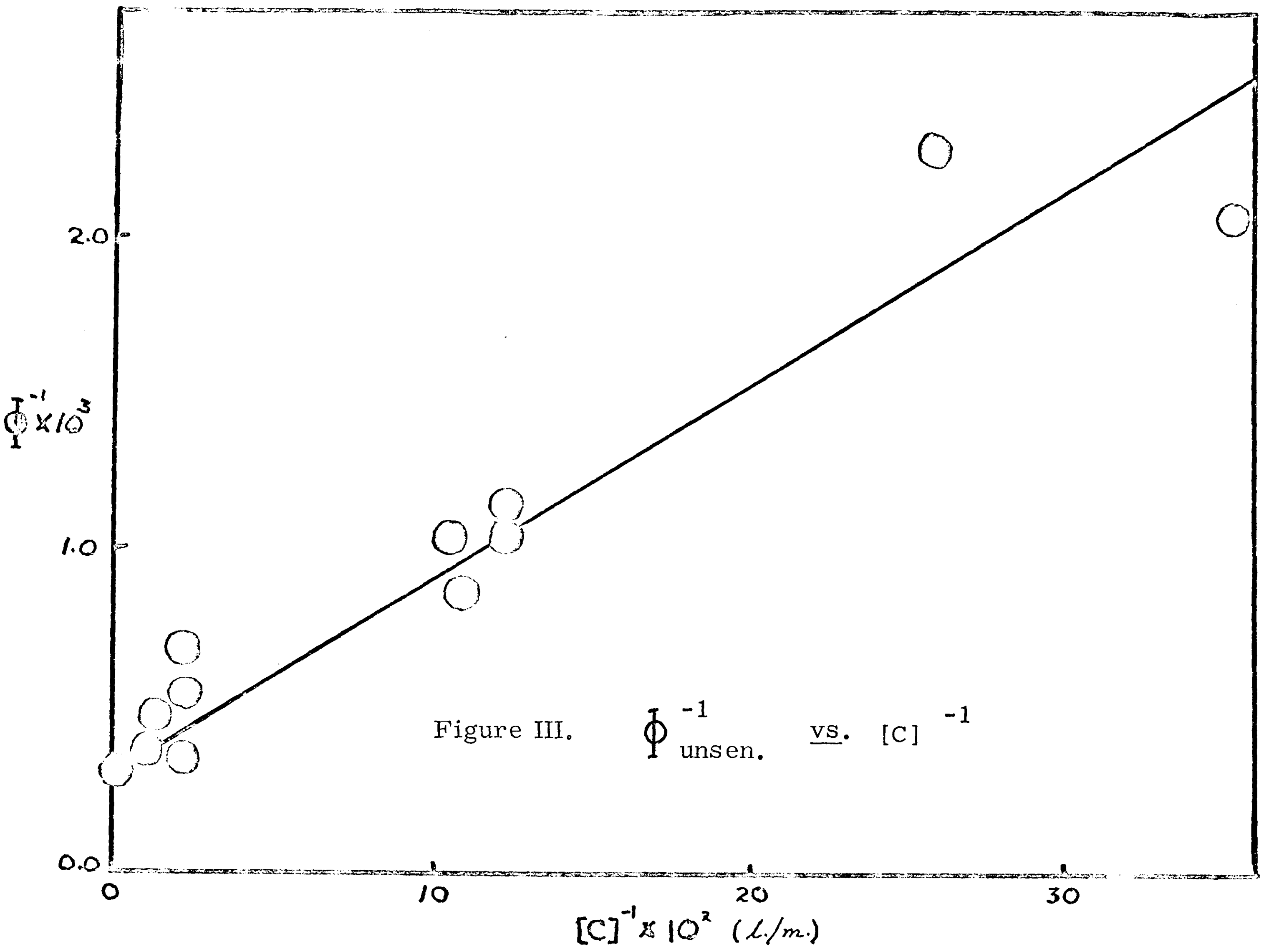


Figure III. $\Phi^{-1}_{\text{unsen.}}$ vs. $[C]^{-1}$

of a $\pi \rightarrow \pi^*$ transition with essentially no $n \rightarrow \pi^*$ mixing in the lowest triplet state (18). Thus, both the lowest excited singlet and triplet states of coumarin have $\pi \rightarrow \pi^*$ configurations.

Plotting $\Phi^{-1}_{\text{unsen.}}$ vs. $[C]^{-1}$ in Figure III, we can extract the ratio $k_{15}/k_{12} = 2.1 \times 10^{-3}$ m./l. From the quenching data of the last section we calculated $k_{12} = 3.2 \times 10^{8}$ l. mole^{-1} sec^{-1}. Thus $k_{15} = 6 \times 10^{5}$ sec.$^{-1}$, which is in poor agreement with coumarin's several second triplet lifetime in an ethanol glass.

The large experimental variation in the unsensitized dimerization quantum yields and the short triplet lifetime calculated from them suggest a build up of triplet quencher, probably derived from a primary photodecomposition product. A photoproduct like VI present in 10^{-4}M. concentration and quenching at a diffusion controlled rate can easily account for the apparent short lifetime and the experimental scatter of Φ_{unsens}.

Flash Spectroscopic Studies

Flash spectroscopy was used in a search for intermediates in the sensitized and direct photodimerization systems. No species with lifetimes greater than 10^{-6} sec. (other than the benzophenone triplet in the sensitized system) were detected by their absorption between 3600 and 5800 Å. Coumarin concentration ranged between 10^{-4} and 10^{-2} M. In a separate experiment benzene solutions of coumarin were flashed with the analyzing lamp beam monitoring the coumarin concentration. We found that more than 95% of the coumarin has returned to the ground state within 50 microsecond after the flash. This observation seems to contradict the suggested production of VI as the mode of energy wastage. However, in this experiment the excitation source was a Xenon-Mercury flash lamp. This lamp has a substantial output in the visable and near U.V. regions where VI should absorb strongly. Under these conditions VI could be photocyclized back to coumarin, establishing a p.s.s. consisting of mainly coumarin in the 15 microsecond flash lifetime.

SUMMARY

The conclusions following our study of the photosenstized and direct photodimerization of coumarin are now summarized.

The *trans* coumarin photodimers, II and III result from triplet coumarin, both by direct irradiation and by photosensitization. It seems likely that an intermediate triplet complex (excimer) precedes a biradical eventually closing to II. The complex apparently decays to product or starting material in a ratio of 5.3. Although other explanations are possible, we feel that coumarin's low intersystem crossing yield of 2.2×10^{-2} is best accounted for by a facile photocleavage of coumarin. The postulated cleavage product should readily revert to coumarin. We find no evidence for self quenching of singlet coumarin. Consistency of the quantum yields at high concentration is contrary to singlet excimer formation in benzene as a significant energy wastage path. We also have shown that singlet energy transfer from coumarin to benzophenone does not contribute measurably to the dimerization quantum yield. Energy transfer to benzophenone from a weakly fluorescing species, possibly an impurity in the solvent, occurs by emission-reabsorption. The mechanism which, in our opinion, best accounts for all of the experimental observations is outlined below.

$$\mathrm{C} + h\nu \longrightarrow {}^{1}\mathrm{C}^{*} \tag{1}$$

$$^{1}\mathrm{C}^{*} \longrightarrow \mathrm{VI} \longrightarrow \mathrm{C} \tag{18}$$

$$^{1}\mathrm{C}^{*} + \mathrm{C} \longrightarrow \mathrm{I} \tag{4}$$

$$^{1}\mathrm{C}^{*} \longrightarrow {}^{3}\mathrm{C}^{*} \tag{5}$$

$$\mathrm{B} + h\nu \longrightarrow {}^{1}\mathrm{B}^{*} \longrightarrow {}^{3}\mathrm{B}^{*} \tag{7}$$

$$^{3}\mathrm{B}^{*} + \mathrm{C} \longrightarrow \mathrm{B} + {}^{3}\mathrm{C}^{*} \tag{8}$$

$$^{3}\mathrm{C}^{*} \longrightarrow \mathrm{C} \tag{15}$$

$$^{3}\mathrm{C}^{*} + \mathrm{C} \longrightarrow {}^{3}\,(\mathrm{complex})^{*} \tag{12}$$

$$^{3}\,(\mathrm{complex})^{*} \longrightarrow 2\mathrm{C} \tag{13}$$

$$^{3}\,(\mathrm{complex})^{*} \longrightarrow \mathrm{IIa} \longrightarrow \mathrm{II} \tag{19}$$

This sequence contains the essential features proposed by Hammond, Stout and Lamola (4). Deleted are the singlet energy transfer from coumarin to benzophenone and energy wastage from a singlet excimer. The unique features we have introduced are: (a) a photoreaction of coumarin accounting for the singlet energy wastage; and (b) proposal of a triplet complex decaying to either ground state coumarins or a biradical, IIa, closing to II.

EXPERIMENTAL

MATERIALS

Coumarin - MCB reagent grade coumarin was recrystalized twice from ligroin (bp. 30 - 60°C) - benzene; mp. 69°C.

Benzophenone - MCB reagent grade benzophenone was either recrystalized once from ligroin or three times from ethanol; mp. 49°C.

trans-α,α-Dimethylstilbene was prepared and purified by Dr. Lelia M. Coyne (13).

trans-Dichloroethylene - MCB practical grade (bp. 48 - 50°C) was distilled through a 2' spinning band column. A constant boiling fraction, bp. 49.5°C, collected was 99% trans isomer and 1% cis isomer.

Benzene - Either benzene purified by sulfuric acid treatment (12), or MCB spectro quality without further treatment, was used. Both grades gave the same results.

Determination of Quantum Yield for Coumarin Dimerizations

A. Preparation of Samples. Benzene solutions of the system under study were delivered into constricted Pyrex test tubes by a calibrated syringe. The tubes had been previously washed with Orvis water soluble soap, carefully rinsed with distilled water

C. Actinometry for Quantum Yield - Two procedures were employed. The majority of the quantum yields were measured with potassium ferrioxalate (20) . Subsequent measurements were based on a relative comparison with the initially determined values. In some of the initial experiments benzophenone - benzhydrol actinometry (21) was used. The values from these two methods differed by a factor of 2. The source of the difference was not located. The ferrioxalate determined values are believed to be more reliable.

C. Analysis of Irradiated Samples. Two or three aliquots of each particular solution were analyzed with a Beckmann DU spectrophotometer at 3050 and 3150 Å. Samples were diluted by an appropriate factor with spectro benzene using a calibrated micro-syringe. Dilutions were made so that the absorbances were in the 0.8 to 0.2 range. Conversions were usually of the order of 10 to 25%. The deviations reported with the data represent the reproducibility of the determinations.

Flash Spectroscopy of Coumarin and Benzophenone - Coumarin Systems - The samples were placed in 10 cm. flash cells with jackets containing appropriate filter solutions so that coumarin or benzophenone could be selectively excited by a xenon flash lamp. The cells were degassed to about 5 x 10^{-6}mm. pressure by several freeze thaw cycles. The apparatus and techniques have been described elsewhere (22).

Fluorescent and Phosphorescent Emission Studies.

A. Quenching of Coumarin Fluorescence by Benzophenone. The total emission spectra of coumarin and coumarin-benzophenone solutions were measured with a photoelectric spectrometer consisting of a Jarrell-Ash-Ebert scanning monochromator(f/9), an EMI 9558 photomultiplier tube and appropriate recording electronics. Excitation was supplied by a General Electric AH4 mercury lamp with filters suitable for isolation of the 3130 Å line.

B. Phosphorescent Emission from Coumarin was measured at 77°K on the above instrument with a "rotating can" which separates the phosphorescence from the total emission. Some of the work was also done using an Aminco-Bowman spectrofluorometer with a phosphorescence attachment.

C. Phosphorescence Lifetimes were measured on an apparatus constructed by Mr. George F. Vesley. The coumarin samples in an ethanol glass at 77°K were excited by a xenon flash lamp. A $NiSO_4$ - $CoSO_4$ filter solution passing a band between 3400 - 2900 Å was placed between the lamp and the sample. For 3660 Å excitation, Corning 737 and 052 glass filters were used. The total emission from the samples was passed through a #3389 Corning glass filter which transmitted wave lengths $>$ 4200 Å to an RCA I P-21 photo tube. The photo tube output was amplified and displayed on an oscilloscope. Lifetimes were calculated from photographs of the oscilloscope display. This technique has been previously described (22).

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PART II

ASYMMETRIC INDUCTION DURING ENERGY TRANSFER

INTRODUCTION

One has only to scan a list of recent chemical publications to sense the substantial amount of work being done in photochemistry. Current interest in this rapidly expanding field has prompted publication of a number of excellent reviews and monographs (1, 2, 3). In order to properly discuss any photochemical mechanism, we must intimately understand the various photophysical processes which accompany and influence the efficiency of the chemical conversion. Our studies on one such process, bimolecular energy transfer, are the subject of this thesis.

Transfer of electronic excitation takes place between a donor (or sensitizer) and acceptor (or substrate)[a]. The overall process may be represented as:[b]

$$D + h\nu \longrightarrow D^* \qquad (1)$$

$$D^* + A \longrightarrow D + A^* \qquad (2)$$

Commonly encountered examples of energy transfer include sensitization and quenching of phosphorescence, fluorescence, and photochemical reactions.

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[a] We use the terms of the above pairs interchangeably.

[b] Throughout this thesis we use an asterik (*) at the upper right of a symbol denoting that that species is in an electronically excited state; The number at the upper left represents the spin multiplicity of that state.

Theoretically and experimentally, there seems to be two classes of mechanisms by which reaction 2 occurs in the liquid phase. A weak dipole-dipole coupling between donor and acceptor states over large distances (e.g., 50 - 100 Å) is effective for energy transfer when both transitions of the transfer pair are fully allowed and when the donor fluorescence and acceptor absorption spectra overlap. (14) Examples of this are:

$$^{1}D^{*} + {}^{1}A \longrightarrow {}^{1}D + {}^{1}A^{*} \qquad (3)$$

and

$$^{1}D^{*} + {}^{3}A \longrightarrow {}^{1}D + {}^{3}A^{*} \qquad (4)$$

Other transfers, not allowed by the above mechanism, apparently occur by an exchange interaction (4, 6). This mechanism is efficient only when the orbitals of the transfer pair overlap in space. The maximum rate of transfer in this instance is that of a diffusion controlled reaction. The most familiar example is triplet-triplet transfer,

$$^{3}D^{*} + {}^{1}A \longrightarrow {}^{1}D + {}^{3}A^{*}. \qquad (5)$$

When singlet energy transfer (reaction 3) is not efficient by the first mechanism, it may occur through the latter interaction.

In most systems studied, the acceptor energy levels are nearly isoenergetic with or lower than those of the donor. Otherwise, the reverse reaction, back transfer, would be the dominant reaction.

This restriction applies well to rigid molecules; those which do not undergo drastic changes in configuration upon excitation followed by relaxation. Aromatic hydrocarbons are an excellent example of this class. The above restriction breaks down when the acceptor is a "flexible " molecule. Examples of the latter are compounds which undergo facile photochemical isomerization, such as alkenes, conjugated dienes, stilbenes, etc. Theoretical calculations (5) and experimental results both suggest that upon electronic excitation, flexible molecules relax to lower energy configurations, substantially differing from those of the ground or spectroscopic states (7). Vibrational relaxation accompanying this distortion is very fast compared to other processes, eliminating the possibility of back-transfer.

"Flexible" acceptors are peculiar in another way. Hammond and Saltiel (7) discovered that the cis → trans isomerization of stilbene could be effected by triplet sensitizers having excitation energies far below the spectroscopic level of cis-stilbene. This effect has been subsequently observed and well documented for virtually every "flexible" acceptor investigated (7, 8). The discrepency in the donor and acceptor energies is apparently not compensated by thermal activation energy (7). Rather it is believed that low energy donors transfer to a non-spectroscopic acceptor state, arrived at through intimate donor-acceptor interaction.

Nuclear motion of the acceptor is believed to be concurrent with energy transfer. This is contrary to the Franck-Condon postulate which states that internal molecular motion is slow compared to electronic excitation. by interaction with the radiation field. This restriction may, however not be valid for energy transfer, where the transfer pair may intimately interact for a long interval on the nuclear motion time scale.

Triplet-triplet energy transfer is presumably due to an exchange interaction, which is large only when orbitals of the transfer pair overlap in space. Thus, the probability of transfer should be a function of the relative donor-acceptor orientation, and should have a maximum value for some preferred configuration. A preference of this type has been demonstrated spectroscopically for the benzophenone-phenanthrene-d_{10} pair (6). Roy and El-Sayed suggest that in the "best" relative orientation, the C-O axis is parallel to the phenanthrene plane.

These studies are also aimed at gaining a better insight into the intimate details of donor-acceptor interactions influencing energy transfer. Our approach to this problem is quite different. Rather than a total reliance on spectroscopic measurements, we employ a technique commonly and effectively used by physical-organic chemists: The affect of systematic variation of structure and its influence on reaction rates. For example, a donor-acceptor pair is selected.

The donor might be modified structurally, for example, by changing its bulk or polarity. Variation in the rate constant for energy transfer should indicate which structural parameters enhance or hinder the process. From this we attempt to infer characteristics of the transition state leading to energy transfer.

There is considerable evidence that the donor energy is the most important rate determining parameter for non-Franck-Condon transfer (7). To observe a valid steric or polar effect during transfer to a given acceptor, a comparison is best made between different donors having the same energies. Optically active donors and acceptors are ideal for this study. The overall energy requirements are identical for transfer from an optically active donor, (+)D, to an enantiomorphic acceptor pair, (+)A and (-)A. Only the relative geometries are different. A typical system might consist of an optically active donor, (+)D, and a racemic acceptor pair, (+)A and (-)A, which undergo a photochemical transformation. The following scheme should apply:

$$(+)D + h\nu \longrightarrow (+)D^{*} \qquad (6)$$

$$(+)D^{*} + (+)A \xrightarrow{k_7} (+)D + (+)A^{*} \qquad (7)$$

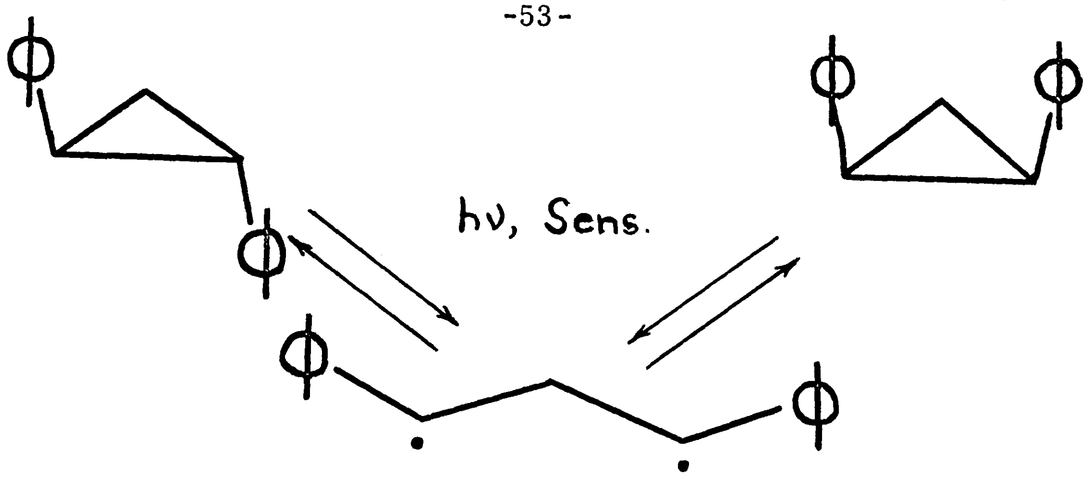
$$(+)D^{*} + (-)A \xrightarrow{k_8} (+)D + (-)A^{*} \qquad (8)$$

$$(\pm)A^{*} \longrightarrow \text{Products (either active or racemic)} \qquad (9)$$

If the donor interacts with (+)A and (-)A differently during energy transfer, $k_7 \neq k_8$. One isomer of the acceptor pair will be consumed faster, leaving the residual starting material partially optically active. Although the above scheme is considerably simplified, it contains the basic steps used in describing systems we have studied.

The sensitized trans → cis conversion of 1,2-diphenylcyclopropane, II, was selected for the asymmetric induction attempt. The system is well suited for this type of experiment in that: 1. the mechanism of the reaction seemed to be reasonably well understood (8); 2. rate constants for transfer from a number of different sensitizers were far below those of a diffusion controlled process; 3. centers of excitation and asymmetry are superimposed; 4. optically pure trans-II apparently has a large specific rotation (11); 5. the absolute configuration of trans-II is known (10, 11); 6. the product of isomerization is symmetric; and 7. previous work suggests that steric effects may be more pronounced in the system (8).

The photochemical trans → cis isomerization of II can be effected with sensitizers or by direct excitation (9). This apparently takes place by formation of an intermediate biradical, 1-3-diphenyltrimethylene, which closes to trans- and cis-II in the ratio 65:35, respectively.



Direct excitation leads to other products, such as 1,3-diphenylpropenes, but in lower quantum yields than the isomerization. The reverse reaction, formation of cis- and trans-II from 1,3-diphenylpropenes has also been reported (9).

RESULTS

Isomerization of (±)trans-1,2-diphenylcyclopropane with (+)N-acetyl-1-(1-naphthyl)-ethylamine.

Optically active (+)N-acetyl-1-(1-naphthyl)-ethylamine (I) was used as a sensitizer to effect the stereochemical trans ⟶ cis isomerization of (±)trans-1,2-diphenylcyclopropane (II). A benzene solution originally containing 0.012 M. (+)I and 0.1 M. (±)II was irradiated until a cis/trans photostationary (p.s.s.) of 1.03 was established. The p.s.s. for naphthalene is 0.92 (8). The sensitizer was removed from the irradiated solutions by alumina chromatography, and cis and trans isomers were separated by vapor phase chromotography (v.p.c.). The specific rotation of the trans isomer was + 28 ± 2° (c. 10.7, benzene) and that of the cis compound was 0.004 ± 0.004°.

The v.p.c. trace also showed the production of a small amount of a side product, believed to be a 1,3-diphenylpropene (9).

The kinetics for the production of cis-II and development of optical rotation were followed by periodically opening and analyzing irradiated samples (2 ml.) of (+)I (7.5×10^{-3}M.) and (±)trans-II (0.46 M.). The amount of cis-II formed was determined from a v.p.c. trace of the irradiated mixture. The rotations of the irradiated samples were large enough so that separation into the pure components was not necessary, Subtraction of the sensitizer rotation from the observed rotation gives the induced rotation.

The data from a typical run are given in Table I and are plotted in Figures I and II.

Effect of Sensitizer Concentration on Extent of Induced Rotation.

The sensitizer concentration was varied, holding the substrate concentration constant. The data in Table II are plotted in Figure III. The variations, apparently within experimental uncertainity, show no dependence of $[\alpha]_{d}^{25}$ trans-II upon concentration of (+)I. The (+)I concentrations used are the high and low limits experimentally possible with this system.

Effect of Substrate Concentration on Induced Rotation.

That data of Table III, plotted in Figure IV, indicate a slight increase in $[\alpha]_{d}^{25}$ with increasing substrate concentration. We feel that the variation is outside the experimental uncertainity.

Photostability of (+)I.

The photostability of (+)I was checked by irradiation of (+)I in benzene or methanol solution, following the rotation and the U.V. absorption spectra. Table V contains these data. After 29 days irradiation the absorption at 3150 Å decreased by about 3%.

TABLE I

Isomerization of (±)trans-II[a] Sensitized by (+)I[b]

Irradiation time (hrs.)	% cis-II formed	Rotation induced (degrees, 1 dm. tube)	$[\alpha]_d^{25}$ trans-II
5	1.86	0.20	1.4
15.5	7.1	0.53	5.5
25.5	9.5	0.64	6.9
42.5	14.2	0.86	9.8
75	17.2	0.90	11.6
112	19.0	0.98	12.5
170	31.2	1.48	22.4
200	29.4	1.36	20.2
310	35.0	1.46	23.3
310	38.2	1.50	25.8
360	36.5	1.45	25.3

Table I (continued)

Irradiation time (hrs.)	% _cis_-II formed	Rotation induced (degrees, 1 dm. tube)	$[\alpha]_d^{25}$ _trans_-II
480	37.6	1.45	24.6
530	38.5	1.57	26.7

[a] 0.46 M.

[b] 7.5×10^{-3} M.

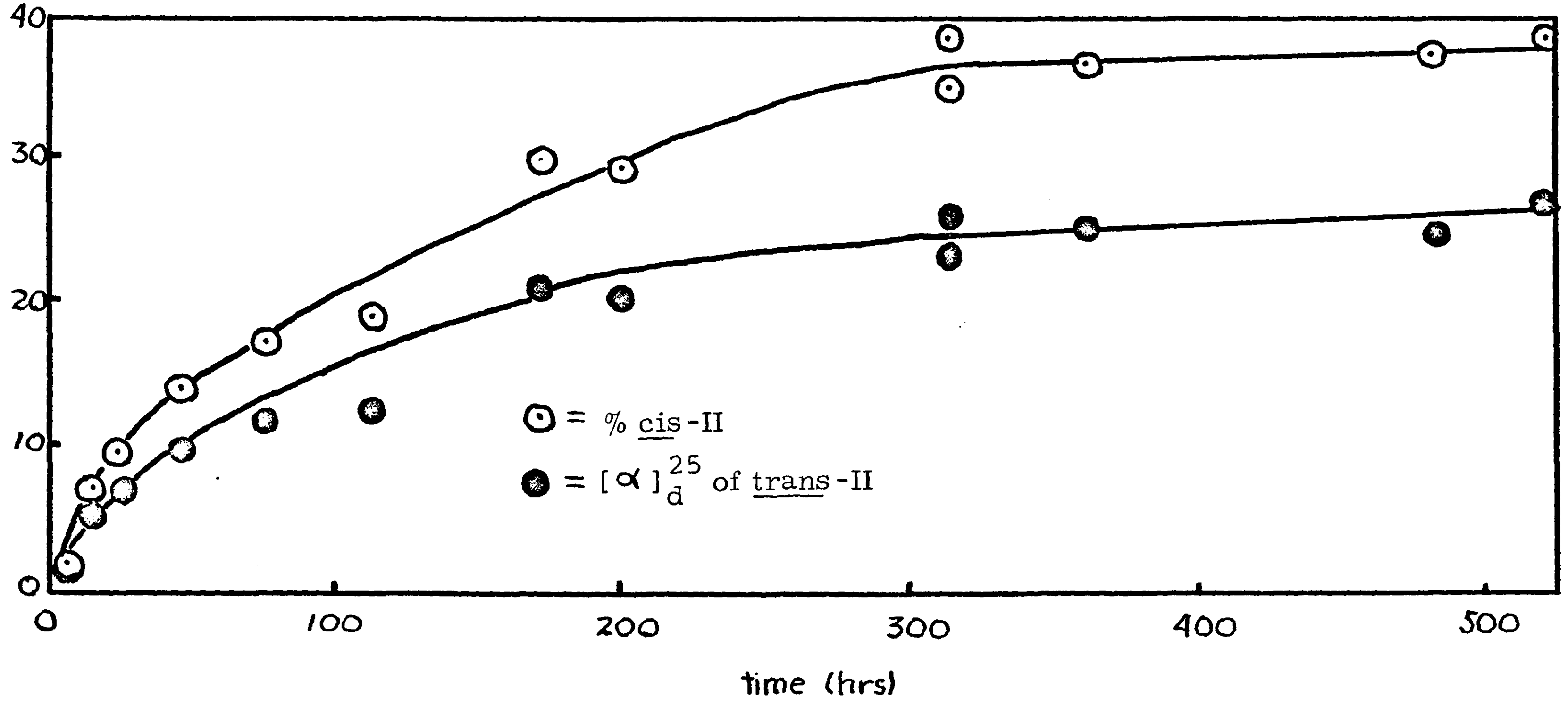


Figure I. Development of optical activity, ●; % cis isomer, ⊙ .

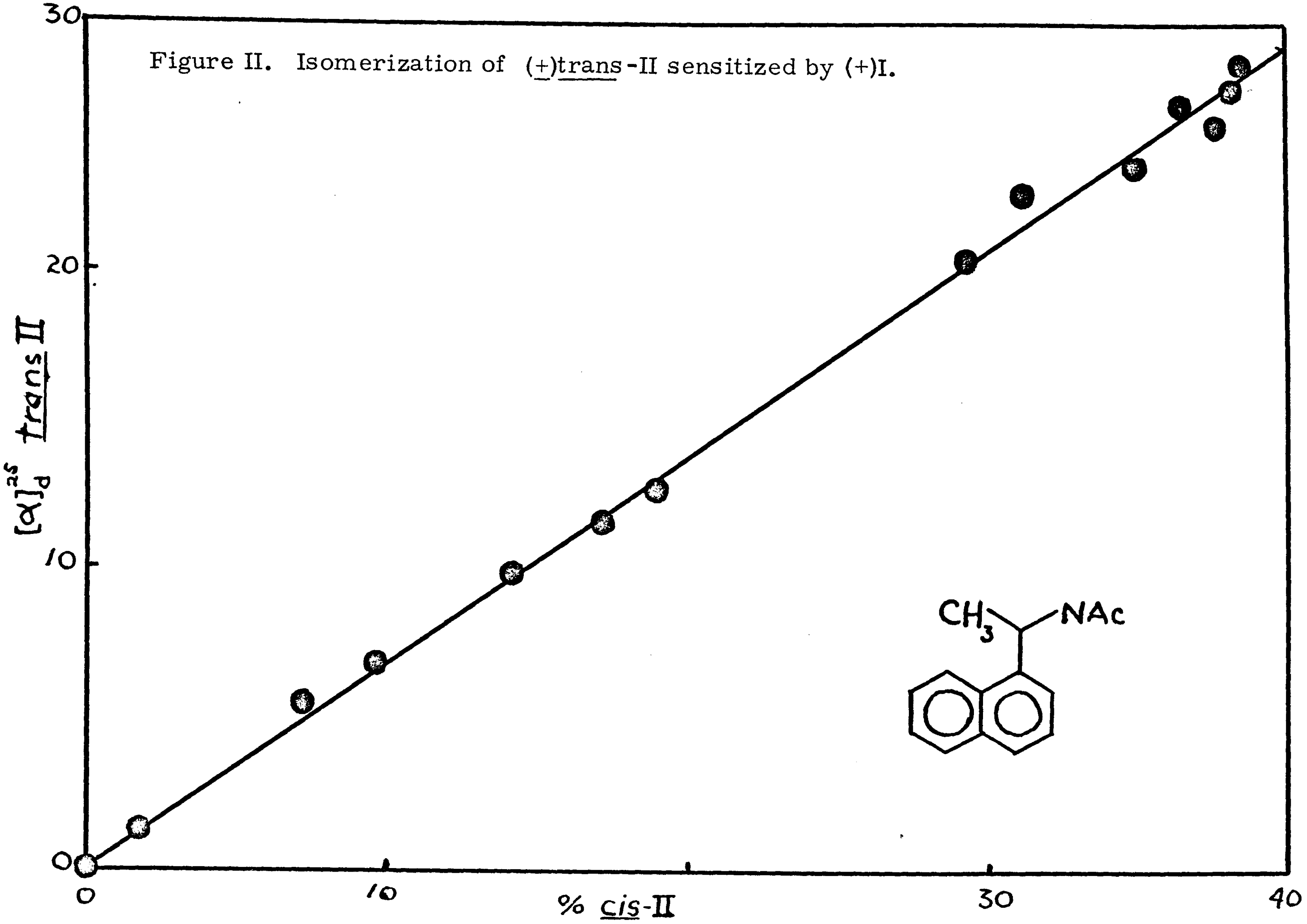


Figure II. Isomerization of (+)trans-II sensitized by (+)I.

TABLE II

Isomerization of (±)trans-II[a] sensitized by (+)I. Effect of concentration of (+)I.

conc. (+)I (m/1)	Irradiation time (days)	% cis-II	Induced Rotation (degrees, 2 dm. tube)	Specific Rotation of trans-II (degrees)
3.34×10^{-2}	2	2.2	0.16	1.6
	1	13.7	0.70	8.1
	7	14.9	0.64	7.5
	-	15.3	0.60	7.1
	2.9	32.7	1.13	16.8
	5	35.5	1.28	20.0
	-	40.5	1.24	20.8
2.35×10^{-2}	0.6	4.4	0.31	3.2
	0.9	5.6	0.39	4.1
	1.2	17.4	0.85	10.3
	2.7	22.4	1.03	13.8

Table II (continued)

conc. (+)I (m/1)	Irradiation time (days)	% <u>cis</u>-II	Induced Rotation (degrees, 2 dm. tube)	Specific Rotation of <u>trans</u>-II (degrees)
	4.8	28.5	1.14	15.9
0.80×10^{-2}	0.5	3.6	0.24	2.5
	1.0	8.3	0.31	3.4
	3.0	8.7	0.47	5.05
	9.0	31.5	0.69	10.1
0.85×10^{-2}	2.0	13.3	0.65	7.5
	4.0	20.2	0.83	10.4
	5.0	20.4	0.82	10.2
	7.0	27.5	1.06	14.7

[a] 0.254 M.

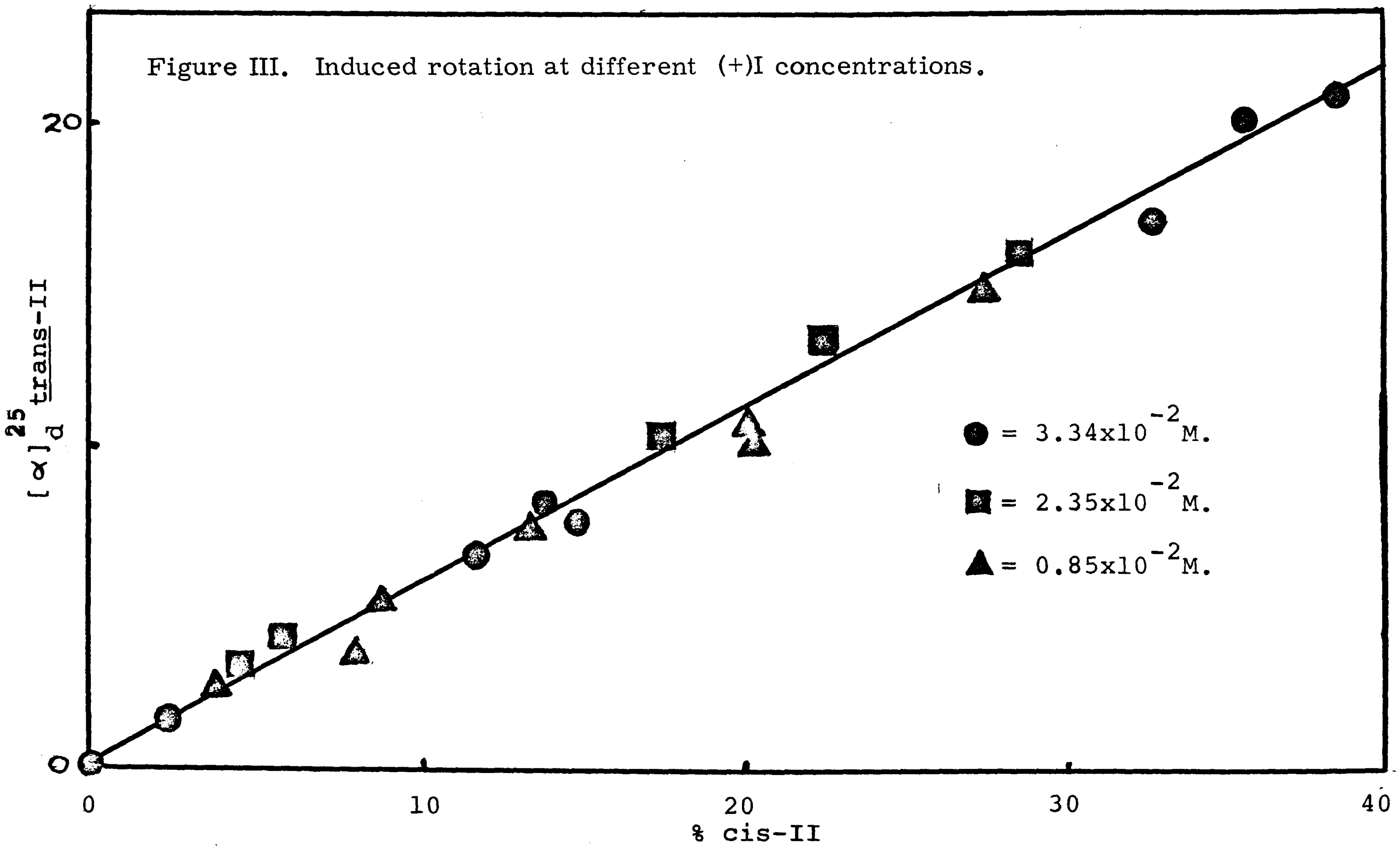


Figure III. Induced rotation at different (+)I concentrations.

TABLE III

Effect of Substrate Concentration on Specific Rotation

trans-II conc. (m/l)	(+)I conc. (m/l)	Irradiation time (days)	% *cis*-II	Induced Rotation (degrees)	$[\alpha]_d^{25}$ *trans*-II (degrees)
1.02	4.7×10^{-2}	1	4.4	1.20	3.14
		2.7	11.9	3.10	8.77
		4	15.4	3.71	11.0
		6	27.6	5.89	20.2
		11	33.4	6.41	24.1
0.46	0.75×10^{-2}	0.21	1.86	0.20	1.4
		0.65	7.1	0.53	5.5
		1.0	9.5	0.64	6.9
		1.8	14.2	0.86	9.8
		3.1	17.2	0.90	11.6
		4.8	19.0	0.98	12.5
		7.1	31.2	1.48	22.4

Table III (continued)

trans-II conc. (m/l)	(+) I conc. (m/l)	Irradiation time (days)	% cis-II	Induced Rotation (degrees)	$[\alpha]_d^{25}$ trans-II (degrees)
		8.4	29.4	1.36	20.2
		13.0	35.0	1.46	23.3
		13	38.2	1.50	25.8
		15	36.5	1.45	25.3
		20	37.6	1.45	24.6
		22	38.5	1.57	26.7
0.254	See Table II.				

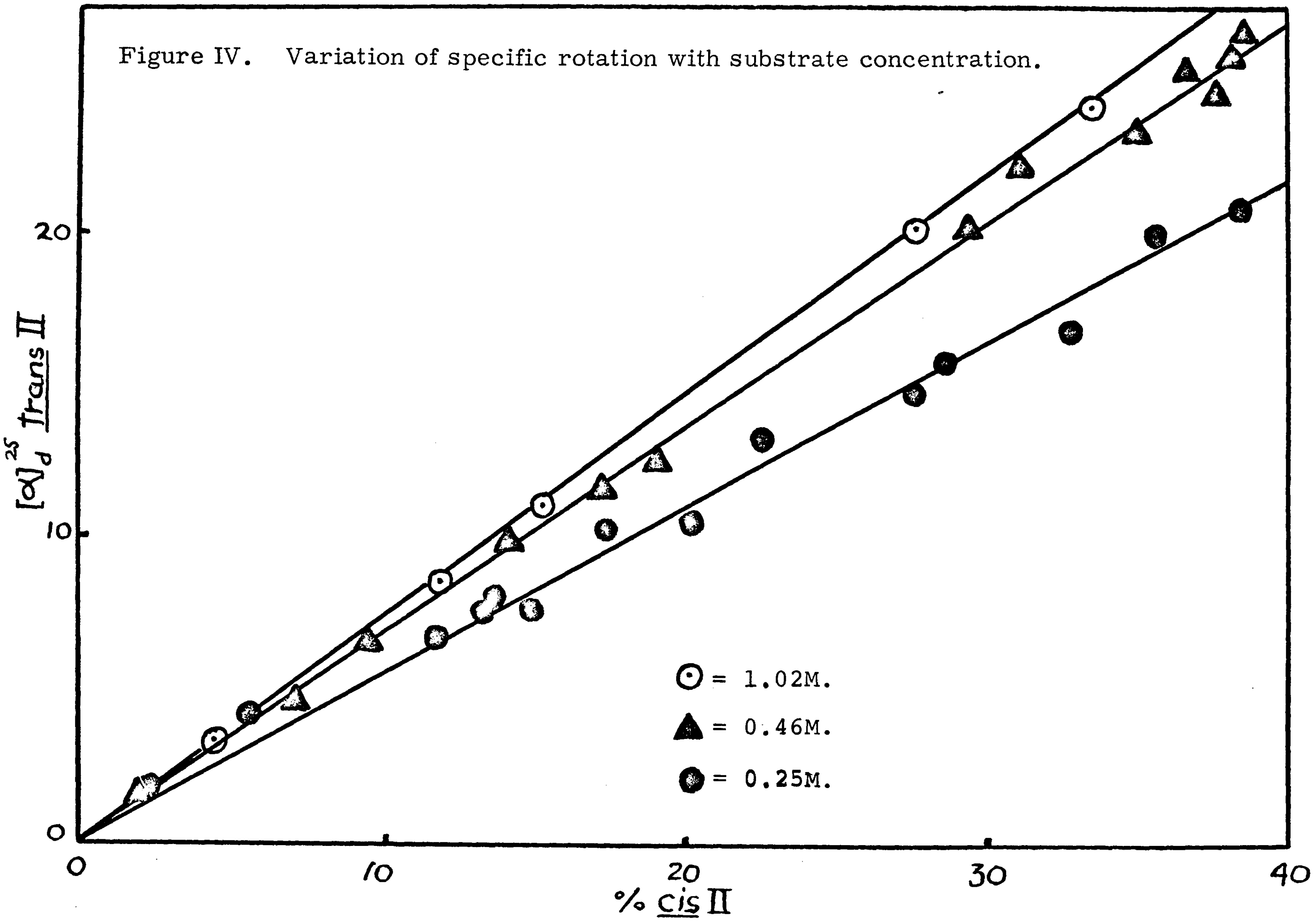


Figure IV. Variation of specific rotation with substrate concentration.

Upon prolonged irradiation, slight decomposition was noted by production of yellow coloration in the samples.

TABLE V

Irradiation of (+)I in Methanol

Irradiation time (days)	Rotation (°) in 2 dm. tube	Absorption at 3150 Å [a]
0	0.64 ± 0.01	0.54
13	0.62 ± 0.02	0.54
29	0.53 ± 0.06	0.53

[a] Diluted by 150.

Solvent Effect on Induced Rotation.

Table VI contains the results for the trans → cis conversion of (±)trans-II sensitized by (+)I in methanol. The data are plotted in Figure V along with a line representing the slope obtained with benzene as a solvent. The ratio of specific rotations of (+)trans-II in methanol and benzene is 1.23, respectively. The sensitizer is apparently less selective between (+) and (-)trans-II in this more polar and hydrogen-bonding solvent.

TABLE VI

Isomerization of trans-II[a] by (+)I[b] in Methanol

Irradiation time (days)	% cis-II formed	Induced Rotation (degrees, 1 dm. tube)	$[\alpha]_d^{25}$ trans-II
1	3.5	0.17	1.71
2	19.2	0.65	8.05
5	15.6	0.53	6.48
7	23.9	0.79	10.3
13	25.0	0.78	10.4

[a] 0.49 M.

[b] 7.5×10^{-3} M.

Effect of Temperature on Induced Rotation.

A substantial and rather interesting change in the induced rotation is evident from the data in Table VII. The values of $[\alpha]_d^{25}$ in Figure VI extrapolated to the photostationary state at 25°C. are 43.0, 33.8 and 11.2 for the respective temperatures 2, 25 and 85°C. The quantum yields are not comparable. A different apparatus was used for the measurements at each temperature. We note that the induced rotation decreases considerably with increasing temperature.

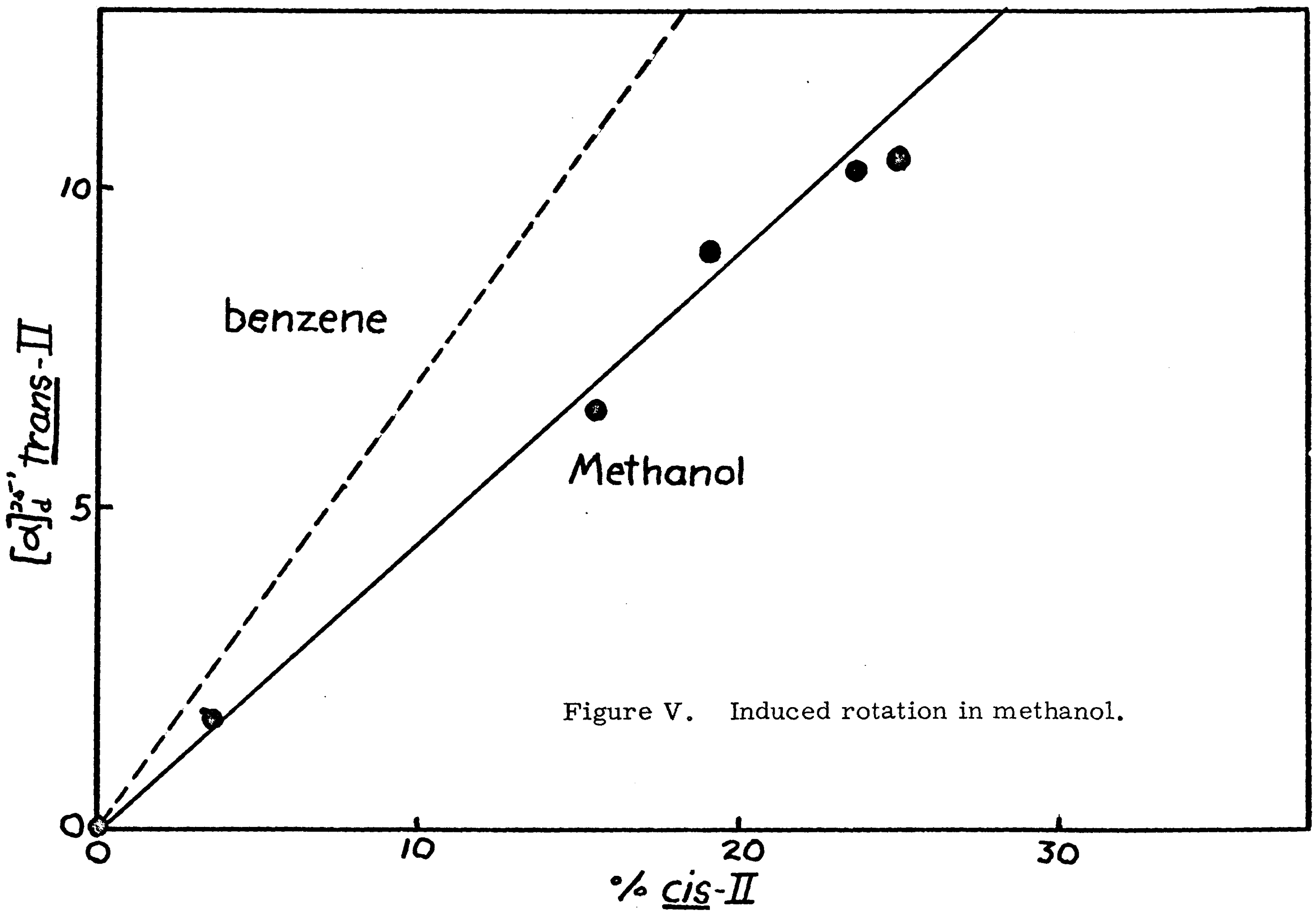


Figure V. Induced rotation in methanol.

Unfortunately, side reactions become more important at elevated temperatures. Samples irradiated at 85°C. discolored more rapidly than those at 2 and 25°C. (+)I in benzene is photostable upon prolonged irradiation at elevated temperatures.

Beer's Law Measurements.

Spectra of (+)I, (±)*trans*-II and their combination demonstrate obedience to Beer's law. The data in Table VIII gives no indication of complex formation between sensitizer and substrate.

Sensitization of the Asymmetric Induction System by Benzophenone. and Triphenylene.

We used benzophenone and triphenylene as primary sensitizers, S, to form triplet (+)I. The following sequence should apply.

$$S + hv \longrightarrow {}^{1}S^{*} \longrightarrow {}^{3}S^{*} \qquad (11)$$

$$ {}^{3}S^{*} + (+)I \xrightarrow{k_{12}} S + {}^{3}(+)I^{*} \qquad (12)$$

$$ {}^{3}S^{*} + \underline{\text{trans}}\text{-II} \xrightarrow{k_{13}} S + \underline{\text{cis}}\text{-II} \qquad (13)$$

$$ {}^{3}(+)I^{*} + \underline{\text{trans}}\text{-II} \xrightarrow{k_{14}} (+)I + \underline{\text{cis}}\text{-II} \qquad (14)$$

$$ {}^{3}(+)I^{*} \xrightarrow{k_{15}} (+)I \qquad (15)$$

In these experiments concentrations of S, (+)I and *trans*-II were chosen so that at least 99% of the incident light is absorbed by S, which undergoes reaction 11 with near unit efficiency. DeBoer has

TABLE VII

Isomerization of (±)trans-II[a] sensitized by (+)I[b]; Effect of Temperature

Temp. (^{o}C)	% cis-II formed	Induced Rotation (degrees, 2 dm. tube)	$[\alpha]_{d}^{25}$ trans-II
2	1.6	0.20	1.02
	9.1	1.44	7.95
	14.4	2.11	12.3
	24.0	3.18	20.9
2.5	See Table I.		
85	4.2	0.09	0.47
	5.5	0.26	1.38
	8.4	0.34	1.85
	14.8	0.60	3.52
	17.4	0.58	3.50

[a] 0.515 M.

[b] 2.2×10^{-2}M.

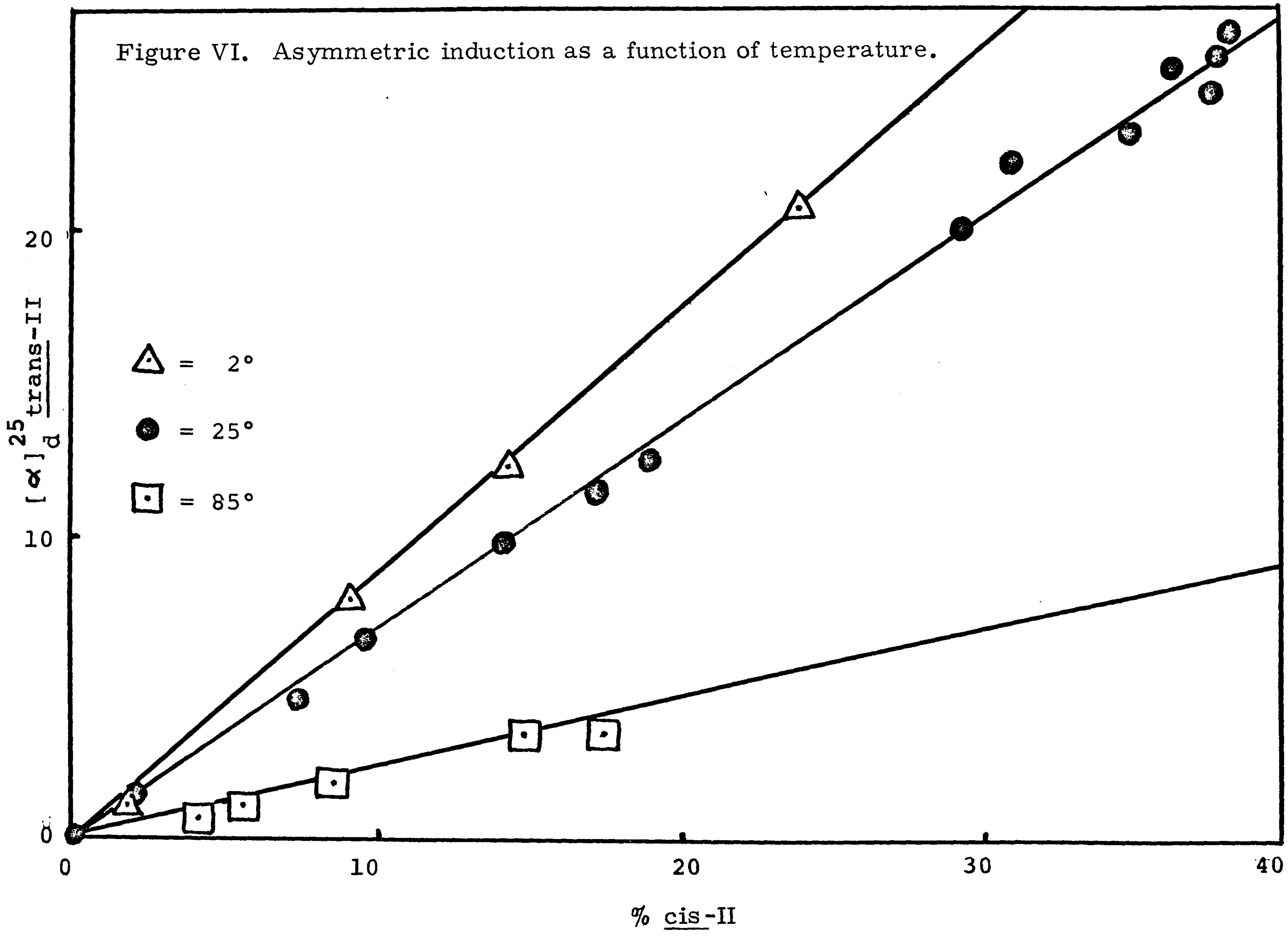


Figure VI. Asymmetric induction as a function of temperature.

TABLE VIII

Spectra of (±)*trans*-II and (+)I in Cyclohexane

		Absorption at wave length =					
conc. (+) I m/l	conc. (±) *trans*-II m/l	3000	3050	3100	3130	3200	3300
0.00	0.51	0.07	0.04	0.025	0.020	0.010	0.005
8.0×10^{-4}	0.00	0.62	0.34	0.165	0.260	0.030	0.00
8.0×10^{-4}	0.51	0.77	0.40	0.210	0.285	0.050	0.01

measured k_{13} to be 10^4 and 10^3 for triphenylene and benzophenone, respectively. Transfer from S to (+)I should be diffusion controlled. With (+)I and trans-II concentration respectively 8.0×10^{-3}M. and 0.25 M., virtually all of the triplets from S will be transferred to (+)I. The presence of S insures that energy transferred to trans-II comes from triplet (+)I. In all experiments of this type, less than 0.1% isomerization occurred even after irradiation for 15 days, a period sufficient to effect at least 10% conversion in the absence of either S or (+)I.

Quenching Studies.

Several conjugated dienes were used to partially quench the trans ⟶ cis isomerization of II. In preliminary experiments it was found that 0.05 in piperylene decreases the isomerization rate of II (0.5 M.) by a factor of 2. The sensitizer (+)I, however, was rapidly consumed in a photoreaction with piperylene.

We found (+)I to be unreactive during irradiation in the presence of butadiene, 1,3-cyclohexadiene and 2,5-dimethyl-2,4-hexadiene (III). The quantum yield for the sensitized photodimerization of butadiene and III is not significant compared to the trans → cis-II quantum yield under the conditions used. We would have easily detected 5% diene-dimer formation.

Table IX contains the data for butadiene quenching of the (+)I sensitized *trans* ⟶ *cis*-II conversion, indicating that $\Phi_o : \Phi = 1.12$. Stephenson (15) finds that the ratio of fluorescence intensities of naphthalene in the absence and presence of 0.05 M. butadiene, I_o:I, is 1.08.

We find that 0.017 M. 1,3-cyclohexadiene quenches the (+)I sensitized isomerization of 0.51 M. *trans*-II by 19%. In this sytem we noted that most of the diene was converted to dimers before 1% *cis*-II appeared.

The most detailed quenching experiments were done with 2,5-dimethyl-2,4-hexadiene, III. In this case we compare the extent of fluorescence quenching of (+)I with the isomerization quenching of *trans*-II sensitized by (+)I. Table XI and XII contain these data which are plotted in Figures VII and VIII.

Similar behavior is noted for III quenching of the naphthalene sensitized isomerization. (See Table X). We find that 1.1×10^{-2}M. III decreases the isomerization rate by 75%. Under these conditions 72% of the naphthalene fluorescence is quenched by III.

There apparently is no measurable fluorescence quenching of (+)I (5×10^{-3}M) by 0.5 M. *trans*-II. A slight decrease in the (+)I emission intensity in the presence of 0.25 M. *trans*-II can easily be accounted for by the substrate's partial absorption of the exciting band.

TABLE IX

Butadiene quenching of *trans*-II[a], sensitized by (+)I[b].

Diene conc. (m/l)	Irradiation time (days)	% *cis*-II formed	$\Phi_o : \Phi$
0.00	2	1.2	
	9	7.4	
	12	7.6	
	16	7.6	
	16	12.8	
0.048	2	1.2	1.00
	9	6.7	1.10
	12	6.7	1.13
	16	11.4	1.12

[a] conc. = 0.5 M.

[b] conc. = 0.015 M.

TABLE X

Naphthalene[a] sensitized isomerization of *trans*-II[b]. Quenching by III.

III conc. (m/l)	Irradiation time (days)	% *cis*-II formed	$\Phi_o : \Phi$
0.00	1.0	0.61	1.00
	2.0	1.16	1.00
	3.16	1.83	1.00
	5.25	2.62	1.00
	5.8	3.03	1.00
1.1×10^{-2}	1.0	0.14	4.35
	2.0	0.26	4.46
	3.16	0.45	4.07
	5.25	0.73	3.59
	5.8	0.82	3.70
		Average =	4.03

[a] Sensitizer conc. 1.9×10^{-2} M. [b] Substrate conc. = 0.51 M.

TABLE XI

Isomerization of trans-II[a] sensitized by (+)I[b].

Quenching by 2,5-dimethyl-2,4-hexadiene.

Diene conc. (m/l.)	Irradiation time (days)	% cis-II formed	$\Phi_o : \Phi$	
0.00	1	1.14	1.00	
	2	2.29	1.00	Ave. =
	3	3.20	1.00	1.00
	4	4.25	1.00	
	5	5.35	1.00	
1.0×10^{-3}	1	1.01	1.13	
	2	2.08	1.10	Ave. =
	3	2.74	1.17	1.13
	4	3.78	1.12	
	5	4.75	1.12	
5.0×10^{-3}	1	0.635	1.79	
	2	1.37	1.67	Ave. =
	3	1.91	1.67	1.67
	4	2.65	1.60	
	5	3.33	1.61	
1.0×10^{-2}	1	0.43	2.67	
	2	0.82	2.79	Ave. =
	3	1.20	2.67	2.68
	4	1.63	2.61	
	5	2.03	2.63	
2.0×10^{-2}	1	0.24	4.76	
	2	0.46	4.97	Ave. =
	3	0.70	4.57	4.64
	4	0.97	4.38	
	5	1.18	4.54	

[a] Substrate conc. = 0.51 M.; [b] Sensitizer conc. = 0.047 M.

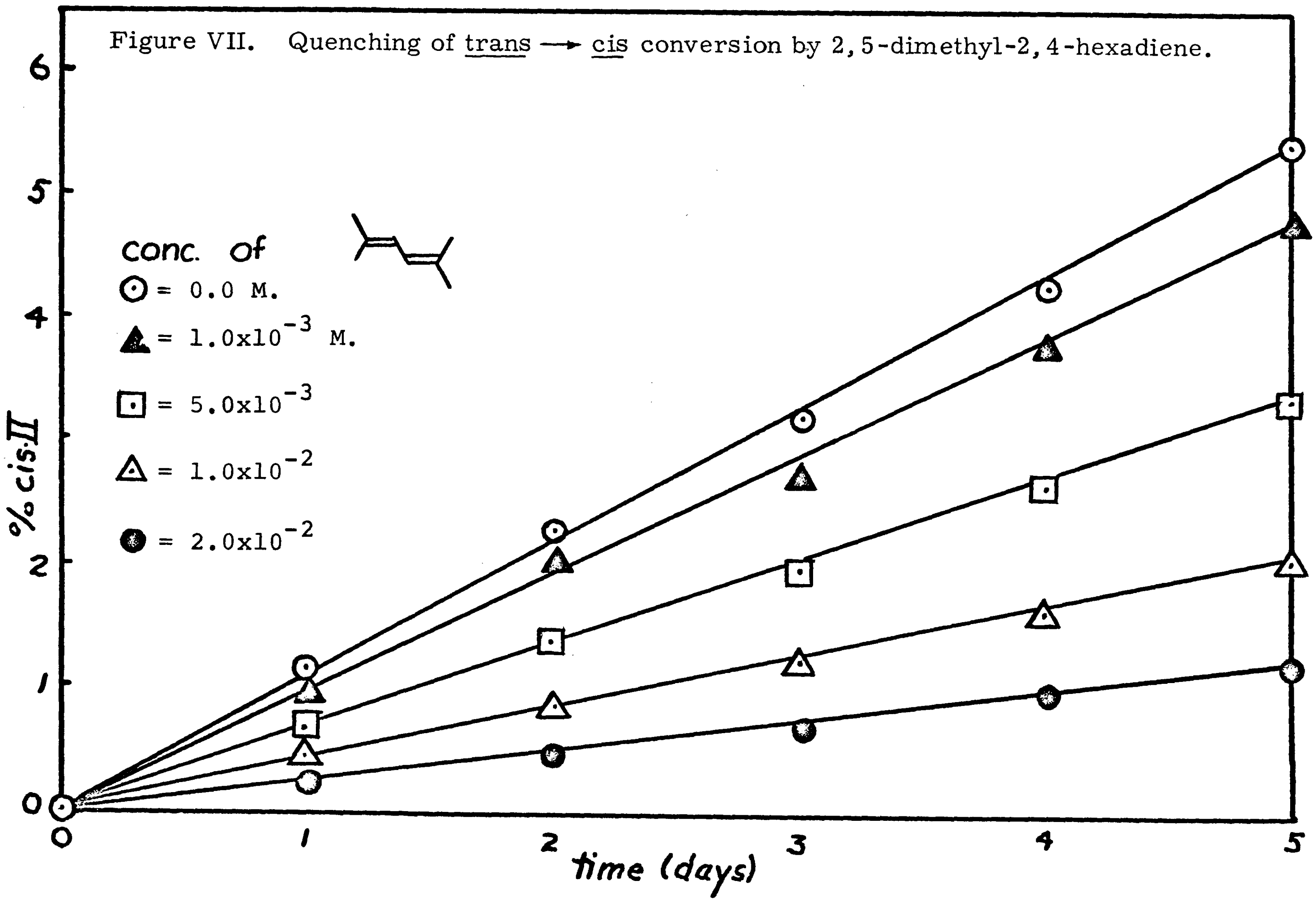


Figure VII. Quenching of trans ⟶ cis conversion by 2,5-dimethyl-2,4-hexadiene.

TABLE XII

Fluorescence quenching of (+)I[a] by III.

Diene conc. (m/l)	Relative Fluorescence Intensity	I_o:I
0.00	17.4	1.00
1.0×10^{-3}	16.0	1.09
3.0×10^{-3}	12.7	1.37
5.0×10^{-3}	10.1	1.72
1.0×10^{-2}	7.5	2.32
1.0×10^{-2}	6.7	2.60
2.0×10^{-2}	4.0	4.35

[a] (+)I conc. = 1.0×10^{-4} M.

Relative trans → cis Quantum Yields.

Relative quantum yields for the trans → cis conversion sensitized by (+)I are given in Table XIII. These were determined by simultaneous irradiation of sensitizer and substrate at various concentrations. Relative Φ^{-1} and 1/(trans-II) are plotted in Figure IX.

TABLE XIII

Relative trans → cis-II Quantum Yields vs. trans-II Concentration

conc. trans-II (m/l)	Irradiation time(days)	% cis-II formed	$\frac{\text{moles cis-II}}{\text{day}}$
1.0	2.0	1.63	2.44×10^{-5}
1.0	2.84	2.21	2.34×10^{-5}
1.0	3.25	2.53	2.33×10^{-5}
0.5	2.0	2.01	1.51×10^{-5}
0.5	2.84	2.66	1.41×10^{-5}
0.5	3.25	3.10	1.40×10^{-5}
0.25	2.0	2.37	8.90×10^{-6}
0.25	2.84	3.28	8.65×10^{-6}
0.25	3.25	3.75	8.65×10^{-6}
0.10	2.0	2.97	4.45×10^{-6}
0.10	2.84	4.07	4.30×10^{-6}
0.10	3.25	4.71	4.35×10^{-6}
0.05	2.0	6.07	4.6×10^{-6}
0.05	2.84	9.06	4.8×10^{-6}
0.05	3.25	5.60	2.6×10^{-6}

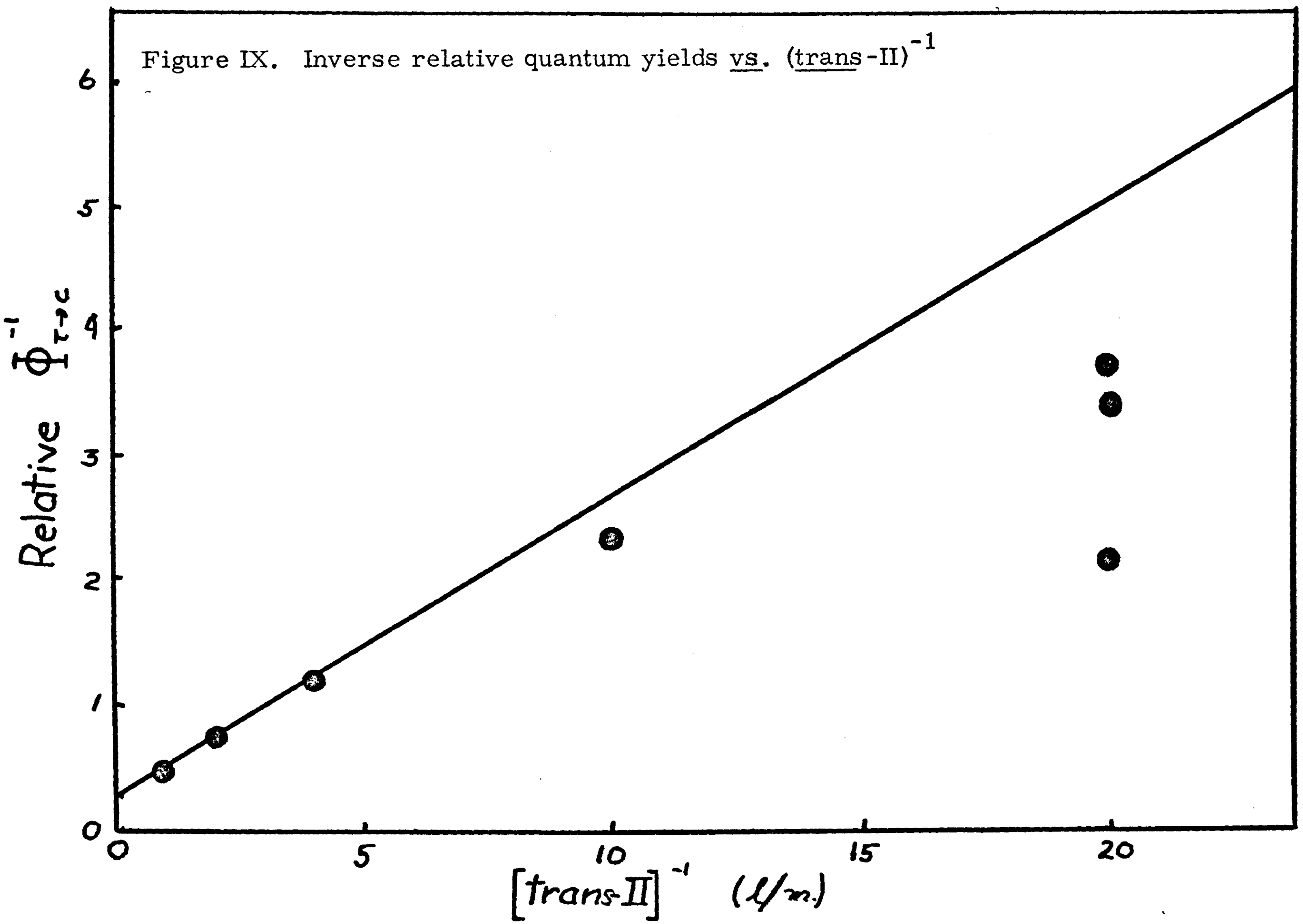


Figure IX. Inverse relative quantum yields vs. (trans-II)$^{-1}$

Benzophenone Sensitized Isomerization; Quenching by 2,5-dimethyl-2,4-hexadiene (III).

The *trans* → *cis* isomerization of II can be sensitized by benzophenone, B, (8). Ratios of $\Phi_o : \Phi$ in Table XIV suggest that triplet energy transfer from benzophenone to *trans*-II is responsible for the isomerization. The following scheme applies to this system:

$$\begin{array}{lllll}
\mathrm{B} + h\nu & \longrightarrow {}^1\mathrm{B}^* \longrightarrow {}^3\mathrm{B}^* & & & (11) \\
{}^3\mathrm{B}^* + \underline{\text{trans}}\text{-II} & \xrightarrow{k_{13}} & \mathrm{B} + \mathrm{T} & & (13) \\
{}^3\mathrm{B}^* + \mathrm{III} & \xrightarrow{k_{21}} & \mathrm{B} + \mathrm{III} & & (21) \\
{}^3\mathrm{B}^* & \xrightarrow{k_{19}} \mathrm{B} & & & (19)
\end{array}$$

The quantum yield for isomerization is:

$$\Phi_{\underline{\text{trans}} \rightarrow \underline{\text{cis}}} = \Phi_{ic} \left(\frac{k_{13}\,[\underline{\text{trans}}\text{-II}]}{k_{19} + k_{21}\,[\mathrm{III}] + k_{13}\,[\underline{\text{trans}}\text{-II}]} \right) \left(\frac{k_{25}}{k_{24} + k_{25}} \right)$$

Thus,

$$\frac{\Phi_o}{\Phi} \equiv \left(\frac{k_{19} + k_{21}\,[\mathrm{III}] + k_{13}\,[\underline{\text{trans}}\text{-II}]}{k_{19} + k_{13}\,[\underline{\text{trans}}\text{-II}]} \right)$$

The initial ratio of quantum yields is 21, decreasing to about 10 as the benzophenone is consumed in a side photoreaction in both systems at about the same rate. The first order decay constant, k_{19}, for benzophenone triplets is 10^6 sec^{-1} (22). Transfer from benzophenone to III should be diffusion controlled. We take 5×10^9 $\mathrm{l.\ mole}^{-1}\ \mathrm{sec}^{-1}$ as the rate constant for reaction 21 (7).

TABLE XIV

Benzophenone[a] sensitized isomerization of trans-II[b];

Quenching by 2, 5-dimethyl-2, 4-hexadiene (III)

Diene conc. (m/1)	Irradiation time (days)	% cis-II formed	$\Phi:\Phi$ quenched	ratio - benzophenone: trans-II[d]
0.00	0.5	0.19	22	0.015
	2	0.53	20	0.014
	5	0.71	8.4	0.009
	7	0.89	9.4	0.012
	14	0.83	10.4	0.008
1.1×10^{-2}	0.5	0.0085		0.017
	2	0.026		0.013
	5	0.085		0.013
	7	0.095		0.009
	14	0.078		0.008

[a] 0.02 M.

[b] 0.51 M. in benzene

[c] Uranium glass filter transmitting 3340 Å

[d] By v.p.c. analysis

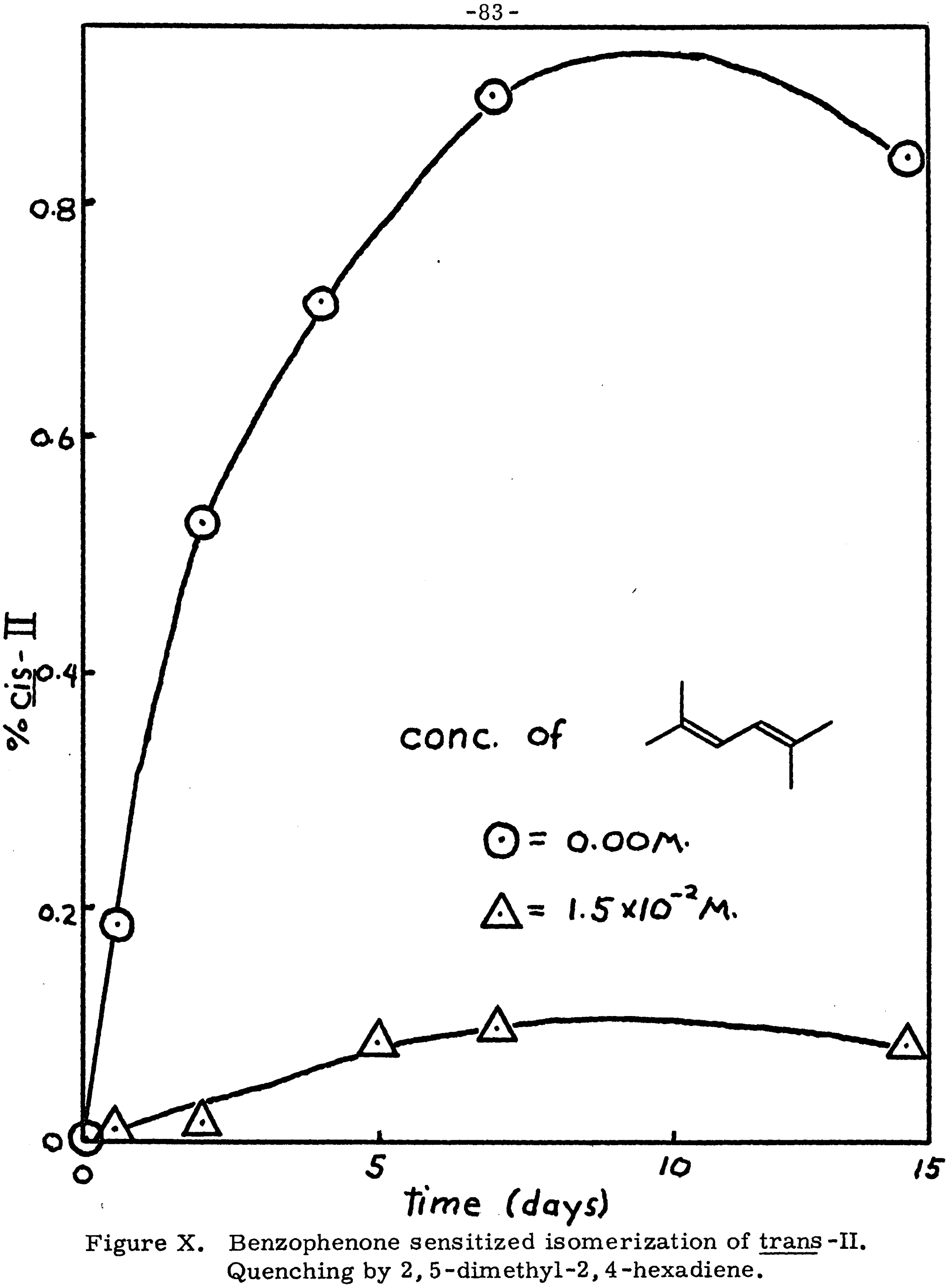


Figure X. Benzophenone sensitized isomerization of trans-II. Quenching by 2, 5-dimethyl-2, 4-hexadiene.

Substituting these values into the above expression we calculate $k_{13} = 3.8 \times 10^{6}$ l. mole $^{-1}$ sec. $^{-1}$. DeBoer's measurements of k_{13} for p-methylbenzophenone, a sensitizer almost identical to benzophenone in energy and structure, give a value of about 7×10^{3} l. mole^{-1} sec^{-1}. This value seems to be inordinately low in comparison with other sensitizers of similar energy and nature (8). Our determination of k_{13} seems to be more in accord with DeBoer's rate constants for a number of phenyl conjugated ketones.

Isomerization of cis-II by (+)I.

The cis → trans isomerization of II was effected by (+)I sensitization. Production of trans-II and its rotation were monitored. Results of these experiments in Table XV are plotted in Figure XI. By inspection, we note that the initially formed trans-II is optically inactive. An initial $[\alpha]_{d}^{25}$ trans-II of 0.5° would have been detected, or about 1/70 of that resulting from transfer to the trans-II isomers.

TABLE XV

Isomerization of <u>cis</u>-II sensitized by (+)I.

Substrate conc. (m/l)	% <u>trans</u>-II formed	Induced Rotation (degrees, 2 dm. tube)	$[\alpha]^{25}_{d}$ <u>trans</u>-II (degrees)
1.28	0.0	0.00	0.00
1.28	1.0	0.00	0.00
1.28	3.0	0.01	0.67
1.28	6.8	0.07	2.06
1.28	10.0	0.15	3.00
0.41	15.8	0.13	5.2
0.41	24.7	0.36	8.75
0.41	29.6	0.64	13.4
0.41	30.1	0.90	18.7
0.41	30.0	0.82	17.1

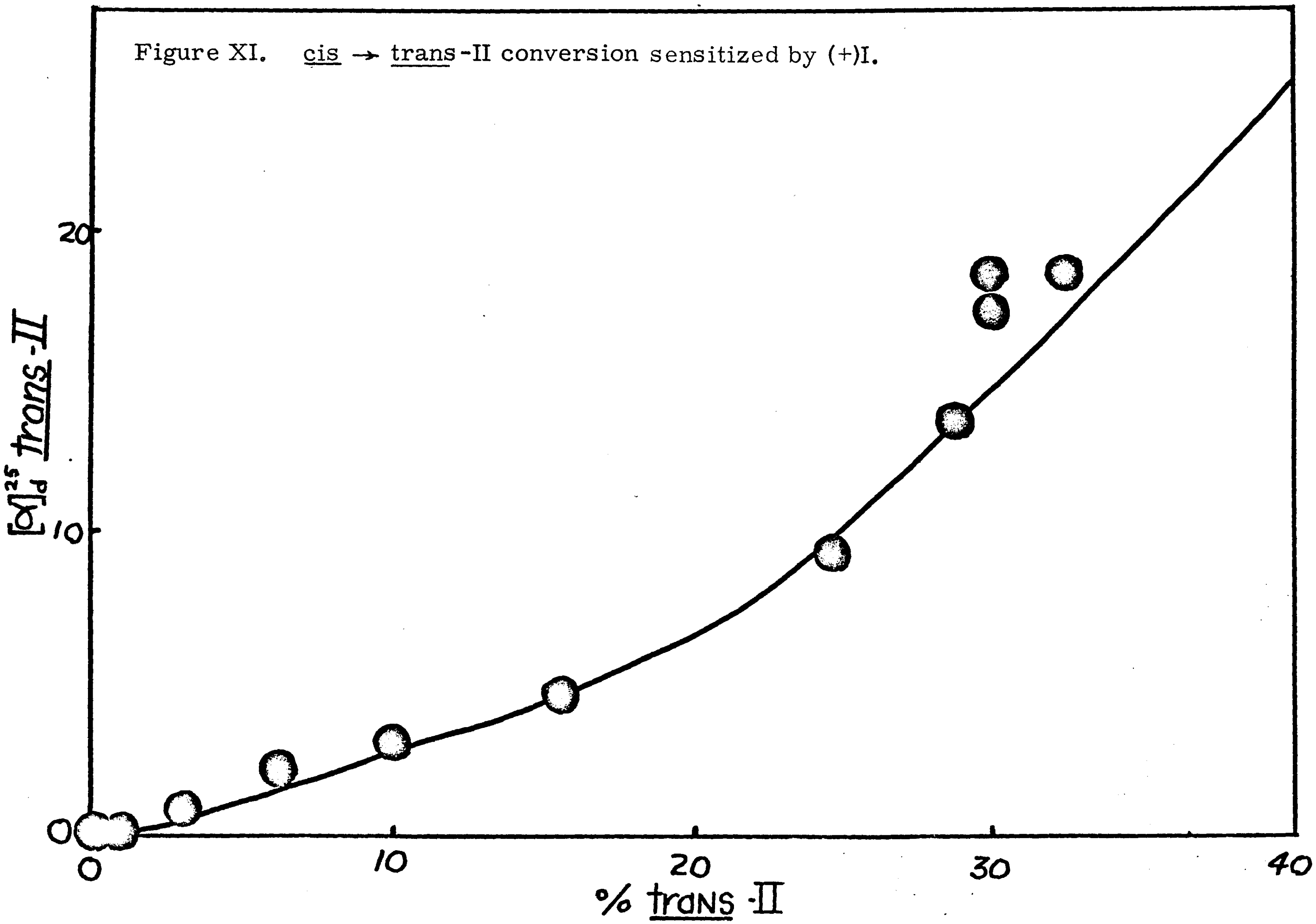
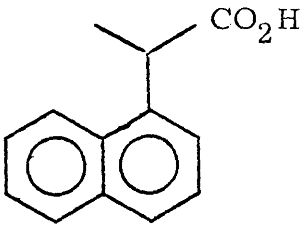


Figure XI. cis → trans-II conversion sensitized by (+)I.

Variation of the Asymmetric Group.

We synthesized a number of other optically active naphthalene sensitizers, varying the nature and position of the substituent group. Included are the compounds shown below.



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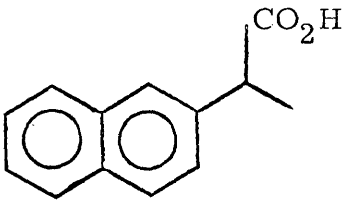

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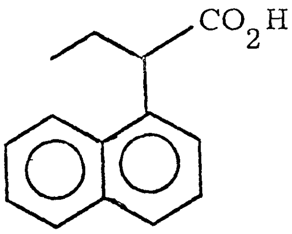

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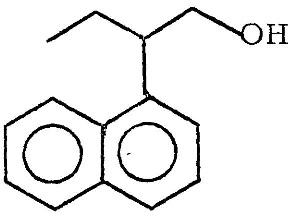
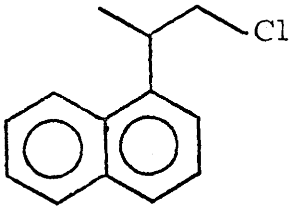


VII



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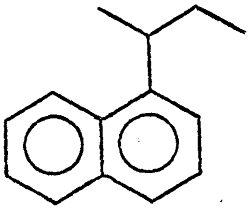

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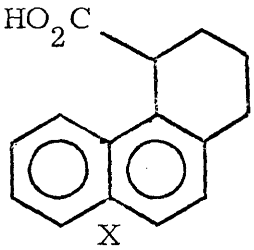
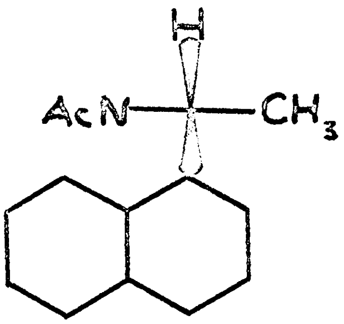


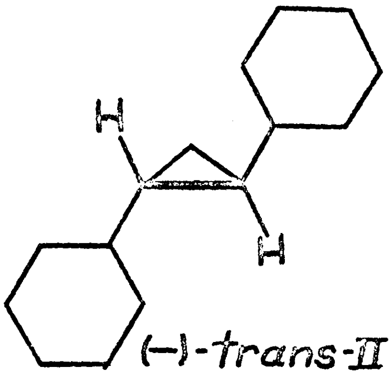
X

Data for the sensitized isomerization of trans-II are given as follows: Compound IV: Table XV, Figure XV; Compound V: Table XVI, Figure XVI; Compound VI: Table XVII, Figure XVII; Compound VII: Table XVIII, Figure XVIII; Compound VIII: Table XIX; Compound IX: no isomerization of trans-II observed; Compound X: Table XXI. In Table XX we summarize the compounds, their configurations and the extent of asymmetric induction extrapolated to the *trans*-*cis* photostationary state of naphthalene. We presume that each of these naphthalene derivatives gives a similar p.s.s. With each sensitizer the reaction proceeds very slowly after about 40% conversion.

Absolute Configurations of Substrate and Sensitizers.



(+)R- I



(-)-trans-II

Absolute configurations for most of the sensitizers have been determined, either by ORD or by stereospecific synthesis. Configuration for IV, V and VI are calculated by Brewster's Rules (23) and agree with those of the corresponding phenyl compounds (23,24). Table XXII contains these data. In the figure above we show the absolute configurations of (+)I and (-)*trans*-II. The latter was determined by stereospecific synthesis (11) and by degradation to a compound of known configuration (10). The specific rotation of optically pure (+)*trans*-II is at least 117° and may be as high as 148°. (11).

TABLE XV

Isomerization of (±)*trans*-II[a]

Sensitized by (+)2-(1-naphthyl) propanoic acid (IV).[b]

Irradiation time (hrs.)	% *cis*-II formed	Induced Rotation (degrees, 2 dm. tube)	$[\alpha]_d^{25}$ *trans*-II
16	5.3	-0.10	-1.26
41	8.6	-0.26	-3.2
65	15.6	-0.36	-5.00
89	18.0	-0.41	-5.93
161	20.8	-0.48	-7.10
305	30.5	-0.57	-9.75
569	37.2	-0.61	-11.6
905	46.4	-0.60	-13.6
881	42.0	-0.61	-12.6

[a] conc. = 0.41 M.

[b] conc. = 2×10^{-2} M.

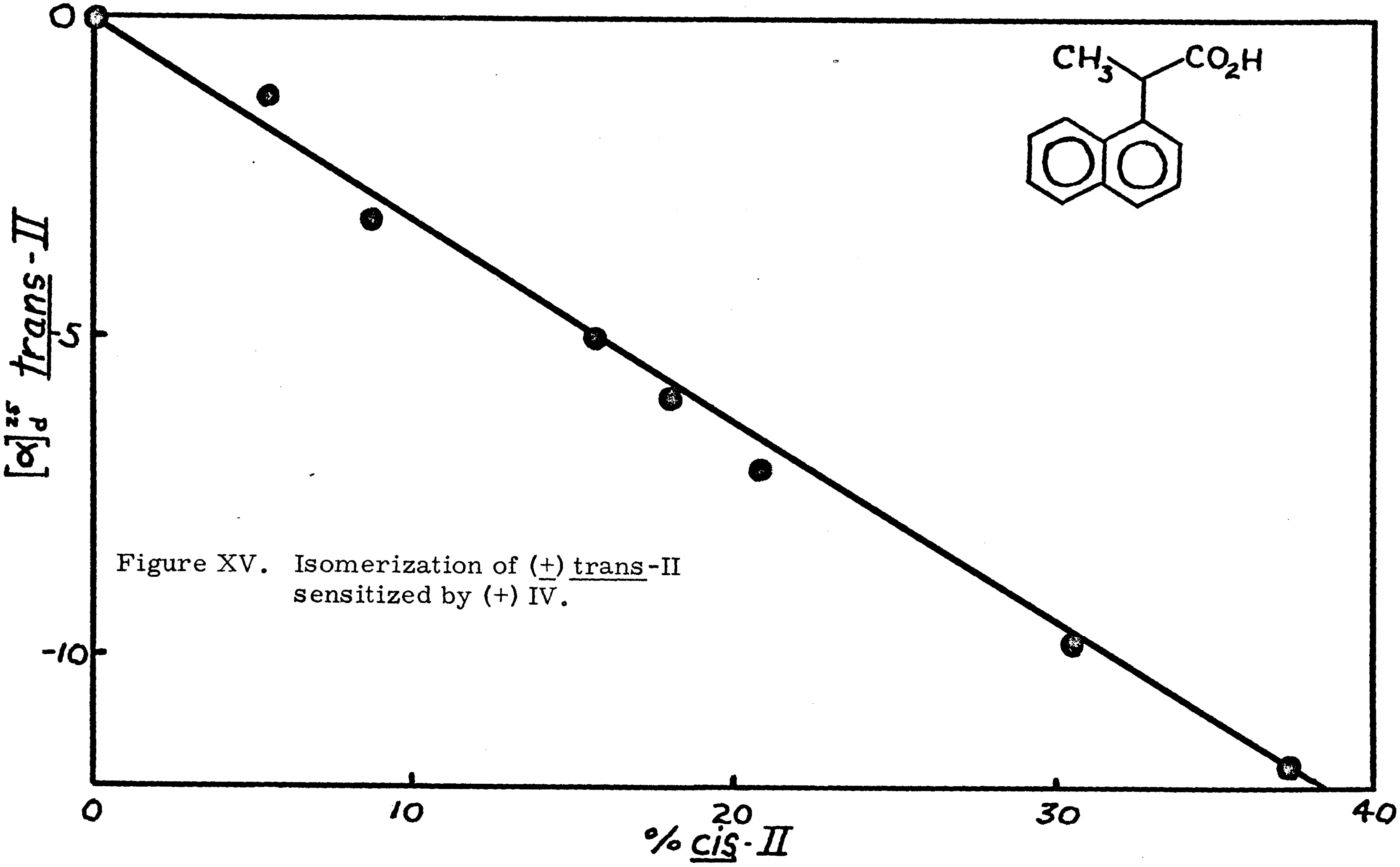


Figure XV. Isomerization of (±) trans-II sensitized by (+) IV.

TABLE XVI

Isomerization of (±)trans-II[a]

Sensitized by (+)2-(2-naphthyl) propanoic acid (V).[b]

Irradiation time (hrs.)	% cis-II formed	Rotation Induced (degrees, 2 dm.tube)	$[\alpha]_d^{25}$ trans-II
230	17.4	-0.04	-0.55
19	2.4	+0.01	+0.20
140	8.0	-0.037	-0.40
160	11.9	-0.040	-0.45
460	27.3	-0.055	-0.78
1104	35.0	-0.080	-1.20
360	25.5	-0.055	-0.75
312	24.5	-0.080	-1.00
1244	37.4	-0.080	-1.27

[a] conc. = 0.49 M.

[b] conc. = 8.0×10^{-3} M.

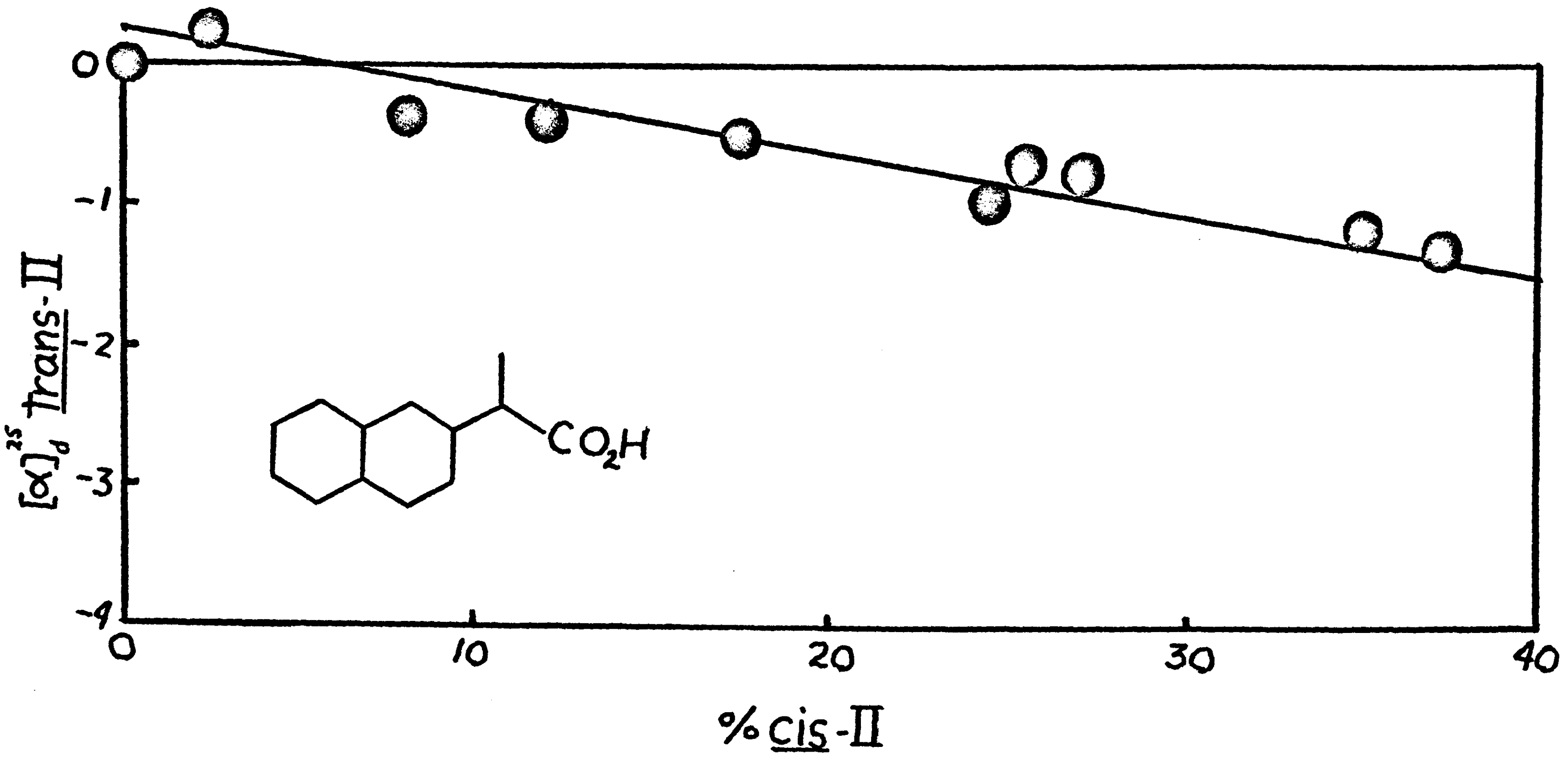


Figure XVI. Isomerization of (±)trans-II sensitized by (+)V.

TABLE XVII

Isomerization of *trans*-II[a]

Sensitized by (+)2-(1-napthyl)-butanoic acid (VI)[b].

Irradiation time (hrs.)	% *cis*-II formed	Induced Rotation (degrees, 2 dm. tube)	$[\alpha]_d^{25}$ *trans*-II
156	16.3	-0.34	-3.8
236	20.0	-0.35	-4.40
456	27.9	-0.47	6.45
600	36.1	-0.51	-7.0
1000	39.0	-0.46	-6.6
72	8.0	-0.15	-1.6
288	20.0	-0.44	-4.95

[a] 0.49 M.

[b] 9.4×10^{-3} M.

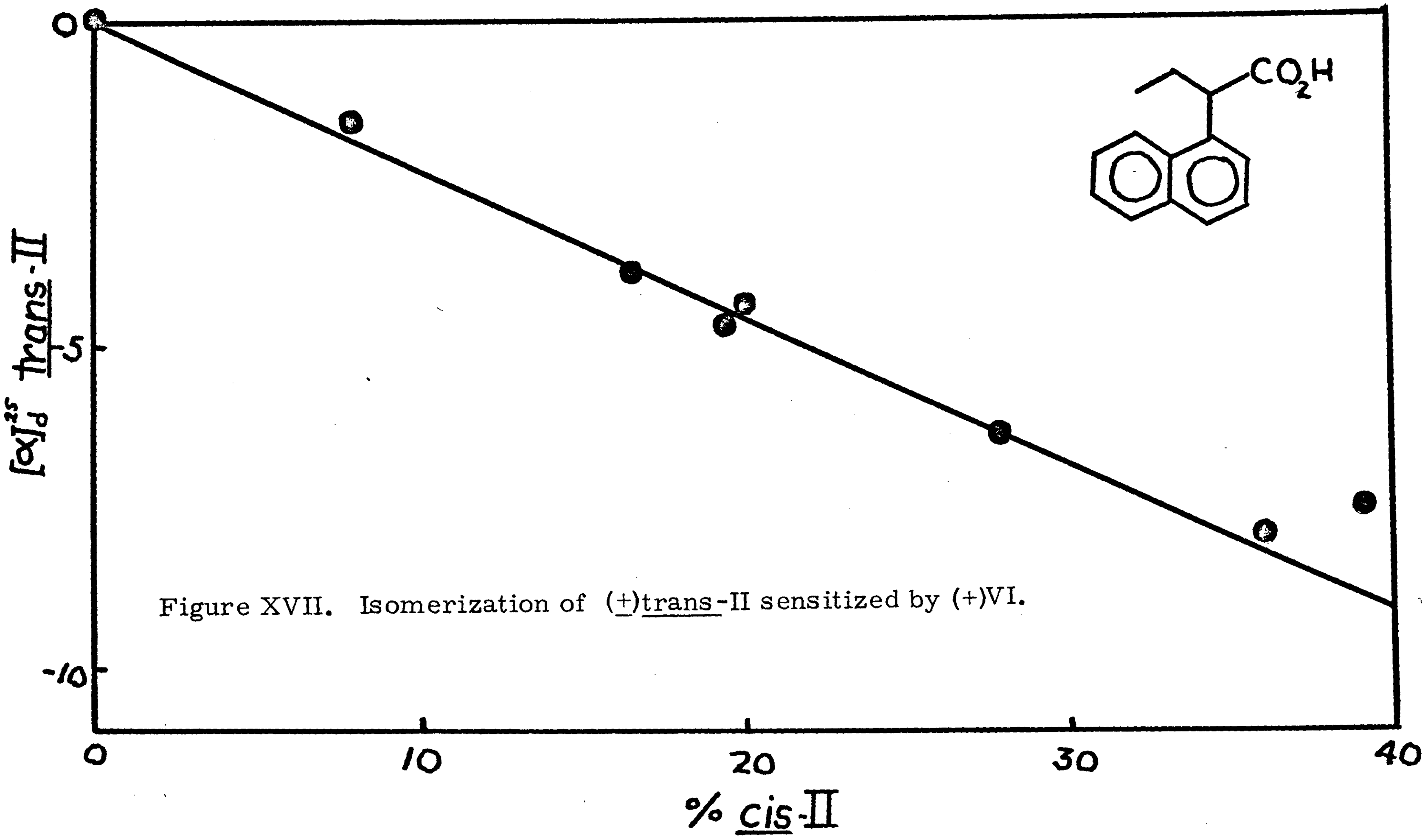


Figure XVII. Isomerization of (±)trans-II sensitized by (+)VI.

TABLE XVIII

Isomerization of (±)*trans*-II[a]

Sensitized by (+)2-(1-naphthyl)-butanol-1 (VII)[b]

Irradiation time (hrs.)	% *cis*-II formed	Induced Rotation (degrees, 2 dm. tube)	$[\alpha]_d^{25}$ *trans*-II
78	11.2	+0.12	2.4
186	14.6	+0.13	3.0
372	22.9	+0.08	2.1
500	29.0	+0.12	3.5
12	2.4	+0.04	0.70

TABLE XIX

Isomerization of (±)*trans*-II[a]

Sensitized by (+)1-chloro-2-(1-naphthyl)-propane (VIII)[c]

Irradiation time (hrs.)	% *cis*-II formed	Induced Rotation (degrees, 2 dm. tube)	$[\alpha]_d^{25}$ *trans*-II
30	5	0.00	0.00
75	21.2	0.00	0.00
200	34.1	0.01	0.00

[a] 0.49 M.

[b] 1.6×10^{-2} M.

[c] 2.5×10^{-2} M.

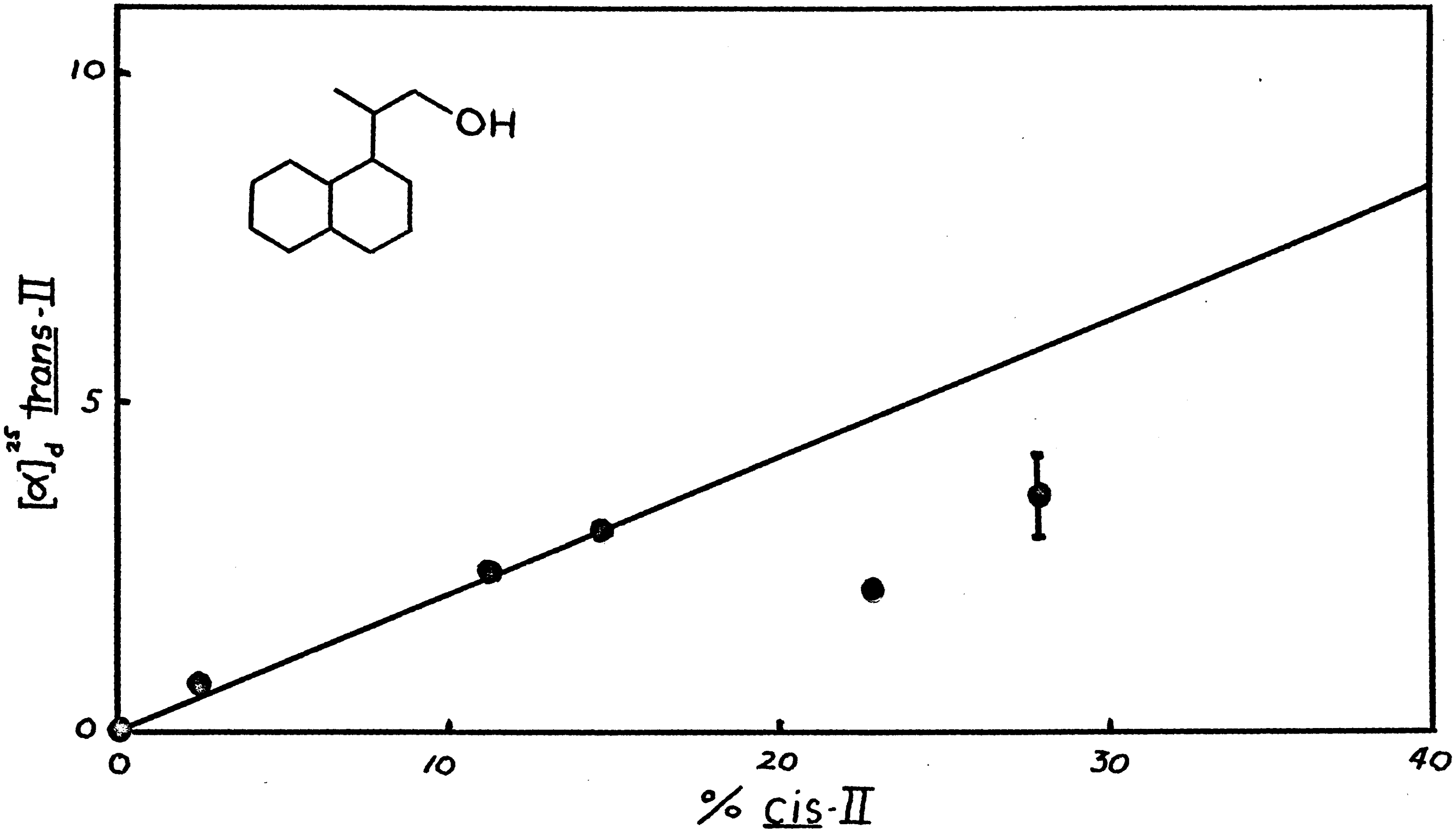
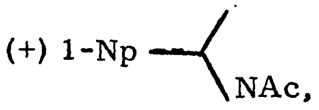
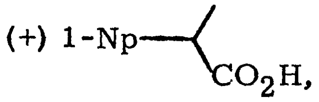
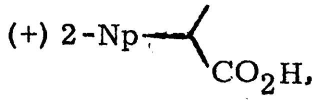
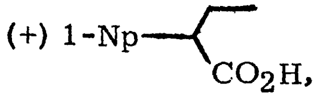
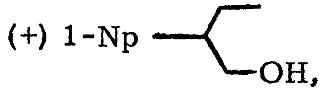
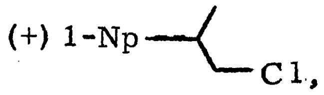
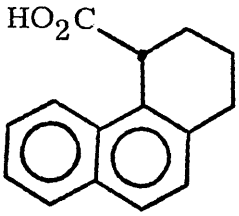
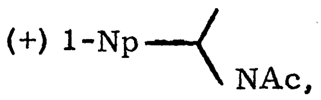


Figure XVIII. Isomerization of (+)trans-II sensitized by (+)VII.

TABLE XX

Sensitizers, their Configurations, and Rotations they induce into *trans*-II at the p.s.s.

Compound		Configuration	Specific Rotation of *trans*-II at p.s.s.
	(+) I	(+) R	+ 28
	(+) IV	(+) S	+ 14
	(+) V	(+) S	- 1.2
	(+) VI	(+) S	- 9
	(+) VII	(+) S	+ 6
	(+) VIII	(+) S	0.00
	(+) X	----	0.00
 (Methanol)	(+) I	(+) R	+ 15

Isomerization of (±)trans-3-methyl-1-phenylpentene-1 (XI) Sensitized by (+)I.

Ten tubes were prepared, each containing 1.0 ml. (±)trans-XI, 20 mg. (+)I and 4 ml. benzene. All were irradiated for 3 days with a 450 w. lamp enclosed in a pyrex cooling well. Concentrations were such that the sensitizer absorbed 99% of the incident light. After irradiation, the samples were combined, the solvent was boiled off, and the remaining substrate was fractionated on a spinning band collumn. The following fractions were obtained. Compositions were measured by v.p.c. analysis and rotations were determined on an electric polarimeter with a 4 cm. cell.

Fraction	Volume, (ml)	Composition, % cis-XI	Rotation (degrees + 0.004)
1	1.25	93	+0.068
2	4.2	64	+0.046
3	2.0	5	+0.020

The specific rotation of (+)trans-XI is greater than +50° (19). The cis isomer of the same absolute configuration should have the same sign and similar magnitude of rotation (24). Possibly, the small observed rotations arise from side products, amounting to about 5% of the total substrate. The latter were produced during the sensitized irradiation and were detected by v.p.c. analysis. This experiment would have detected a difference in rate constants of transfer to the optical isomers of trans-XI (k_{+t} and k_{-t}) if the latter differed by more than 1%. The failure to observe an induction is perhaps not surprising. The rate constants for transfer in this system are probably within an order of magnitude of diffusion control (20), and the substrate asymmetric center is removed from the area to which energy is transferred. This reaction takes place by triplet energy transfer (15 , 20).

DISCUSSION

Introduction

Racemic trans-1, 2-diphenylcyclopropane, (±)trans-II, becomes optically active during irradiation in the presence of optically active sensitizers. These sensitizers also effect the trans → cis stereochemical isomerization of this substrate, presumably by energy transfer (8). This result conveys strong supports to the view that intimate contact between donor and acceptor are necessary for some energy transfer mechanisms (4). This type of system should be extremely useful for exploring the detailed donor-acceptor interactions affecting energy transfer. Before discussing some of the implications of these experiments, we will digress, reconsidering some of the fundamental aspects of this reaction. First, we examine the nature of the reaction leading to the stereochemical isomerization. The linearity of the plot in Figure II suggests that the trans → cis isomerization and asymmetric induction have a common source. For each increment in the extent of isomerization there is a corresponding increase in the specific rotation of the substrate.

Indentity of the Donor Excited State

The interaction effecting trans → cis isomerization is between excited singlet (+)I and ground state trans-II. Results of the quenching experiments demonstrate this conclusively. Besides being excellent quenchers for triplet species (7), conjugated dienes efficiently quench the fluorescence of many aromatic hydrocarbons (15). The 2,5-dimethyl-2,4-hexadiene, III, quenches the (+)I sensitized trans → cis-II conversion and the fluorescence of (+)I to the same extent, as shown in Figure VIII. The following equations show the expected consequence of addition of diene to the asymmetric induction system.[a]

$$S + h\nu \longrightarrow {}^{1}S^{*} \tag{16}$$

$$ {}^{1}S^{*} \xrightarrow{k_{17}} S + h\nu' \tag{17}$$

$$ {}^{1}S^{*} \xrightarrow{k_{18}} {}^{3}S^{*} \tag{18}$$

$$ {}^{3}S^{*} \xrightarrow{k_{19}} S^{*} \tag{19}$$

$$ {}^{1}S^{*} + D \xrightarrow{k_{20}} S + D \tag{20}$$

$$ {}^{3}S^{*} + D \xrightarrow{k_{21}} S + D \tag{21}$$

$$ {}^{1}S^{*} + t \xrightarrow{k_{22}} S + T \tag{22}$$

$$ {}^{3}S^{*} + t \xrightarrow{k_{23}} S + T \tag{23}$$

$$ T \xrightarrow{k_{24}} t \tag{24}$$

$$ T \xrightarrow{k_{25}} c \tag{25}$$

---

[a] For clarity in the above sequence, we have omitted several steps which do not affect the conclusions of this discussion. We simply designate the sensitizer, S; diene, D; (±) trans-II, t; cis-II, c; and the intermediate formed from c or t by interaction with S* as T. The validity of the latter assumption is discussed in the following section of this thesis.

The quantum yield for fluorescence is

$$I = \frac{k_{17}}{k_{17} + k_{18} + k_{20}[D]} \qquad (26)$$

The ratio of intensities in the absence and presence of D is given by equation 27.

$$\frac{I_o}{I} = \frac{k_{20}[D]}{k_{17} + k_{18}} + 1 \qquad (27)$$

According to this mechanism I_o/I should be linear with [D]. This is verified in Figure VIII (p. 105) and has also been demonstrated for a number of other hydrocarbons (15).

The trans → cis quantum yield is

$$\Phi_{t \rightarrow c} = \left(\frac{k_{22}[t]}{k_{17} + k_{18} + k_{20}[D] + k_{22}[t]}\right)\left(\frac{k_{25}}{k_{24} + k_{25}}\right)$$

$$+ \left(\frac{k_{18}}{k_{17} + k_{18} + k_{20}[D] + k_{22}[t]}\right)\left(\frac{k_{23}[t]}{k_{23}[t] + k_{21}[D] + k_{19}}\right)\left(\frac{k_{25}}{k_{24} + k_{25}}\right) \qquad (28)$$

This rather complex expression of five factors can be simplified by removal terms which do not contribute significantly to Φ. Let us examine the last three factors. Factor 3, the sensitizer intersystem crossing ratio, is about 0.3 (15) and will be smaller when $[D] > 0$. DeBoer's values for k_{23} and k_{19} are 1×10^3 l. mole^{-1}sec. and

1.4×10^4 sec.$^{-1}$, respectively. Triplet transfer from naphthalene to conjugated dienes (reaction 21) is diffusion controlled. The last term, the fraction of T decaying to c is 0.35 (8). We are now prepared to eliminate triplet energy transfer from naphthalene sensitizers to diphenylcyclopropanes as a significant mechanism leading to isomerization. This is suggested by the negative results using p-methylbenzophenone, thioxanthone and triphenylene to sensitize the isomerization of trans-II in the presence of (+)I.[a]

First we look at one extreme: the case in which there is no singlet transfer contribution. The triplet contribution to Φ then is given by the last three factors of 28. The ratio of quantum yields in the absence and presence of D is

$$\frac{\Phi_o\,(\text{triplet})}{\Phi\,(\text{triplet})} = \frac{k_{21}[D]}{k_{19} + k_{23}[t]} + 1 \qquad (29)$$

In our experiments with naphthalene as a sensitizer (Table X) $[D] = 1.1 \times 10^{-2}$M. Assuming a triplet mechanism $\Phi_o : \Phi$ should be about 3×10^3. Far from this, the measured value is 4.03. Similar results are obtained using butadiene, 1,3-cyclohexadiene and 2,5-dimethyl-2,4-hexadiene (III) with (+)I as a sensitizer. These results strongly suggest that triplet energy transfer is not significant in the

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[a] In a latter section of this discussion we show how this result demonstrates triplet energy transfer from benzophenone, thioxanthone and triphenylene to trans-II.

trans ⟶ cis-II isomerization sensitized by naphthalene compounds. $\Phi_o : \Phi$ for these systems is, however, in excellent agreement with I_o:I, implicating a singlet energy transfer. Removing the terms involving triplet transfer from 28,

$$\Phi_{t \rightarrow c} = \left(\frac{k_{22}[t]}{k_{17} + k_{18} + k_{20}[D] + k_{22}[t]}\right)\left(\frac{k_{25}}{k_{24} + k_{25}}\right) \tag{30}$$

The small value of Φ (e.q., 10^{-4} at $[t] = 0.2$ M.) allows a further simplification of 30.

$$\Phi_{t \rightarrow c} = \left(\frac{k_{22}[t]}{k_{17} + k_{18} + k_{20}[D]}\right)\left(\frac{k_{25}}{k_{24} + k_{25}}\right) \tag{31}$$

now,

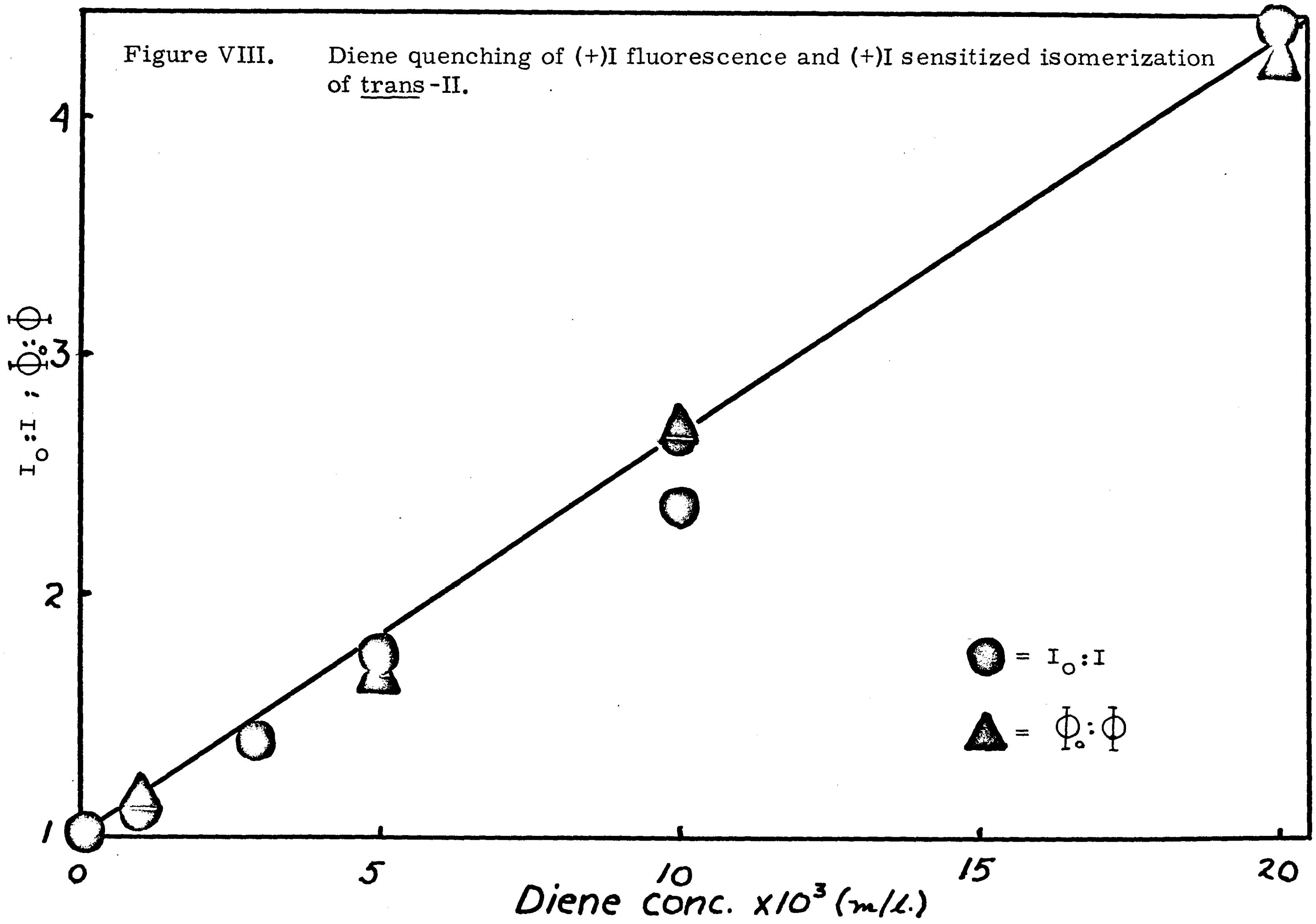
$$\frac{\Phi_o}{\Phi} = 1 + \frac{k_{20}[D]}{k_{17} + k_{18}} \tag{32}$$

We note that equation 27 and 32 are identical in form. Thus,

$$\frac{\Phi_o}{\Phi} = \frac{I_o}{I} \tag{33}$$

Examination of Tables XI and XII and Figure VIII shows this excellent correlation for the (+)I, trans-II and III system. These results verify that the mechanism leading to both isomerization and asymmetric induction involves interaction of excited singlet sensitizer and trans-II.

Figure VIII. Diene quenching of (+)I fluorescence and (+)I sensitized isomerization of trans-II.



Nature of the Singlet Energy Transfer.

Before we speculate on the detailed mechanism of this seemingly unprecedented process, we present our evidence discounting some other possibilities.

Direct absorption by the substrate is eliminated by the absence of a sensitizer concentration effect. The additivity of the absorption spectra of (+)I and trans-II indicates no appreciable formation of ground state sensitizer-substrate complex. The latter could absorb light, effecting the isomerization of II.

This system clearly does not possess the stringent requirements necessary for Forster or collisional transfer. The excitation energy of the naphthalene singlet is 90 Kcal. Both isomers of II have their lowest U.V. absorption mexima at 105 Kcal. Transfer to the acceptor's spectroscopic state is endothermic by 15 Kcal.

We prefer to describe the reaction of excited sensitizer with substrate as an electronic energy transfer. Our bases are: 1. The intermediate formed from substrate appears to undergo similar reactions to that produced by triplet energy transfer and by direct excitation(a) (8, 9); 2. Before closure to cis- or trans-II, the intermediate becomes free of the sensitizer asymmetric environment;(b)

(a) See "Product of the Transfer Reaction" section.

(b) This is concluded from results of the isomerization of cis-II sensitized by (+)I, discussed in the "Schenck Mechanism" section of this thesis.

3. The low quantum yields for isomerization and fluorescence quenching appear to be of the same order of magnitude. Dienes efficiently quench hydrocarbon fluorescence, but do not undergo comparably efficient photoreactions by this quenching (15). The latter suggests that dienes do not pass through electronic excited states while degrading singlet energy.

We find ourselves in need of a new mechanism. Unfortunately, knowledge of this system is rather limited. As it stands, we feel that the best explanation is afforded by a non-Franck-Condon singlet transfer mechanism. The detailed mechanism might be envisioned as being similar to that proposed by Hammond and Saltiel for non-vertical triplet energy transfer to "flexible" acceptors (7). The apparent deficiency in energy between the excited sensitizer and the spectroscopic levels of the acceptor is circumvented by transfer to a lower energy, non-spectroscopic level, arrived at through skeletal distortion of the acceptor. The efficiency of this process should be low and would certainly require an intimate donor-acceptor interaction. This transfer is shown diagramatically in Figure XX. Also shown is the analogous non-vertical triplet transfer. Figure XX represents a highly simplified model of the acceptor potential functions. It consists of bimolecular potential functions, which represent the energy as the 1,2-bond is cleaved. Rotation of the 2,3- and 1,3-bonds is not shown. However, this rather crude model contains most of the essential

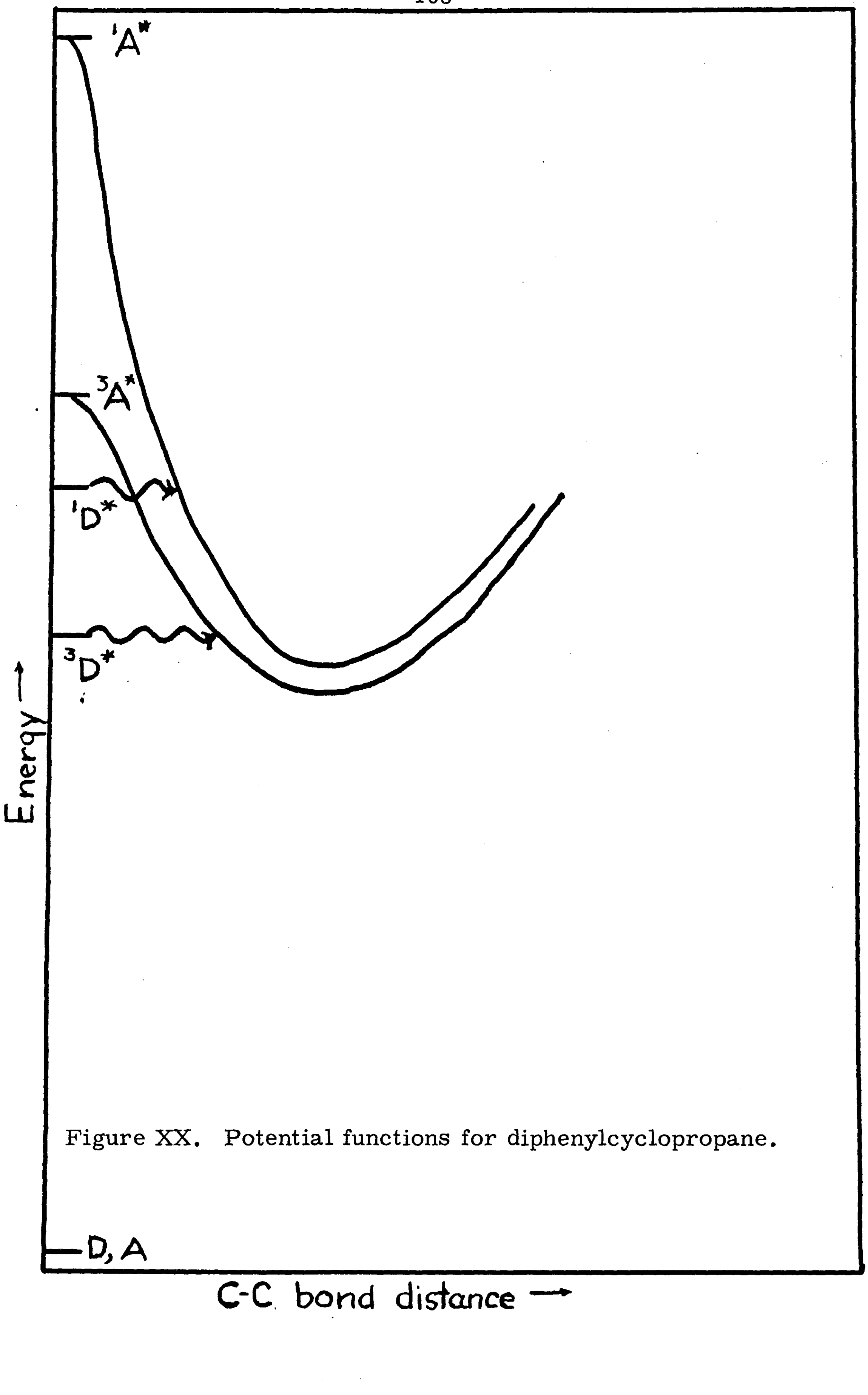


Figure XX. Potential functions for diphenylcyclopropane.

properties and facilitates our discussion.

It might be argued that a non-vertical process, which is already quite inefficient for triplet transfer, should be negligible for the comparable singlet mechanism, since excited singlet lifetimes are usually several orders of magnitude shorter than triplet lifetimes. Diphenylcyclopropanes may, however, be especially vulnerable to non-vertical singlet transfer. For this type of mechanism, the factor which regulates the rate of transfer is reasonably the amount of acceptor distortion required.

As the 1,2-bond is opened, the singlet and triplet potential functions of II must converge. In the intermediate, 1,3-diphenyltrimethylene, the singlet and triplet energy levels should be nearly the same due to the weak interaction between the end positions. Thus, the singlet potential function must decrease much more rapidly than its triplet counterpart, as the 1,2-bond scission takes place. For a given "endothermicity", the singlet transfer may not require as much distortion as the comparable triplet process. Singlet transfer might then have a comparable efficiency in spite of the sensitizer's short singlet lifetime.

The detailed interactions assisting non-vertical energy transfer might be similar to those responsible for charge transfer (c.t.) complex formation. Van's (17) observations relating to quenching of naphthalene fluorescence by amines supports this interesting possibility. The diene quenching of hydrocarbon fluorescence can also apparently be explained by a c.t. interaction(15). A c.t. complex between excited sensitizer and ground state substrate is an acceptable intermediate or transition state by which a substantial asymmetric induction could be obtained. The large perturbation should also assist the acceptor to a non-spectroscopic state. The intermediate closing to products must, however, be able to diffuse free of the donor's asymmetric environment, as indicated by the *cis*-II isomerization results.

On the Schenck Mechanism.

The asymmetric induction system provides an excellent test for the Schenck mechanism (16). This mechanism proposed for sensitized photoreactions is outlined below.

$$S + h\nu \longrightarrow S^* \qquad (34)$$

$$S^* + A \longrightarrow \cdot S\text{-}A\cdot \text{ (biradical)} \qquad (35)$$

$$\cdot S\text{-}A\cdot \longrightarrow \cdot S\text{-}B\cdot \qquad (36)$$

$$\cdot S\text{-}B\cdot \longrightarrow S + \text{products} \qquad (37)$$

The excited sensitizer interacts with the acceptor or substrate, forming a covalently bonded biradical. The intermediate biradical then interconverts to an assemblage which cleaves to sensitizer and product. The fact that we do observe an asymmetric induction in the *trans* → *cis* conversion does suggest the operation of a Schenck mechanism, as shown in Figure XXI. However, results for the reverse reaction are contrary to this. The *cis* → *trans*-II conversion sensitized by (+)I yields optically inactive *trans*-II. Data in Table XV and Figure XI show that the first formed *trans*-II is racemic and that the rotation induced increases with the extent of the *trans* → *cis* back reaction. In this experiment we would have detected an initially induced rotation of 1/70 of that for the *trans* → *cis* conversion. This indicates that the intermediate leading to isomerization, presumably 1,3-diphenyltrimethylene, becomes kinetically free of the optically active sensitizer. If there is covalent bonding between sensitizer and substrate, the bottom sequence in Figure XXI should apply. We suspect that the most favorable transition states for transfer to *cis*- and *trans*-II have many similarities. For example, consider our preferred transition state discussed in the next sections. This is also the transition state by which the Schenck mechanism should operate. The excited sensitizer, (+)I*, when approaching either *cis*- or *trans*-II "sees" a similar assemblage, as shown in Figure XXI. (+)I should show the same preference for one side of *cis*-II as it does for one isomer of *trans*-II. Once the biradical is formed with *cis*- or *trans*-II, only one isomer of *trans*-II can result upon the closure - cleavage. Thus, isomerization by the Schenck mechanism should produce optically active *trans*-II to about the same extent starting from either *cis*- or *trans*-II. That the initially formed *trans*-II is racemic is contrary to

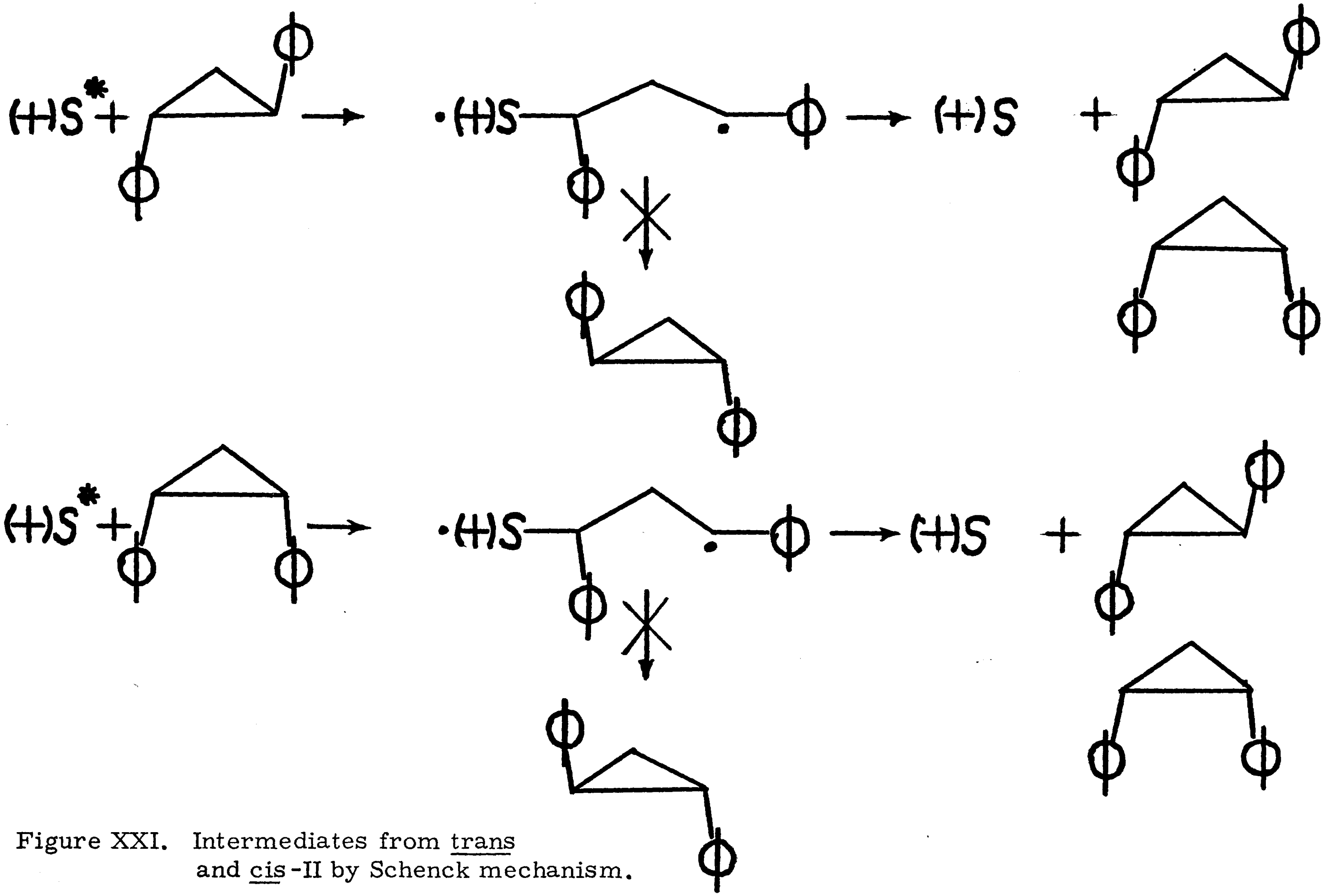


Figure XXI. Intermediates from trans
and cis-II by Schenck mechanism.

formation of a biradical intermediate. This objection, however, can be circumvented by proposing cleavage of the biradical into sensitizer and diphenyltrimethylene, which diffuses free of the sensitizer before closure. We feel that such a sensitizer-substrate biradical should also close, forming stable adducts. These are not formed, since material is not consumed even after prolonged irradiation for 30 days. The latter observation combined with the cis-trans isomerization results does seem to rule out the operation of a Schenck mechanism for this system.

Product of the Transfer Reaction.

Triplet energy transfer to cis- and trans-II apparently gives a common intermediate, 1,3-diphenyltrimethylene (8). Direct excitation of either isomer of II leads to the production of the same intermediate, or one which has a decay path common to that produced by triplet energy transfer. We infer this by comparison of predicted and measured stationary states by direct excitation. At the p.s.s.,

$$\frac{[\text{trans-II}]}{[\text{cis-II}]} = \frac{\epsilon_{\text{cis}}\ f_{\text{trans}}}{\epsilon_{\text{trans}}\ f_{\text{cis}}}$$

where ϵ_{cis}, ϵ_{trans} are the extinction coefficients and f_{trans}, f_{cis} are the fractions of intermediate decaying to trans- and cis-II. The ratio of extinction coefficients at 2537 Å is 0.233; the decay ratio of the intermediate formed by triplet transfer is 1.86 (8). We predict a p.s.s. composition of 0.45 for the direct excitation of II with 2537 Å light. The measured value is approximately 0.65 (9). This is in good agreement, considering that the excitation source was an unfiltered low pressure mercury arc.

This brings up another interesting point. DeBoer (8) has examined the decomposition of trans-3,5-diphenyl-1-pyrazoline, XII, which produces cis- and trans-II. The XII → II conversion was effected thermally, by direct excitation, and by triplet sensitization. These results (Table XXI) were used to infer that the thermal decomposition and direct excitation produce singlet 1,3-diphenyltrimethylene, which closes primarily to trans-II. The explanation tendered was that the rate of closure is much greater than that of internal rotation of the biradical. On the other hand, sensitization produces triplet biradical. Here, spin relaxation must precede closure to product, allowing the biradical to equilibrate.

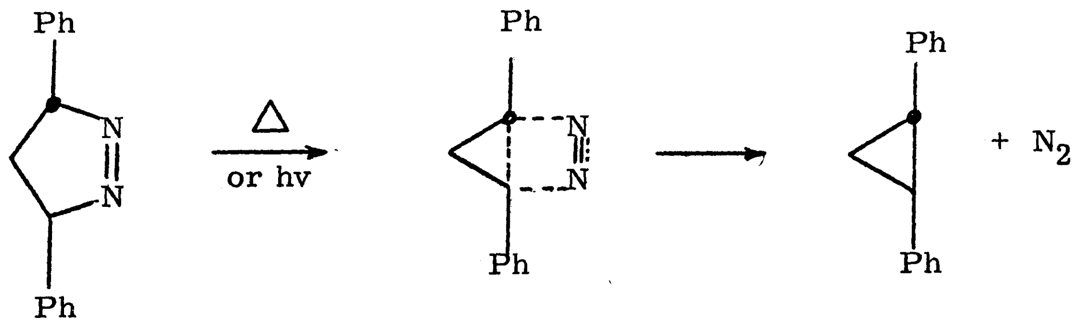
TABLE XXI

Decompositions of trans-3,5-diphenylpyrazoline.

Method	%trans-II[a]
Thermal decomposition	91.1
Direct excitation	90.0
Sensitized decomposition	65

[a] The other product was cis-II.

We offer an alternative explanation. The thermal decomposition of XII could take place by a concerted mechanism, as shown below:



A competing path, giving the biradical, could account for the incomplete stereospecificity observed. Evidently, the thermal decomposition and direct excitation of XII have common paths, not shared by the sensitized decomposition of XII and the sensitized and direct excitation of cis- and trans-II.

The intermediate formed by singlet energy transfer from naphthalene to cis- and trans-II appears to have the same decay paths as that produced by direct excitation and by triplet sensitizers.(a) This is not surprising since the excited singlet and triplet potential functions of 1,3-diphenyltrimethylene should closely converge as the biradical opens to its equilibrium configuration.

(a) This calculation is presented in the next section.

Rate Constants for Transfer.

An approximate value for the rate constant for transfer from naphthalene to trans-II is calculated by equation 31. DeBoer's value for $\Phi_{t \rightarrow c}$ is 10^{-4} at 0.177 M. substrate concentration. The singlet lifetime of naphthalene is taken to be 2.2×10^{-8} sec. (18). Thus, $k_{22} = 2.5 \times 10^{4}$ l. mole^{-1} sec^{-1}. This rate constant does not seen to vary by more than an order of magnitude with the different naphthalene sensitizers. Similarity of the quantum yields suggests this.

The ratios of rate constants $k_{(+)t} : k_{(-)t}$ are evaluated as follows. The system can be described by these reactions:

$$(+)\underline{trans}\text{-II} \longrightarrow (-)\underline{trans}\text{-II} \qquad (39)$$

$$(+)\underline{trans}\text{-II} \longrightarrow \underline{cis}\text{-II} \qquad (40)$$

$$(-)\underline{trans}\text{-II} \longrightarrow (+)\underline{trans}\text{-II} \qquad (41)$$

$$(-)\underline{trans}\text{-II} \longrightarrow \underline{cis}\text{-II} \qquad (42)$$

$$\underline{cis}\text{-II} \longrightarrow (+)\underline{trans}\text{-II} + (-)\underline{trans}\text{-II} \qquad (43)$$

At the p.s.s.,

$$\text{Rate}_{39} + \text{Rate}_{40} = \text{Rate}_{41} + \frac{\text{Rate}_{43}}{2} \qquad (44)$$

$$\text{Rate}_{41} + \text{Rate}_{42} = \text{Rate}_{39} + \frac{\text{Rate}_{43}}{2} \qquad (45)$$

$$\text{Rate}_{40} + \text{Rate}_{42} = \text{Rate}_{43} \qquad (46)$$

where

$$\text{Rate}_{39} = k_{(+)t}\,[(+)\underline{trans}\text{-II}]\,[D^{*}]\,\frac{f_{trans}}{2}\text{, etc.} \qquad (47)$$

By manipulation of the above expressions, it can be shown that at the p.s.s.

$$\mathrm{Rate}_{39} = \mathrm{Rate}_{41}, \quad \mathrm{Rate}_{40} = \frac{\mathrm{Rate}_{43}}{2}, \quad \frac{\mathrm{Rate}_{39}}{\mathrm{Rate}_{40}} = \frac{f_{\underline{\mathrm{trans}}}}{f_{\underline{\mathrm{cis}}}} \tag{48}$$

The specific rotation at the p.s.s., $\alpha_{\mathrm{p.s.s.}}$, is

$$\alpha_{\mathrm{p.s.s.}} = \frac{(100)^2 \, a_{\mathrm{p.s.s.}}}{[c_o] \; 1 \; (\% \; \underline{\mathrm{trans}}\text{-II})_{\mathrm{p.s.s.}}}, \tag{49}$$

where a, $[c_o]$, and 1 are the observed rotation, the initial concentration of (±)trans-II and the polarimeter tube length, respectively.

$$a = \left([(+)\underline{\mathrm{trans}}\text{-II}] - [(-)\underline{\mathrm{trans}}\text{-II}] \right) \frac{\alpha_o \; 1}{100}, \tag{50}$$

giving

$$\left(\frac{[(+)\mathrm{trans}\text{-II}] - [(-)\mathrm{trans}\text{-II}]}{[(\pm)\underline{\mathrm{trans}}\text{-II}]} \right)_{\mathrm{p.s.s.}} = \frac{\alpha_{\mathrm{p.s.s.}}}{\alpha_o} \tag{51}$$

where α_o is the specific rotation of the optically pure isomer.

Substituting expressions 47, etc. into 51,

$$\frac{\alpha_{\mathrm{p.s.s.}}}{\alpha_o} = \frac{k_{(+)t} - k_{(-)t}}{k_{(+)t} + k_{(-)t}} \tag{52}$$

$\alpha_{\mathrm{p.s.s.}}$ is extrapolated from the experimental data plots, using the form of the curve derived in the appendix.

The ratios $k_{(-)t} : k_{(+)t}$ for the various sensitizers are given in Table XXII.

TABLE XXII

Sensitizers and ratio of transfer rate constants

Sensitizer[a]	$k_{(+)t} : k_{(-)t}$[b]
(-)I	1.50
(+)IV	1.20
(+)V	1.02
(+)VI	1.15
(-)VII	1.10
(+)VIII	1.00
(+)X	1.00
(-)I[c]	1.20

[a] See page 87 for structures; benzene solvent.

[b] Specific rotation of optically pure (+)trans-II taken as 140°.

[c] Methanol solvent.

Kinetic Analysis of the Mechanism.

The validity of our mechanism is demonstrated by the excellent agreement between calculated and measured specific rotations at various trans → cis conversions. The calculated values were determined through solution of the differential rate equation for this system. Here, I gratefully acknowledge Professor S. I. Chan for his derivation of these equations,[a] which are:

$$\frac{[(+)t]}{[(+)t]_o} = c_1 e^{\lambda_1 t} + c_2 e^{\lambda_2 t} + c_3$$

$$\frac{[(-)t]}{[(+)t]} = c_4 e^{\lambda_1 t} + c_5 e^{\lambda_2 t} + c_6$$

$$\frac{[c]}{[(+)t]_o} = c_7 e^{\lambda_1 t} + c_8 e^{\lambda_2 t} + c_9$$

The coefficients are combinations of energy transfer rate constants and decay fractions of the intermediate formed by energy transfer. From the previous expressions we note that

$$r \equiv \frac{k_{(+)t}}{k_{(-)t}} = \frac{\alpha_o - \alpha_{p.s.s.}}{\alpha_o + \alpha_{p.s.s.}} \quad \text{and}$$

$$k_c = 2\,k_{(+)t}\,\frac{f_c}{f_t}\left(\frac{[(+)t]}{[c]}\right)_{p.s.s.}$$

---

[a] See the appendix for this derivation.

The decay ratios are calculated from the relative initial rates.

$$W_o \equiv \left(\frac{d\,[\,(-)t]}{d\,[\,(+)t]} \right)_{t\,=\,o} = \frac{f_t \;-\; f_t.r \;-\; 2f_c.r}{f_t.r \;-\; f_t \;-\; 2f_c}$$

Using $\alpha_o = 140$, (which we see later gives the best comparison between calculated and experimental data) the initial slope, W_o, is 3.25. Solving for the decay fractions, $f_t = 1.86f_c$. Since $f_t + f_c = 1$, $f_c = 0.35$; $f_t = 0.65$. These are exactly the values for intermediate produced by triplet energy transfer (8).

The good agreement between calculated and experimental rotations at various conversions is shown in Figures XXII and XXIII. The data are for the (+)I sensitized system. Parameters which give the best correlation are:

$$\alpha_o = 140 \pm 5^o$$

$$\frac{k_{(-)t}}{k_{(+)t}} = 1.50$$

$$\frac{k_{(-)t}}{k_c} = 2.33$$

Variation of the Asymmetric Group.

A number of optically active naphthanene sensitizers were prepared, varying the size, polarity and position of the asymmetric substituent. Most of these compounds effected the trans ⟶ cis conversion of (±)trans-II. Quantum yields are of the same order of magnitude, indicating that the various substituents do not grossly

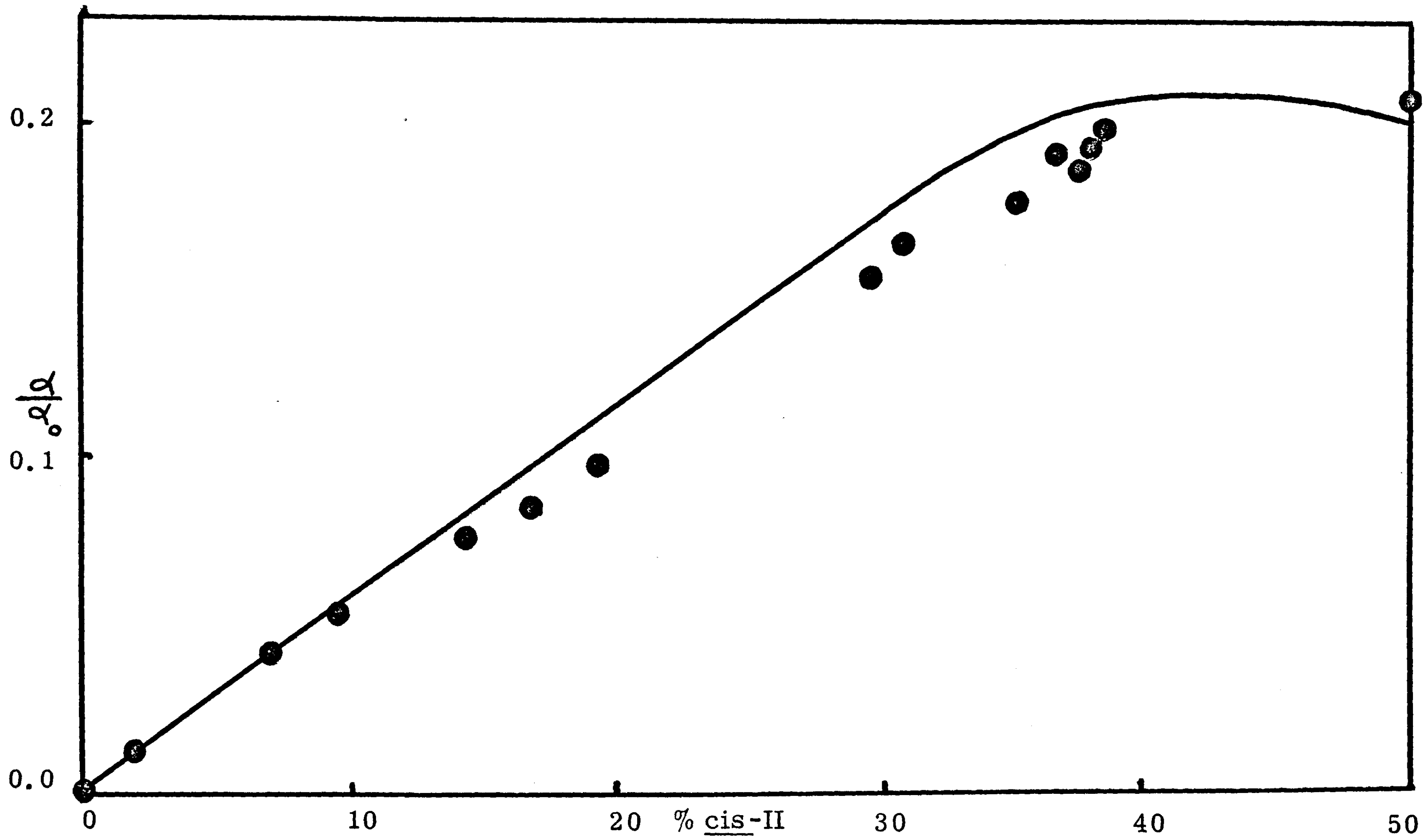


Figure XXII. Theoretical curve and experimental data for (+)I. sensitized trans → cis-II conversion.

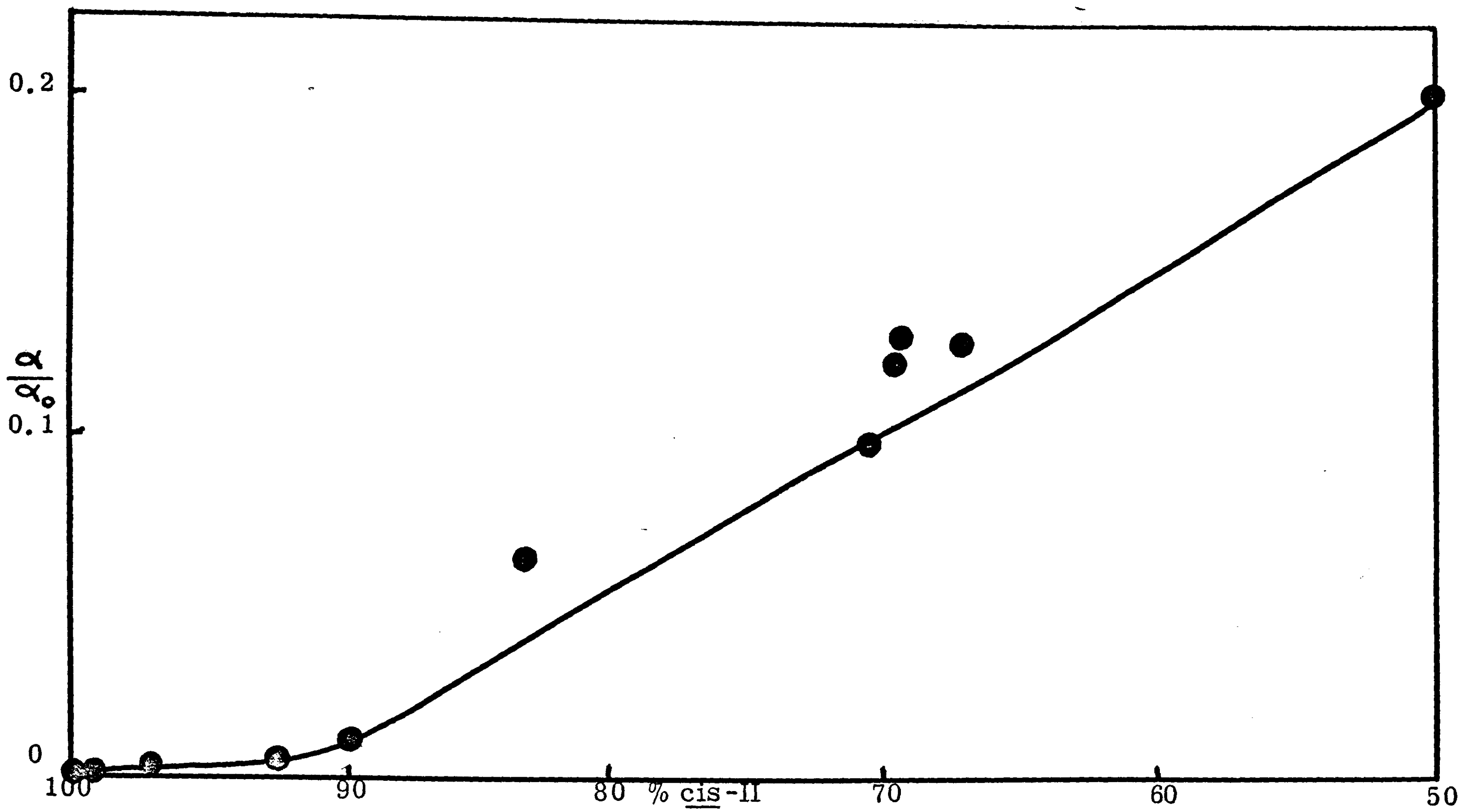


Figure XXIII. Theoretical curve and experimental points for the <u>cis</u> → <u>trans</u>-II conversion by (+)I.

affect the rates of transfer. The extent of asymmetric induction for each is given in Table XX. These values are extrapolated to the p.s.s., of naphthalene using the form of the curve previously derived. We assume that the p.s.s. does not change significantly with the subtle changes in structure. This is apparently true for naphthalene and (+)I and has also been shown to be valid for other naphthalene sensitizers (8). This extrapolated value represents, besides the induction at the trans-cis-II p.s.s., the p.s.s. between the optical isomers of trans-II.

The data for the different sensitizers suggest some interesting points. Most conspicious is the large difference between (+)2-(1-naphthyl) propanoic acid, IV, and (+)2-(2-naphthyl) propanoic acid, V. The former compound is 8.5 times more selective between (+) and (-) substrate. That such a seemingly small change in sensitizer structure dramatically alters the selectivity between substrate isomers, is consistent with our belief that a very specific donor-acceptor configuration are requisite for effective energy transfer. The small influence of the asymmetric group of (+)V suggests that the asymmetric center of the acceptor approaches nearer to the 1-positions of the naphthalene ring during transfer. This seems reasonable since the electron density of the excited orbital is highest at this position. A crude approximation is afforded by the Huckel treatment. Coefficient magnitudes of the 5th and 6th orbitals are:

position	c_i	c_i^2
1	0.425	0.180
2	0.262	0.069
9	0.000	0.000

The magnitude of c_i^2, the excited electron distribution should be a crude measure of the transfer efficiency at that position. It is reasonable to presume that the presence and variation of the asymmetric substituent will not drastically alter the most important configurations for transfer. Evidently, the majority of transfers take place through a relatively small number of configurations.

Another interesting comparison is between IV and VI. Addition of a methyl group to the aliphatic chain decreases the selectivity by only 30%. From examination of scale molecular models, it is noted that the carboxyl and ethyl groups of VI have nearly the same steric requirements. Thus, we conclude that simple steric interactions alone do not adequately account for the observed selectivity. Sensitizer (+)VIII is sterically similar to (+)VI, but the former compound apparently does not distinguish between the enantiomers of *trans*-II.

Sensitizers (+)I, (-)IV, (-)V, (-)VI, having the same absolute configurations, preferentially transfer to (-)<u>trans</u>-II. The alcohol, VII, prepared from optically active VI, does not follow this trend. It displays similar selectivity as (+)VI, but its preference is reversed. Apparently, we cannot easily predict the extent of asymmetric induction, or even the isomer to which transfer is favored, by comparison to other sensitizers. The extent of asymmetric induction seems to be no simple function of bulk, polarity, or configuration of the optically active sensitizer.

One characteristic is noted. Sensitizers producing an asymmetric induction have acidic hydrogens. Possibly this polar and hydrogen-bonding group assists selection between acceptors directly, or by enhancing the asymmetry of the environment. A hydrogen bonding substituent might hinder rotation of the optically active group by bonding to the naphthalene ring in the excited state. The sensitizer, being held in a more rigid conformation, should show greater selectivity. If self hydrogen-bonding is important, the induced rotation should be solvent dependent. Isomerization of <u>trans</u>-II sensitized by (+)I in methanol proceeds similar to the reaction in benzene. The extent of asymmetric induction is 46% less in methanol.

A sensitizer, (+)X, with rigidly fixed conformation did not produce optically active <u>trans</u>-II during the <u>trans</u>-<u>cis</u>-II conversion.

This compound was anticipated to show a large selectivity, being a "rigid" version of (+)IV or (+)VI. However on closer examination we note that the side of the naphthalene ring not obstructed by the carboxyl group is essentially planar and presents a rather bland asymmetric environment. Acceptors approaching this side "see" a relatively symmetric donor. This might suggest that preferential transfer takes place on the side of naphthalene opposite of the polar group.

Speculation on the Configuration and Nature of the Transition State.

The ultimate goal of this work is, of course, determination of the relative orientations of donor and acceptor during energy transfer. Since the absolute configurations of (+)*trans*-II and most of our sensitizers are known, we should be able to construct a suitable transition state using our results. Some of the criteria we selected for this transition state are:

1. First, an intimate interaction between donor and acceptor. This is demanded by our results. An obvious extention includes substantial interaction of the asymmetric centers.

2. Transfer from the vicinity of the 1-position of the naphthalene nucleus to the 1,2-bond of *trans*-II. Comparison of the 1 and 2 substituted naphthalene sensitizers suggest this preference.

3. Positioning of the plane of the substrate's phenyl rings

orthogonal to the 1, 2-bond, as shown in Figure XXIV. This allows maximum resonance stabilization of the diphenyltrimethylene forming in the transition state.

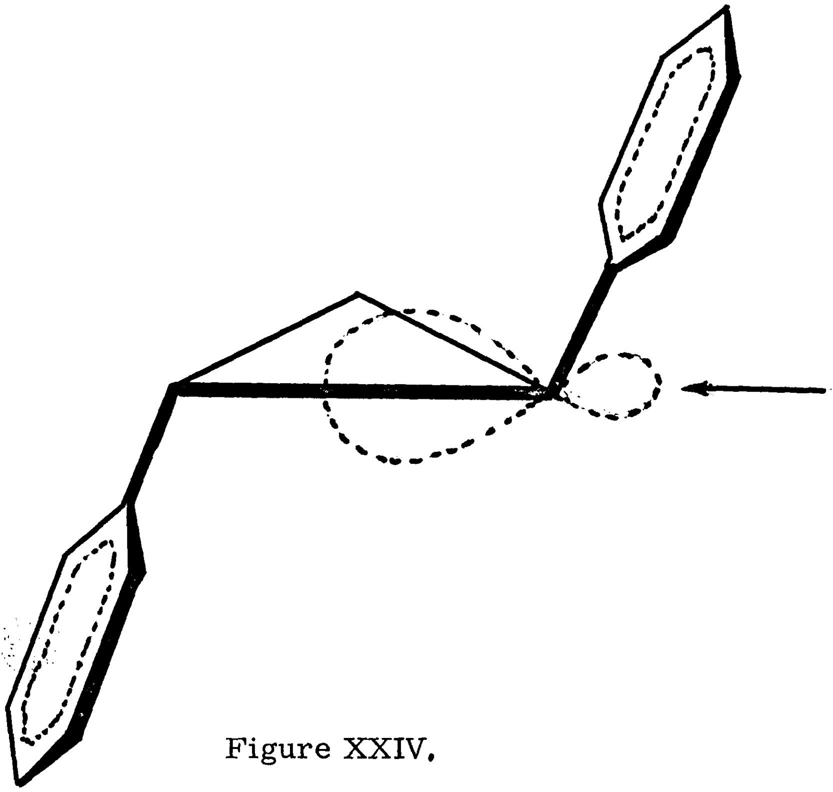


Figure XXIV.

4. The last criteria is more speculative. Energy to the 1, 2-bond might be accomplished with least difficulty by interaction with the non-bonding lobe of the 1, 2-bond, (shown by the arrow in Figure XXIV. This area, being sterically more accessible, allows close approach and overlap with the donor's pi orbitals, particularly the 1-positions.

The sensitizer-substrate combination which best fits these qualifications is shown in the bottom combination of Figure XXV. This relative orientation fulfills each of the above criteria far better than for any other combination. We base this on our lengthy examination with scale molecular models of the sensitizer and both substrate isomers. Our second choice pictured at the top of Figure XXV, fulfills most of our requirements, but overlap between the donor pi clouds and the acceptor orbitals of the 1,2-bond is much smaller than in the lower combination.

In a crude model of our system, the energy transfer reactions can be considered as proceeding through a number of donor-acceptor relative geometries[a]. Some of these configurations provide more efficient transfer than others. Each configuration displays a particular preference for (+) and (-) substrate isomers. Apriori, the configuration most efficient for transfer is not necessarily that which is most selective towards substrate isomers. The obviously large selectivity and the temperature variation studies both suggest that the bulk of the transfers are effected by a relatively small number of donor-acceptor orientations. We interpret the marked

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[a] We use the terms relative geometries, relative configurations donor-acceptor configuration, and configurations to designate the spatial orientation between donor naphthalene ring and the phenyl rings of the acceptor. Using this definition, it seems easier for us to describe how a sterically similar combination between (+)D - (+)A and (+)D - (-)A gives rise to very different electronic interactions between the "sites" of energy transfer, the naphthalene ring and the acceptor 1,2-bond.

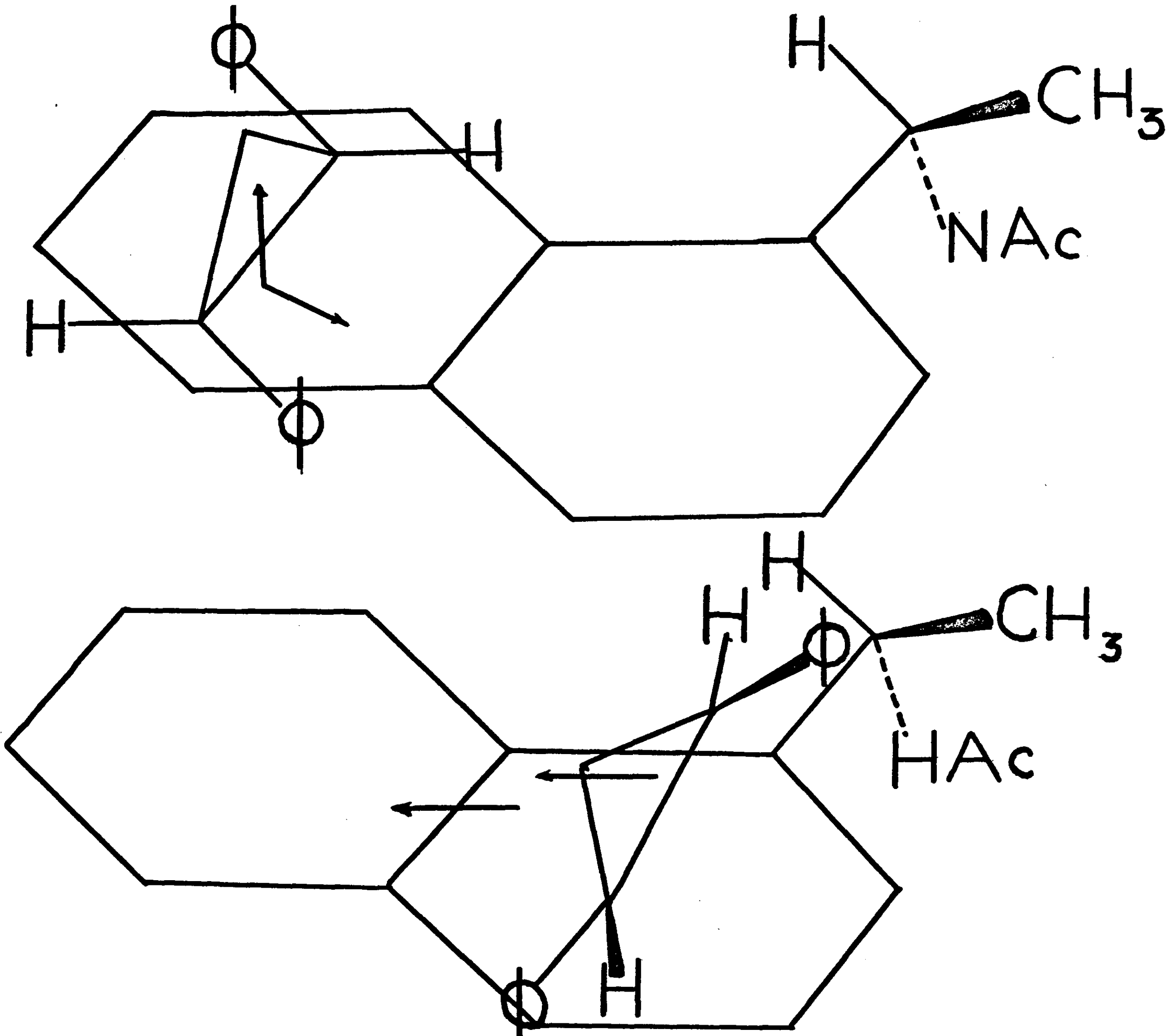


Figure XXV. Probable transition states for energy transfer.

decrease in the induced rotation at higher temperatures as follows: As the temperature is increased, new configurations become more efficient as energy transfer modes. These additional modes, which compete with the set most important at lower temperatures, may display opposite preference between substrate isomers. Their increased participation will diminish the overall extent of asymmetric induction. This is apparently what we observe. An important implication of this result is that the transfer has a substantial activation energy.

We now examine our "best" configuration in detail, exploring how transfer to one isomer might be preferential. Our points are most easily visualized by inspection of a cross section view of the donor-acceptor configuration. Figure XXVI shows this cross section for the two combinations, (+)D - (+)A and (+)D - (-)A. The cut is made through the 1,4-positions of (+)I and through the 1,2-positions of the trans-II isomers (orthogonal to the cyclopropane ring). This profile, representative of the overall fit between donor and acceptor, is quite similar for both combinations. However, the protruding orbitals of the donor and acceptor (shown by the arrows in the cross sections) which overlap for the (+) - (-) pair, are orthogonal in the (+) - (+) combination. For this configuration, transfer between the (+) - (-) pair should be greatly favored.

Thus, we can see how the configuration of the transition state might be elucidated by interpretation of asymmetric induction results. In order to do this effectively, we clearly require a much better understanding of the factors which influence the rates of transfer.

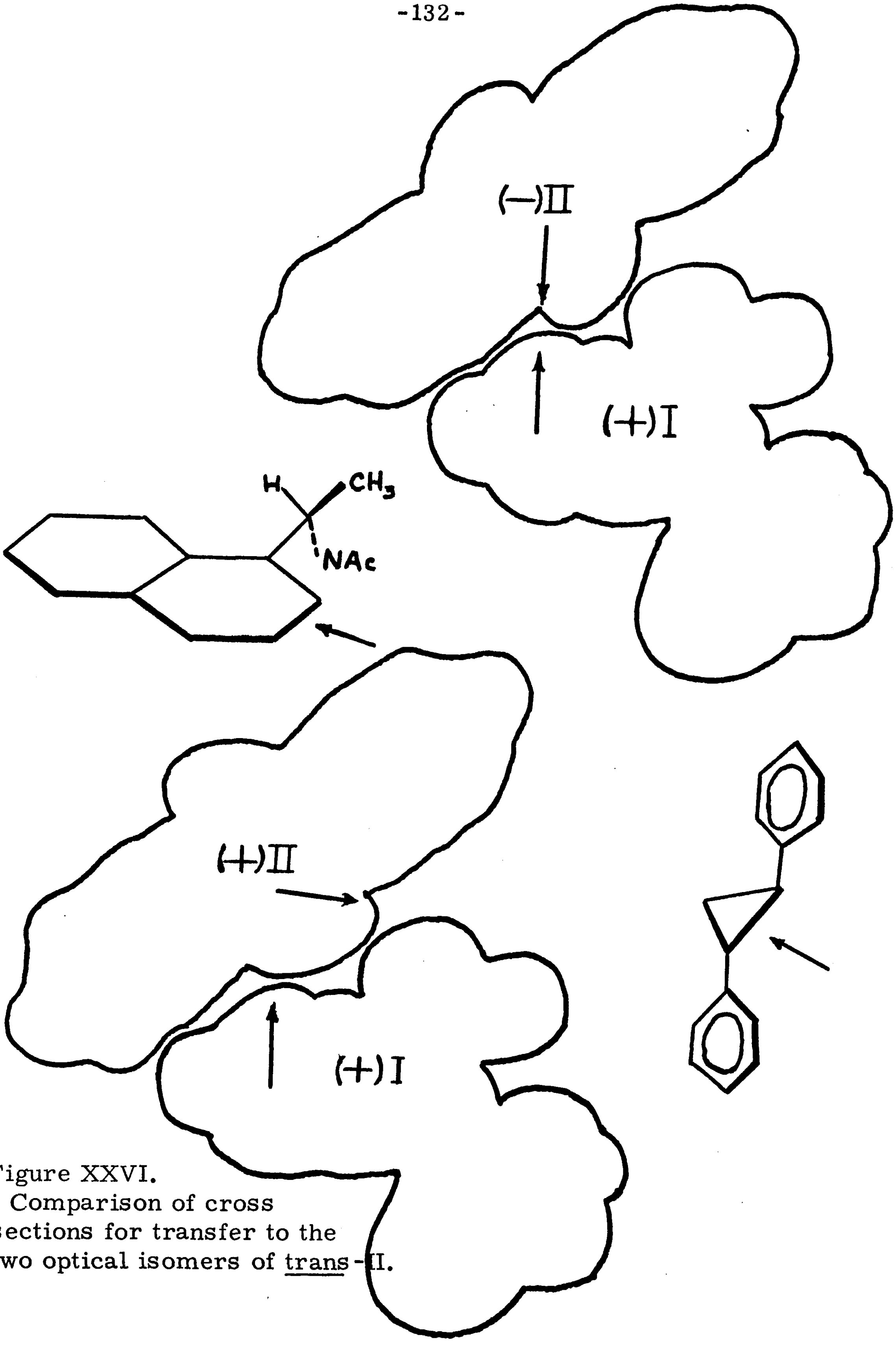


Figure XXVI.
Comparison of cross sections for transfer to the two optical isomers of trans-II.

EXPERIMENTAL

Materials

(±)trans-1,2-Diphenylcyclopropane was prepared by Dr. Charles DeBoer (8). Material was purified by several crystallizations from ethanol-water, followed by distillation at reduced pressure. A constant boiling middle fraction collected was 99.9% trans isomer by v.p.c. analysis. No other components were detected.

cis-1,2-Diphenylcyclopropane was prepared by Dr. Charles DeBoer (8). Material was purified by vacuum distillation and two crystallizations from ethanol-water. Material was 99.98% cis isomer.

(+)N-Acetyl-1-(1-naphthyl)-ethylamine, (+)I. 0.5 g (+)1-(1-naphthyl)-ethylamine was warmed with 0.5 ml. acetyl chloride in 100 ml. benzene. The formed gel was dissolved in 100 ml. hot benzene and 25 ml. sat. Na_2CO_3. Evaporation of the separated benzene layer gave a flocculent ppt. Several crystallizations from heptane-benzene gave 200 mg. fine needles, mp. 155°C, $[\alpha]_d^{25} = +120^\circ$, c. 2.5, $CHCl_3$.

(+)2-(2-Naphthyl)-propanoic acid, (+)V. To 42 g. 2-acetonaphthone and 33 ml. ethyl chloroacetate in 60 ml. dry benzene was added 15 g. powered $NaNH_2$. Reaction was kept below 10°C during the slow addition. After two hours stirring at 25° C. mixture was poured onto 200 g. ice. Layers were separated and the benzene layer was washed with dil. HOAc, H_2O and NaCl solution. Evaporation on a steam bath and distillation of the residue gave 20 g. 2,3-epoxy-3-(2-naphthyl)-1-butanoic acid, ethyl ester, bp. 155-170°C, 2 torr. The ester was hydrolized with 6.5 g. NaOH in 50 ml. H_2O. After 3 hours, mixture was acidified and extracted with ether. Evaporation and recrystallization from benzene yielded 12 g. of the acid. Distillation of the acid at 2 torr. gave 10 g. 2-(2-naphthyl)-propanal. The aldehyde was oxidized by addition of 1.25 g. NaOH in 50 cc. H_2O to a mixture of 1.3 g. aldehyde, 1.25 g. $AgNO_3$, 15 cc H_2O, and 25 cc. EtOH. Mixture was stirred for 2 hours under N_2 atmosphere, filtered, and extracted with Et_2O. Acidification of the aqueous layer gave 1.2 g. acid, mp. 124°C.

This acid was resolved as the quinine salt from ethanol-water and methanol solutions. Eight recrystallizations were required to give constant melting material of constant rotation, mp. 194.5-195°C., $(\alpha)^{25}_{d} = +76.8$ c. 3.45, benz. Material was vacuum sublimed before use as a sensitizer.

<u>(+) 2-(1-Naphthyl) propanoic acid, (+) IV.</u> Five g. 1-naphthalene acetonitrile was added slowly to 1.2 g. powered $NaNH_2$ in 30 ml. benzene. After 3 hours of rapid stirring a thick green ppt. formed. This was cooled to 5° C and 4.5 g. CH_3I was added slowly. This was allowed to stand overnite at 25° C, then refluxed for 3 hours. The reaction mixture was poured on 30 g. ice. The separated organic

layer was evaporated and distilled, giving 86% 2-(1-naphthyl)-propionitrile, bp. 114-115°C, 1 torr.

The nitrile was hydrolized by refluxing in 20 ml. H_2O, CH_3CO_2H, H_2SO_4 (1:1:1 by volume) for 10 hours, poured on 50 g. ice, extracted with ether which was then extracted with aqueous base. Acidification of the basic extract with HCl precipitated the acid. It was crystallized from ethyl acetate-ligroin, yielding 3.8 g. product, mp. 145-147°C. The acid was resolved as its brucine salt, which was crystallized five times from acetone. The recovered oil slowly crystallized, mp. 68-70°C, $[\alpha]_d^{25} = +189^\circ$, c. 2.0 benz. Resolution may not have been complete as the product melted over a 2° C. range.

2-(1-Naphthyl)-butyric acid, VI. Procedure was the same as that for the corresponding propanoic acid except that EtI was added to the sodium salt of naphthalene acetonitrile. Yield of acid was 49 g. from 50 g. nitrile and 60 g. ethyl iodide. The acid was resolved as the brucine salt by 7 recrystallizations from acetone-ether. Mp. of salt 131-135°C. Rotation of acid $[\alpha]_d^{25} = +186^\circ$ c. 6.25 (benz). (+)VI did not crystallize. It was distilled on molecular still before use as a sensitizer.

(+)2-(1-Naphthyl)-butanol, VII. The (+) acid (2.6 g.), VI added to $LiAlH_4$ (0.5 g.) in 70 ml. dry ether, was stirred and refluxed overnite. The oil isolated by distillation at reduced pressure did not crystallize. $[\alpha]_{d}^{25} = +1.86^{\circ}$ c. 2.9 (benz). Material was distilled under reduced pressure before use as a sensitizer.

(+)2-(1-Naphthyl)-butane. The above alcohol was treated with 2.3 g. tosyl chloride in 60 ml. pyridine. After 10 hours, 50 ml. Et_2O was added. The solution was extracted with 0.1 N. HCl, dried over $MgSO_4$, filtered, and evaporated. Yield, 3.3 g. of colorless oil. The tosylate was reduced with 0.4 g. $LiAlH_4$ in 50 ml. ether. The oil isolated from reduction (1.7 g.) was chromatographed on an alumina collumn. $[\alpha]_{d}^{25} = +18^{\circ}$ (c. 2.0 benz.). NMR spectra was consistent with that expected for 2-naphthyl butane, absorptions were at (d): 7.0 (7 protons, m.); 3.1 (1, sextet); 1.4 (2,m.); 1.0 (3,d.); 0.55 (3,t).

1-Chloro-2-(1-naphthyl)-butane. (+) VI was reduced to the corresponding alcohol with $LiAlH_4$ as in the preparation of VII. The isolated alcohol was treated with $SOCl_2$ in ether, allowing about 10 days for reaction. Unreacted alcohol was removed by H_2SO_4 extraction of the product in hexane. The remaining product was chromotographed on alumina and recovered, $[\alpha]_{d}^{25} = +41.2^{\circ}$ c. 3.03 (benz.). NMR consisted of aromatic multiplet, 8,0-7.1, quartet of multiplets 4.3, complex multiplet 3.0-3.8, and doublet, 1.4. The relative intensities are 7/1/2/3. The complexity of the group at 3.0-3.8 may be due to presence of the adjacent asymmetric center.

(+)4-Phenanthene carboxylic acid-4 (H)-1,2,3,4., (+) X.

Naphthalene acetonitrile was condensed with methyl acyrlate, forming the ester nitrile. The latter was hydrolized to the diacid which was then cyclized to the ketoacid. Reductive elimination of the keto acid afforded the desired product, which was resolved as the quinine salt. The details are as follows.

Naphthalene acetonitrile (57 g.), and methyl acrylate (29.5 g.) in 100 ml. benzene was stirred while 3.0 ml. Triton B (40% in methanol) was added drop wise. Stirring was continued overnite. The solution was acidified with dil. NaCl and extracted with water. The separated organic layer was distilled at 0.1 mm pressure and the fraction boiling 170 - 200° C collected; yield 80 g. (93%). NMR was consistent with desired product.

The ester-nitrile (40 g.) was hydrolized to the corresponding diacid by refluxing 8 hours in 300 ml. 1:1:1 (by volume H_2SO_4 - HOAc - H_2O. The hydrolysis mixture was poured onto ice and extracted with ether; the ether extract was extracted with 0.1 N. NaOH, which was then acidified. The precipitated oil was extracted with ether. Evaporation of the solvent left an oil which crystallized with difficulty; mp. 124.5 - 125°C.; yield, 80%. NMR resonances (d) in $DCCl_3$: 13.45 (2), 7.3 (7), 4.5 (1), 2.3 (4).

The diacid (60 g.) dissolved in 400 ml. anhydrous HF was stirred overnite. The reaction mixture was poured onto ice and the crystalline mass filtered quickly and washed with H_2O. The dried precipitate, crystallized from benzene-ethanol (10:1), yielded 41 g. keto acid. NMR absorptions (d) in $DCCl_3$ occur at: 7.5 (7), 4.3 (1), 2.4 (4).

The keto-acid was reduced to X by hydrogenation. Two g. keto-acid, 0.1 g. 5% Pd/C, 1 drop H_2SO_4 in 200 ml. 95% EtOH at 40 p.s.i. H_2 pressure was shaken for 4 hours at 25°C. Work up gave 1.0 g. desired product, mp. 141-142°C. NMR spectrum (CCl_4) consisted of absorptions (d) at: 11.15 (1), 7.4 (7), 4.2 (1), 2.9-1.5 (4).

The acid, X, was resolved as its quinine salt from ethanol-water; mp. 204-204.5°C, $[\alpha]_d^{25} = -8.3^\circ$ (c. 6.0 benz.). The acid, recovered by dil. HCl decomposition of the salt, was crystallized from heptane, mp. 120°.0, $[\alpha]_d^{25} = -8.3^\circ$ (c. 6.3 benz.). The sharp mp. was taken as criteria of optically pure product.

Benzene - two grades of benzene were used. Both gave the same results. The first was prepared by H_2SO_4 extraction of reagent grade benzene and distillation from P_2O_5. The purification has been described in detail (Reference 12, Part I of this thesis).

Experimental Methods.

Preparation of samples. Stock solutions of sensitizers and substrate were prepared in purified or spectro-grade benzene. Two ml. aliquots were placed in 13 mm. pyrex test tubes which had a restriction at the top. All tubes were washed thoroughly with Orvus, rinsed carefully with distilled water, and dried in an oven at 120°C before filling. The solutions were degassed to about 4×10^{-4} torr. by four freeze-pump-thaw cycles.

Irradiations were carried out by placing sealed tubes around the pyrex cooling well of a Hanovia 450w. mercury lamp. For one series, a quartz well with a 4 mm. pyrex filter and a 2.5 mm. layer of 0.05 M. potassium biphthalate soluation was employed, as described by C. DeBoer. This was supposed to eliminate side reactions from direct excitation of the diphenylcyclopropanes.

V.p.c. analysis showed 97% of the original cyclopropanes remained even after 1000 hours irradiation. The other 3% is probably diphenylpropenes.

Analyses

Isomer compositions of the irradiated solutions were measured by v.p.c. analysis on a Loenco Model 15B chromatograph equipped with a thermal conductivity detector. A 10% Apiezon L on Chromosorb W packed collumn at 185-195°C gives a good separation of the isomers. Measurable isomerization does not occur during v.p.c. analysis.

Rotations were determined on a standard optical polarimeter using the sodium D line. One or two dm. tubes were employed. Standard procedure was to average 5 or 6 readings. The zero was determined before and after each series of sample measurements. Rotation could be easily reproduced to ± 0.02°.

The specific rotation is calculated as,

$$[\alpha]_{d}^{25} = \frac{100a}{c \cdot 1}$$

where a = observed rotation, 1 = tube length, and c is the conc. in g/100 ml. For our calculation we used $c = c_o$ (% trans-II).

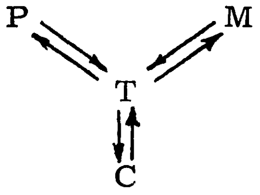
Fluorescence Intensity Measurements

Spectra were determined on an Aminco-Bowman Spectrophotofluoremeter. Samples containing the fluorescent compound ($c = 10^{-3}$ M.), quenchers and solvent were degassed by several freeze-thaw-cycles before sealing.

Appendix

The concentrations of each species as a function of time are derived as follows. For clarity we designate [P] = [(+) trans-II], [M] = [(-) trans-II], [C] = [cis-II].

We are interested in the following system:



which can be represented by the equations:

$$S + h\nu \xrightarrow{I_0} S^*$$

$$S^* \xrightarrow{k_d} S$$

$$S^* + P \xrightarrow{k_p} S + T$$

$$S^* + M \xrightarrow{k_m} S + T$$

$$S^* + C \xrightarrow{k_c} S + T$$

$$T \longrightarrow P$$

$$T \longrightarrow M$$

$$T \longrightarrow C$$

The effective relationships are:

$$P \longrightarrow M \text{ ------ } R_1$$

$$P \longrightarrow C \text{ ------ } R_2$$

$$M \longrightarrow P \text{ ------ } R_3$$

$$M \longrightarrow C \text{ ------ } R_4$$

$$\left.\begin{array}{l} C \longrightarrow P \text{ ------ } R_5 \\ C \longrightarrow M \text{ ------ } R_6 \end{array}\right\} \quad R_5 = R_6$$

These R's can be expressed as:

$$R_1 = k_p f_d [S^*] [P]$$

$$R_2 = k_p f_c [S^*] [P]$$

$$R_3 = k_m f_d [S^*] [M]$$

$$R_4 = k_m f_c [S^*] [M]$$

$$R_5 = k_c f_d [S^*] [C]$$

$$R_6 = k_c f_d [S^*] [C]$$

where f_d = fraction of T decaying to P

f_l = " " " " " M

f_c = " " " " " C

with the specification that

$$f_d = f_l$$

at the s. s.,

$$R_1 + R_2 = R_3 + R_5$$

$$R_3 + R_4 = R_1 + R_6$$

$$R_5 + R_6 = R_2 + R_4$$

at all times,

$$\frac{R_1}{R_2} = \frac{f_d}{f_c}, \quad \frac{R_3}{R_4} = \frac{f_d}{f_c}$$

substituting into the above expressions,

$$R_1 + \frac{f_c}{f_d} R_1 = R_3 + R_5$$

combining the top two expressions,

$$2R_1 + \frac{f_c}{f_d} R_1 = 2R_3 + R_4 \text{ , giving}$$

$$R_1 \left(2 + \frac{f_c}{f_d} \right) = R_3 \left(2 + \frac{f_c}{f_d}\right)$$

or $R_1 = R_3$,

and $R_4 = R_2 = R_5 = R_6$ at the s. s.

Thus:

$$\left(\frac{[P]}{[M]}\right)_{s.s.} = \frac{k_p}{k_m}$$

$$\left(\frac{[P]}{[C]}\right)_{s.s.} = \frac{k_p}{k_c} \frac{f_d}{f_c}$$

The differential expressions are:

$$\frac{d[P]}{d[t]} = R_3 + R_5 - R_1 - R_2$$

$$\frac{d[M]}{d[t]} = R_1 + R_5 - R_3 - R_4$$

$$\frac{d[C]}{d[t]} = R_2 + R_4 - 2R_5$$

These can be simplified by solving the steady state $[S^*]$.

$$\frac{d[S]}{dt} = I_0 - [S^*] (k_d + k_p[P] + k_m[M] + k_c [C]) \approx 0$$

$$\therefore [S^*] = \frac{I_0}{k_d + k_p[P] + k_m[M] + k_c[C]}$$

since $k_d \gg k_p[P] + k_m[M] + k_c[C]$

$$[S^*] \cong \frac{I_0}{k_d} = \text{constant.}$$

Since we are interested in relative rates, the constant is taken to be 1. The differential equations are then

$$\frac{d[P]}{dt} = -[P](f_d + f_c)k_p + [M]f_d k_m + [C]f_d k_c$$

$$\frac{d[M]}{dt} = [P]f_d k_p - [M](f_d + f_c)k_m + [C]f_d k_c$$

$$\frac{d[C]}{dt} = [P]f_c k_p + [M]f_c k_m - [C]2f_d k_c$$

For clarity the following substitutions are made:

$$\frac{d[P]}{dt} = \alpha_1[P] + \beta_1[M] + \gamma_1[C]$$

$$\frac{d[M]}{dt} = \alpha_2[P] + \beta_2[M] + \gamma_2[C]$$

$$\frac{d[C]}{dt} = \alpha_3[P] + \beta_3[M] + \gamma_3[C]$$

Define $z \equiv [P] + [M] + [C]$. Then,

$$\frac{d[P]}{dt} = (\alpha_1 - \gamma_1)[P] + (\beta_1 - \gamma_1)[M] + \gamma_1 z$$

$$\frac{d[M]}{dt} = (\alpha_2 - \gamma_2)[P] + (\beta_2 - \gamma_2)[M] + \gamma_2 z .$$

This gives two non-homogeneous coupled differential equations which can be reduced to a pair of coupled homogenous equations as follows:

$$[P'] = [P] + p$$
$$[M'] = [M] + m$$

p and m are constants chosen such that the differential equations become homogeneous.

1. $$\frac{d[P']}{dt} = \frac{d[P]}{dt}$$
$$\frac{d[M']}{dt} = \frac{d[M]}{dt}$$

2. $$(\alpha_1 - \gamma_1)[P] = (\alpha_1 - \gamma_1)[P'] + (\alpha_1 - \gamma_1)p$$
$$(\alpha_2 - \gamma_2)[P] = (\alpha_2 - \gamma_2)[P'] + (\alpha_2 - \gamma_2)p$$

3. $$(\beta_1 - \gamma_1)[M] = (\beta_1 - \gamma_1)[M'] + (\beta_1 - \gamma_1)m$$
$$(\beta_2 - \gamma_2)[M] = (\beta_2 - \gamma_2\ [M'] + (\beta_2 - \gamma_2)m$$

Hence,

$$(\alpha_1 - \gamma_1)p + (\beta_1 - \gamma_1)m = -\gamma_1 z$$
$$(\alpha_2 - \gamma_2)p + (\beta_2 - \gamma_2)m = -\gamma_2 z$$

Solving for p, m

$$m = \frac{-z[\alpha_2 \gamma_1 - \gamma_2 \alpha_1]}{\xi}$$

$$p = \frac{-z(\beta_1 \gamma_2 - \beta_2 \gamma_1)}{\xi}$$

where $\xi = (\alpha_2 - \gamma_2)(\beta_1 - \gamma_1) - (\alpha_1 - \gamma_1)(\beta_2 - \gamma_2)$.

The homogeneous equations are now

$$\frac{d[P']}{dt} = (\alpha_1 - \gamma_1)[P'] + (\beta_1 - \gamma_1)[M']$$

$$\frac{d[M']}{dt} = (\alpha_2 - \gamma_2)[P'] + (\beta_2 - \gamma_2)[M']$$

The solutions are

$$[P'] = C_1 e^{\lambda t}, \quad [M'] = C_4 e^{\lambda t}$$

substituting these into the differential expressions,

$$C_1 \lambda e^{\lambda t} = [(\alpha_1 - \gamma_1) C_1 + (\beta_1 - \gamma_1) C_4] e^{\lambda t}$$

$$C_4 \lambda e^{\lambda t} = [(\alpha_2 - \gamma_2) C_1 + (\beta_2 - \gamma_2) C_4] e^{\lambda t}$$

or

$$O = (\alpha_1 - \gamma_1 - \lambda) C_1 + (\beta_1 - \gamma_1) C_4$$

$$O = (\alpha_2 - \gamma_2) C_1 + (\beta_2 - \gamma_2 - \lambda) C_4$$

which are non trivial only if

$$\begin{vmatrix} \alpha_1 - \gamma_1 - \lambda & \beta_1 - \gamma_1 \\ \alpha_2 - \gamma_2 & \beta_2 - \gamma_2 - \lambda \end{vmatrix} = O$$

or

$$\lambda^2 - \eta\lambda - \xi = O$$

where

$$\eta \equiv (\alpha_1 - \gamma_1) + (\beta_2 - \gamma_2)$$

The solutions are

$$\lambda_{\substack{1\\2}} = \frac{\eta \pm \sqrt{\eta^2 + 4\,\xi}}{2}$$

Hence

$$[P] = C_1 e^{\lambda_1 t} + C_2 e^{\lambda_2 t} + C_3$$
$$[M] = C_4 e^{\lambda_1 t} + C_5 e^{\lambda_2 t} + C_6$$
$$[C] = C_7 e^{\lambda_1 t} + C_8 e^{\lambda_2 t} + C_9$$

where

$$C_3 = -p\,, \quad C_6 = -m\,.$$

The other coefficients are evaluated using initial boundary conditions with the first and second derivative expressions.

$$C_1 = \frac{(\beta_1 - \gamma_1)(\alpha_2 + \beta_2) - (\alpha_1 + \beta_1)[\lambda_2 - (\alpha_1 - \gamma_1)]}{\lambda_2[\lambda_1 - \lambda_2]}[P_0]$$

$$C_2 = \frac{(\beta_1 - \gamma_1)(\alpha_2 + \beta_2) - (\alpha_1 + \beta_1)[\lambda_1 - (\alpha_1 - \gamma_1)]}{\lambda_1[\lambda_2 - \lambda_1]}[P_0]$$

$$C_4 = \frac{(\alpha_2 - \gamma_2)(\alpha_1 + \beta_1) - (\alpha_2 + \beta_2)[\lambda_2 - (\beta_2 - \gamma_2)]}{\lambda_1[\lambda_2 - \lambda_1]}[P_0]$$

$$C_7 = -(C_1 + C_4) \qquad C_9 = 2[P_0] - C_3 - C_6$$
$$C_8 = -(C_2 + C_5)$$

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PROPOSITIONS

PROPOSITION I

Studies involving electronic energy transfer between donors and acceptors labeled on biological macromolecules are proposed. Experiments of this type should help elucidate the structure as well as function of biological macromolecules.

* * * * * * * * * *

Spectroscopic studies indicate that energy transfer can occur through space between donors and acceptors separated by effective distances of up to 100 Å (1). According to the Forster treatment, the rate constant for energy transfer, k, is

$$k = \frac{6000 \ln 10 \; \eta_D}{128 \; \pi^6 n^4 N \; \tau_D R^6} \int_0^\infty f_D(v) \, \varepsilon_A(v) \, \frac{dv}{v^4}$$

where v is the wave number, η_D is the quantum yield for fluorescence, n is the refractive index of the medium, N is Avogadro's number, τ_D is the lifetime of the excited state, R is the mean distance between donor and acceptor, $f_D(v)$ is the spectral distribution of the donor, and $\varepsilon_A(v)$ is the extinction coefficient of the acceptor.

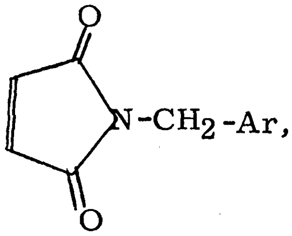
Notably, the efficiency, varies as $1/R^6$. This has been verified experimentally for a number of cases (1).

We propose to label proteins and other biological macromolecules with both donors and acceptors and study the efficiency of energy transfer between the pair. The simplest case would be to label a donor on a molecule which already contains a chromophore in the visable or near U.V. Spectroscopic measurement of the sensitized fluorescence of this chromophore or the quenching of the donor fluorescence should indicate the distance between the transfer pair. Hemoglobin or the cytochromes could be studied by this technique (3). Other enzymes could be labeled with a donor and the substrate with an acceptor. Energy transfer between an enzyme-substrate complex could then be studied. This should be useful in investigating the position of the active site. Allosteric enzymes can be doubly labeled. A change in tertiary structure of the protein by formation or an enzyme-substrate or enzyme-product complex would alter the donor-acceptor distance and hence the efficiency of transfer.

The specificity and activity of these labeled enzymes can be compared to those of the native compounds. This should indicate whether the presence of the label has significantly altered the structure of the protein or its function (4).

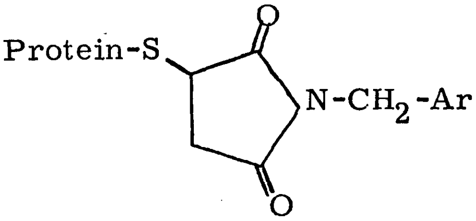
There are a number of reactive groups which can be used to place a label on various amino acid residues (2). When light, specific labeling is desired, N-substituted maleimides appear to be most promising, since this group react specifically with exposed -SH groups of cysteine.

Labels with the below structure would be prepared.



where Ar is an aromatic group

with the desired energy transfer characteristics. The reaction product with a protein is



The second component of the transfer pair could be added using a reagent which is more reactive such as a substituted isocyanate, or one which reacts with other amino acid residues.

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PROPOSITION II

Measurement of carbon-13 hyperfine interactions from the electron spin resonance spectra of non-planar alkyl free radicals will provide information on their detailed electronic structures and nuclear configurations.

* * * * * * * * * *

Extensive measurements have been made on the proton hyperfine splittings of simple alkyl free radicals (1,2a,b). These studies indicate that the unpaired electron is localized in a "p" orbital on a trigonally hybridized carbon atom.

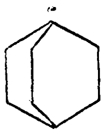
Bicyclic aliphatic free radicals, where the unpaired spin is located at a bridgehead position, should not be able to attain a planar configuration at this position. However, chemical kinetic results on the decarbonylation of aldehydes suggests that 1-bicyclo [2,2,2] octyl (I) and 1-adamantly (II) radicals are more stable that the t-butyl radical, while 1-bicyclo [2,2,1] heptyl (III) is less stable than n-propyl (3).

We propose that ESR carbon-13 splittings be measured for various, non-planar alkyl free radicals. These results will help elucidate free radical structures. The carbon-13 splittings, a^c, should be a sensitive function of the hybridization of the atom bearing the unpaired spin, and we believe a simple correlation exists between a^c and the hybridization. The following relationship is suggested:

$$a^c = a_o^c \lambda + a_p^c (1-\lambda) \tag{1}$$

The first term of 1 is the zero order isotropic hyperfine coupling constant for an electron in a carbon 2s orbital, a_o^c, times the fractional 2s character of that orbital, λ . First order spin polarization of the other orbitals is taken into account by the second term. Reasonably, the spin polarization should decrease as the 2s character of the unpaired spin is increased. Using Hartree-Fock orbitals, a_o^c is calculated to be 1190 gauss (4, 5). a_p^o is measured and calculated to be 41 ± 3 gauss (6). When the odd electron is in an sp, sp^2 or sp^3 like orbital, the predominant splittings will arise from the 2s character of that orbital. This will greatly overshadow the induced spin polarization, approximately by a factor of ten for an sp^2 electron. For very slightly distorted radicals, the relationship developed by Karplus and Fraenkel (4) should be useful for correlating bond angles with observed splittings. The carbon-13 splittings of compounds I-VII are expected to obey 1, giving a correlation as shown in Figure I.

Some model compounds, for which the geometry of the radical should be similar to that of the parent hydrocarbon are shown below.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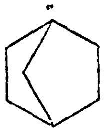
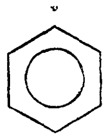
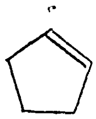
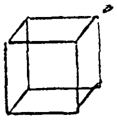
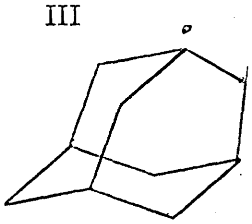

III

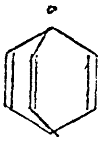

IV


V

$H-C\equiv C\cdot$
VI


VII


II


VIII

Significant deviations from a correlation such as 1 could indicate large distortion in the hydrocarbon geometry upon formation of the radical. Looser, large ring systems should display this trend.

Synthesis of many of the precursors to these radicals will undoubtedly be a difficult task, especially with carbon-13 in the appropriate position. The best way to overcome this is, perhaps, to work with these compounds containing carbon-13 in natural abundance. High radical concentrations should facilitate observation of the widely spaced carbon-13 satellites.

Changes in hybridization upon formation of the radical may be calculated and compared to the experimental value. An elementary calculation might be accomplished with the following assumptions: 1. a first order perturbation in hybridization occurs

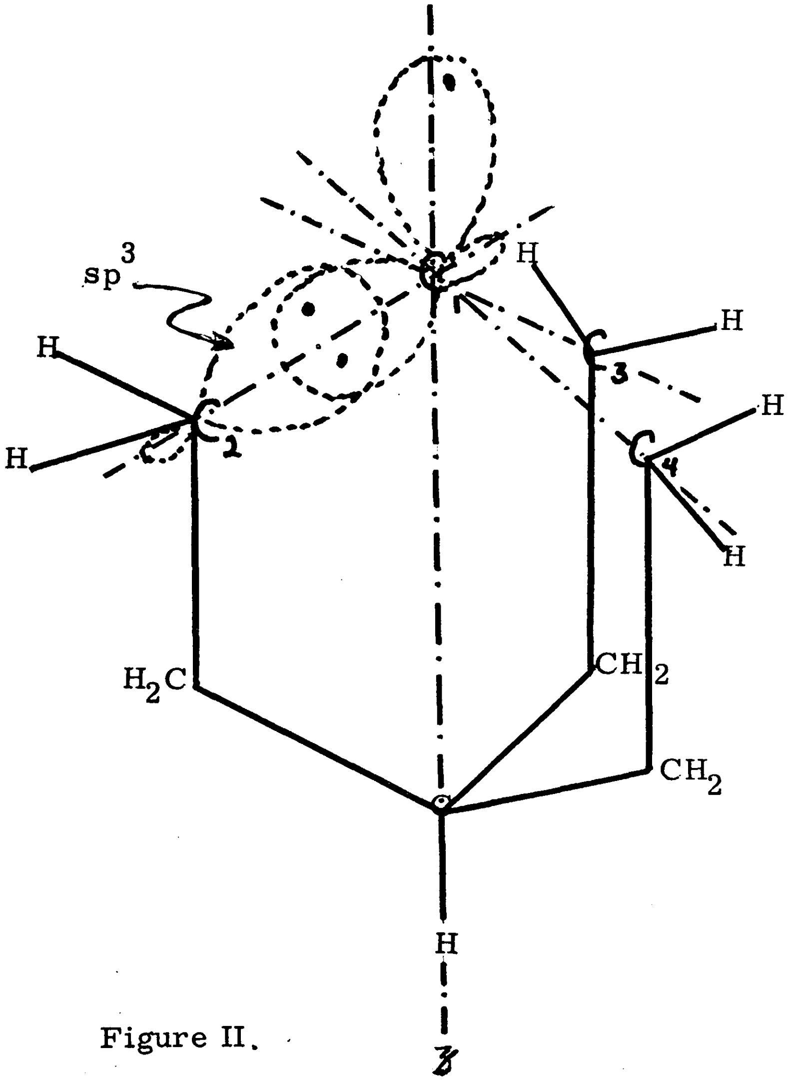


Figure II.

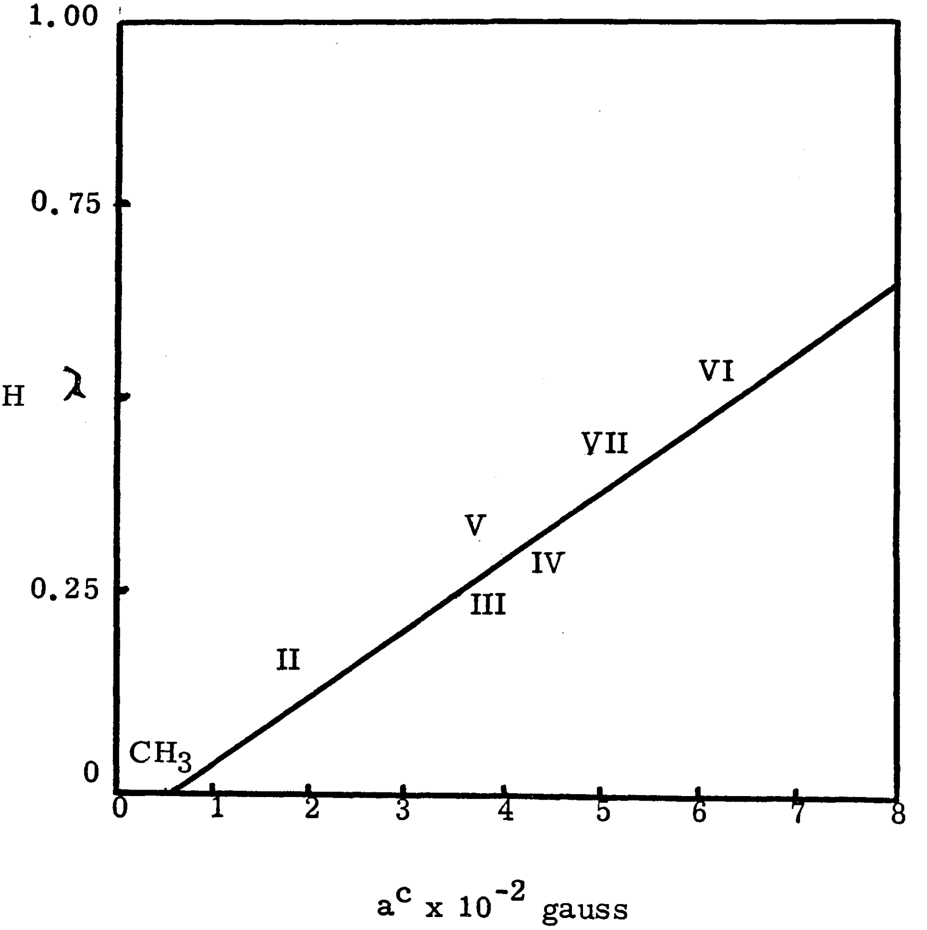


Figure I.

only at the unpaired electron site. Influences on other atoms in the radical are second order, and their hybridizations and positions are taken to be those of the parent hydrocarbon; 2. energy of the system is proportional to the overlap between the atoms in question (i.e., the atom bearing the unpaired spin and those atoms bonded to it.)

With these assumptions, hybridization calculations can be made as follows: 1-bicyclo[2,2,2] octyl is used as an example in Figure II. C_1 is placed in a variable position on the z axis. An expression for the overlap between C_1 and C's 2,3, and 4 is set up and maximized with respect to the position of C_1 and the coefficients of the C_1 atomic orbitals. The s character of the unpaired spin on C_1 is then given by

$$\lambda = 1-3\lambda'$$

where λ' is the 2s coefficient of the other three sigma orbitals of C_1.

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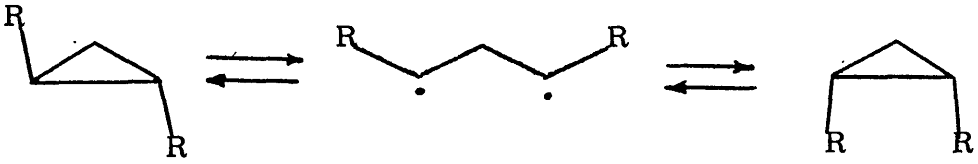
PROPOSITION III

Experiments are proposed to determine whether the trimethylenes formed by electronic excitation of cyclopropanes and by addition of triplet carbenes to alkenes equilibrate before closure to the cyclopropane.

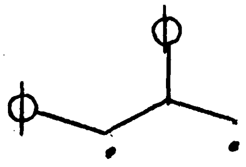
* * * * * * * * * *

Cyclopropanes undergo photochemical transformations by direct excitation and by singlet and triplet energy sensitization (1-4). Upon excitation, the ring is apparently cleaved, forming a trimethylene. This intermediate can then close back to a cyclopropane.

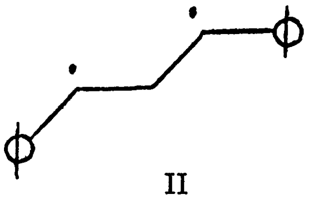


In the above case, where a cis-trans isomerization occurs, a specific decay ratio to cis and trans product is observed. For 1,2-diphenylcyclopropanes, this ratio is apparently the same, whether the intermediate is formed by direct excitation or by singlet or triplet sensitization (1-3).

We propose that the isomeric trimethylenes shown below be prepared and their decay paths compared by the distribution of

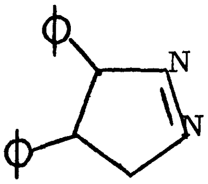


I



II

products formed. Experiments of this type should indicate whether an equilibration between I and II takes place before closure to cis and trans product. The decay paths of II have been previously studied (1, 2). The biradical I could be generated by the sensitized decomposition of III, or by addition of triplet methylene to stilbenes (5).



$$\longrightarrow \quad \mathrm{I} + N_2$$

$$CH_2N_2 \xrightarrow[\text{sens.}]{h\nu} CH_2\text{:(triplet)}$$

$$CH_2\text{:(triplet)} + \text{stilbene} \longrightarrow \mathrm{I}$$

This type of study should assist in understanding the decay paths of photochemically produced intermediates.

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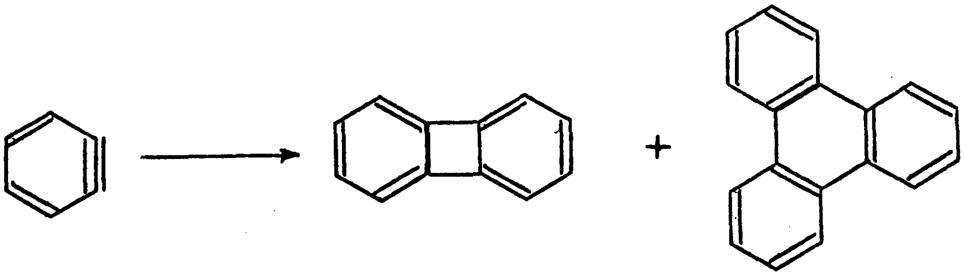
PROPOSITION IV

A mechanism for the formation of triphenylene from benzyne is suggested.

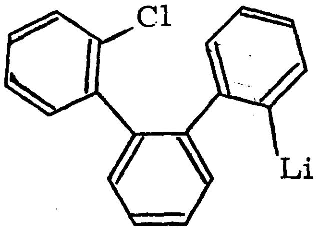
* * * * * * * * * *

An extensive amount of work has been done on the chemistry of arynes (1). In virtually all systems where benzyne (I) is generated as a reactive intermediate, the formation of biphenylene (II) and triphenylene (III) are noted.



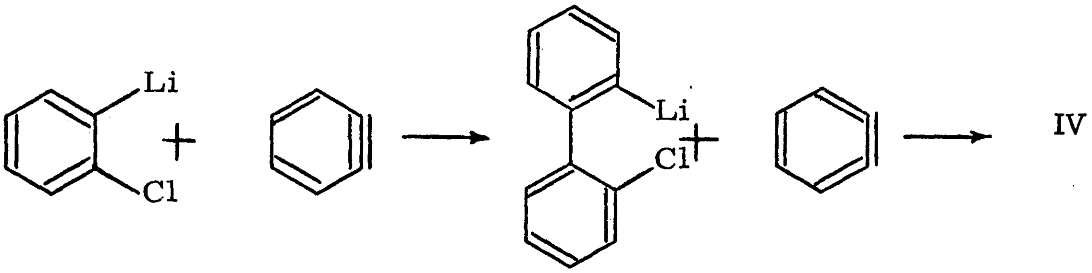
I II III

The absolute and relative yields of II and III vary greatly (1), depending upon the experimental conditions and especially upon the method of production of I. High yields of III are noted when a 1,2-dihaloaromatic is reduced with an alkali metal. There is evidence that the formation of III involves the intermediacy of a precursor such as IV (1).

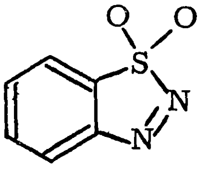


IV

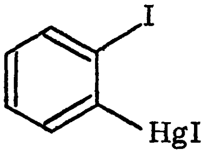
This could be formed by reaction of benzyne with the organometallic as shown below.



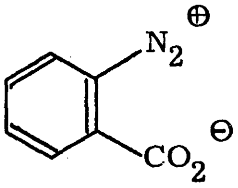
This route is not possible when benzyne is generated under non-alkaline conditions, such as by the thermal or photochemical cleavage of compounds such as V, VI, and VII (2,3). In these systems the yield of II is much greater than in systems where I



V

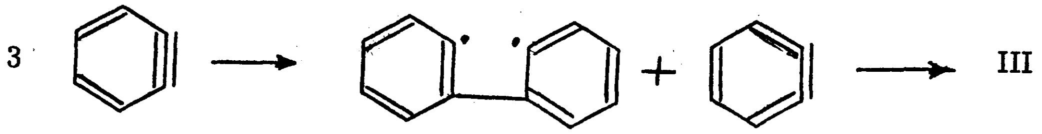


VI

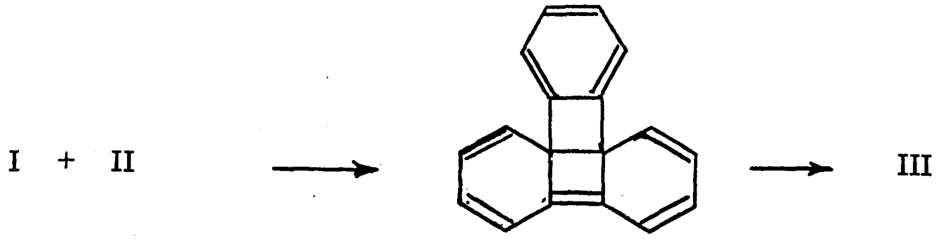


VII

is generated under alkaline conditions. The production of III is still noted, although in smaller yields (ca. 1-2%) (2). It is difficult to imagine the reaction leading to III being termolecular in I, due to the rather short lifetime of I (1). It is equally improbable that a biradical addition reaction (as shown below) could compete with closure to II.



We propose that under non-alkaline conditions, the formation of III takes place by attack of benzyne on biphenylene, possibly as shown below.



This mechanism could be tested by decomposition of compounds V-VII in the presence of added II. If this type of mechanism is correct, the yield of III will increase linearly with the II concentration if I is generated photochemically, and approximately so if I is generated thermally.

The spin state of I might be significant in determining the yield of III. This could be tested by decomposition of benzyne precursors by triplet sensitizers.

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PROPOSITION V

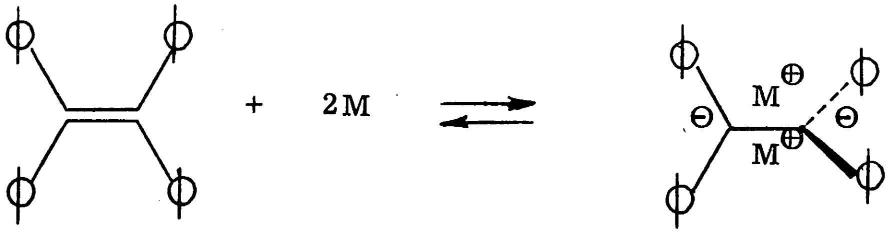
The NMR and ESR spectra of metal adducts of substituted tetraphenylethylenes should indicate whether or not tetraphenylethylene distorts significantly when it forms alkali metal adducts.

* * * * * * * * * *

Virtually all aromatic hydrocarbons preferentially form mono-alkali metal adducts ($K_2 \ll 1$). Ethylenes with attached aromatic groups are peculiar in that they frequently form dianions rather than ion-radicals (1) ($K_2 \gg 1$). The following equlibria apply for the simplest case.

$$2M + H \overset{K_1}{\rightleftarrows} \overset{+}{M}\overset{-}{H}\cdot + M \overset{K_2}{\rightleftarrows} \overset{+}{M_2}\overset{=}{H},$$

where M is an alkali metal and H, the hydrocarbon. One explanation offered for this anomality is that substituted ethylenes undergo a large geometric distortion upon formation of the metal adducts, facilitating formation of dianions (2). A likely possibility might be:



We propose to test this theory by study of the NMR and ESR spectra of anions of tetramesitylethylene. The *ortho* methyl groups of the parent hydrocarbon are non-equivalent in the NMR spectrum, presumably due to steric hinderance to rotation of the phenyl groups (3). If the hydrocarbon distorts to an orthogonal configuration upon formation of its anions, the methyl groups should become equivalent, as they are in dimesityl ketone (3).

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