PART ONE

PHOTOCHEMICAL CIS ⇄ TRANS ISOMERIZATION OF β - STYRYLNAPHTHALENE

PART TWO

PHOTOCHEMISTRY OF N - METHYL - 4 - PYRIDONE AND N - METHYLLUTIDONE

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To My Family

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ABSTRACT

PART ONE

Photochemical cis ⇄ trans isomerization of β-styrylnaphthalene is studied by direct irradiation with light of various wavelengths and irradiation in the presence of sensitizers. A very unusual "negative" wavelength effect on quantum yields of trans → cis isomerization by direct irradiation is observed. The interpretation of this observation is presented in terms of multiple conformers of electronically excited states which are not interconvertible. The study of fluorescence spectra confirms the interpretation. Sensitizers transfer triplet energy quite efficiently to β-styrylnaphthalene. However, benzophenone whose triplet energy is considered to be high transfers triplet excitation preferentially to the cis isomer. Quenching constants, both k_{qc} and k_{qt}, were expected to be diffusion controlled. However, the study of the photostationary states and quantum yields of sensitized isomerization indicates the opposite for the benzophenone. A significant quantum waste is observed and interpreted in terms of localization of excitation in the naphthalene chromophore. The effect was far more pronounced in direct isomerization perhaps because the excited singlets are shorter lived than triplets made by energy transfer. Definitely a singlet mechanism is involved, perhaps in conjunction with other mechanisms, in direct isomerization. This is confirmed by the studies of quantum yields, photostationary states, and side reactions. The studies of solvent effect and concentration effect on quantum yields in direct isomerization are also presented. ^{60}Co γ-ray radiolysis of β-styrylnaphthalene in benzene indicates that the triplet mechanism is responsible for the isomerization of β-styrylnaphthalene in the radiolysis of benzene solution. The detailed study of G values and radiostationary states are presented with the discussions of the nature of the reaction. The implications of above studies in the study of other photoreactions are presented.

PART TWO

The photochemistry of the model compounds for pyrimidine bases, N-methyl-4-pyridone and N-methyllutidone, is reported. Spectroscopic and chemical studies on the irradiations of these compounds in aqueous solutions indicate that the hydration occurs at the α position and leads to ring opening. The products obtained from ring opening undergo some unknown reactions, perhaps photo-oxidations and polymerizations.

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PART ONE

PHOTOCHEMICAL CIS $\rightleftharpoons$ TRANS ISOMERIZATION OF β - STYRYLNAPHTHALENE

INTRODUCTION

In the past few years there have been numerous investigations of photochemical cis ⇄ trans isomerization of olefins (1). The photochemical process can be effected by direct irradiation of olefins or by irradiation in the presence of a sensitizer or a catalyst.

Direct irradiation of solutions containing either isomer leads to photostationary mixture of the two isomers whose composition is mainly determined by relative extinction coefficient if no side reactions occur other than isomerization.

The mechanism of these processes have been discussed frequently and thoroughly (2) even though it is not clear yet. The structure of the electronically excited states is very important to elucidate the course of the reaction but it still can be determined only approximately, and often by methods not easily accessible to the organic chemist. Even when the excited - state structure is known, it is uncertain what criteria control the course of the excited - state reaction.

Mulliken and Roothaan (3) arrived early at the conclusion by extensive quantum mechanical calculations that both the lowest excited singlet state and the lowest excited triplet state of ethylene have energy minima at the configuration in which the planes of the methylene groups are perpendicular to each other .

This geometry is reasonable since the molecular orbital picture of an electronic transition in ethylene is that of an electron jump from the highest filled bonding π orbital into the lowest unfilled π^* orbital and refined calculations indicate that the destabilizing effect of the π^* electron outweighs the bonding energy of the electron left in the π orbital making the ground - state nuclear configuration, in which the two p_z orbitals are parallel and form a π bond, no longer the most stable configuration. Twisting the molecule 90° about the $C_1 - C_2$ axis minimizes the overlap between π and π^* orbitals, and the perpendicular configuration is the most stable for the π, π^* configuration. If one plots the potential energy curve for twisting of ethylene as a function of the angle between the π and π^* orbitals, the result is shown in Figure 1.

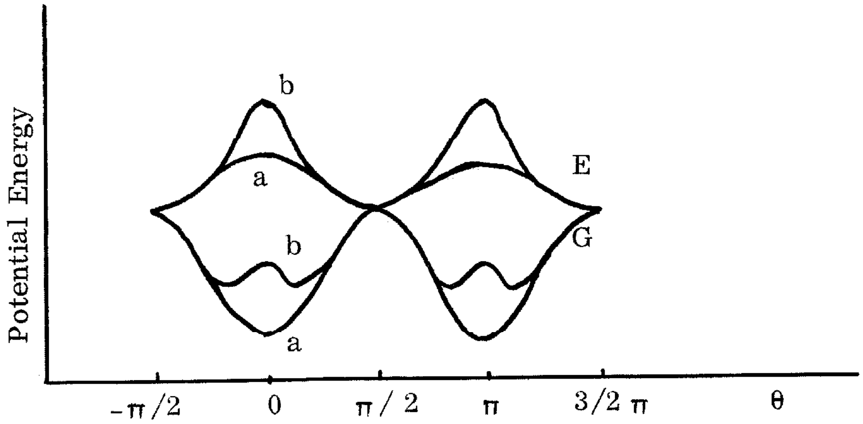


Figure 1 The Potential Energy of (a) Ethylene and (b) A Hindered Ethylene as a Function of Angle Twist. G = Ground State; E = Excited State (7).

Presumably this situation will prevail for substituted olefins as long as the substituent is not in conjugation with the double bond in question. Thus for alkyl - substituted olefins common excited singlet and triplet intermediates would be expected at an angle of twist close to 90° and isomerization would be expected to occur from either of the lowest excited singlet or triplet states.

But for the complex olefins such as cis - and trans - stilbene, substituted stilbenes or diethyl maleate and diethyl fumarate, the calculations for ethylene are not expected to apply. The double bond is now a part of an extensive π system and cannot be treated as an isolated unit (4).

One of the few systems in which most of the tools available to photochemists have been put into use and which is most thoroughly studied is stilbenes.

The mechanism of direct photochemical cis ⇌ trans isomerization of the stilbenes has been disputed by many people extensively. Hitherto available data can be accomodated by either of two mechanisms:

(a) the Lewis mechanism, which assumes that $S^1 - S_0$ radiationless conversion produces a freely rotating, high vibrational level of the ground electronic state and isomerization occurs from this state. Eventually the surplus energy is lost to the medium and the molecule stays either in the cis or the trans form (5). Saltiel et al. (6) support this mechanism from the study of azulene effect on scintillation experiments with stilbenes.

(b) the Förster mechanism, in which the stilbene isomers lose their identity upon $S^1 - T^1$ crossing to interconvertible or common triplet states (4, 8 - 16). However, among those authors, there is divergence of opinion as to the appropriate place where activated processes should be introduced. Birnbaum et al. (7 - 8) and Förster (10) and Yamashita (11) have supported the view that photoisomerization involves an intermediate state, the triplet state in which both parts of the molecule are twisted by 90° at the double bond, common to both cis and trans isomers. In this state there is no energy barrier between two isomers.

According to Zimmerman et al. (17) the above two mechanisms, $S^1 - S_0$ and $S^1 - T^1$ conversion, contradict the experimental results, and it therefore has to be assumed that "the isomerization takes place as an ordinary thermal reaction of an electronic excited state, i. e., thermal interconversion of electronic excited cis* and trans* molecules across a hypothetical energy barrier.

However the following observations make the thermal interconversion and common triplet theories very questionable.

(i) The cis / trans ratio of the photostationary mixture is bigger than that of the thermal equilibrium mixture. (ii) The strong fluorescence is observed from the trans - stilbene but only a weak structureless fluorescence is observed from the cis isomer (5, 12). (iii) Contrary to expectation based on LCAO - MO calculations, analysis of the vibrational structure of the absorption spectra of the two stilbenes led to the conclusion that the stretching frequency of the central ethylenic double bond is practically unaltered upon excitation of either isomer to its lowest excited state (stretching frequencies of ethylenic bond at excited state 1599 cm^{-1} (S), at ground state 1635 cm^{-1} (vs) (12), and henceforth the bond strength of the central double bond is practically unchanged upon excitation which would cause a substantial barrier for rotation between cis^* and $trans^*$ isomer. (iv) It is found that the trans → cis quantum yield decreases as the temperature goes down but that the fluorescence quantum yield increases. These results suggest that there is an activated process in isomerization (2).

Malkin and Fischer (2) and Stegemeyer (14) have supported the view that there is a small barrier to interconversion of isomeric triplet states from temperature dependence of quantum yields and a study of fluorescence. Schulte - Frohlinde et al. (13), and Dyck and McClure (12) favor the view that there is a small activation energy involved in intersystem crossing, at least in the trans system from the spectroscopic data and quantum yield dependence on the temperature, solvent, wavelength and concentration.

Hammond et al. (16) suggest that radiationless decay of the excited singlet must include paths having significant activation energies, one of these paths being production of dihydrophenanthrene. From the comparison of experimental results of photostationary states for direct irradiation and photosensitized processes with 1 - methylstilbene and stilbene, they strongly suggest that the same reactive intermediate, namely triplet state, was involved in the direct as in the sensitized isomerization of the stilbenes. But this is, of course, recognized to be dependent upon the assumption that the efficiency of intersystem crossing is the same for the two isomers which is not necessarily the case. The significance of this result is clouded further by the value of α, the fraction of stilbene triplets which decay to cis - stilbene, used in their interpretation but shown to be off by about 20 - 30 % (18).

As shown above, most of modern discussions of direct isomerization of stilbenes presume that the triplet states of the stilbenes are the principal isomerization pathway but it cannot be proven unequivocally so far with the data available that triplets are involved or that other pathways are not. Also it is very clear that the geometry of the excited states is very important to the elucidation of the mechanism.

If we replace one of the phenyl rings in stilbene with a bigger chromophore such as a naphthyl- , p - nitrophenyl-, or p - bromophenyl-ring, the transition moment of excitation will be more or less localized in those big chromophores rather than spreading all over the molecule. Consequently the ethylene bond would not be effected very much and would maintain planar configuration in the excited states as in the ground state. This would cause the isomerization to be very inefficient, giving poorer quantum yield than stilbene. This phenomenon was observed in the cases of 1 - (p - nitrophenyl) - 2 -(p' - dimethylaminophenyl) - ethylene (13) and p - bromostilbene (15).

The photosensitized cis $\rightleftarrows$ trans isomerization of stilbene, α-methylstilbene, α, β - dimethylstilbene, and 1, 3 - pentadiene was thoroughly studied by Hammond and his co - workers (16, 18 - 26), but the detailed nature of participation of sensitizer in the photochemical process is still debatable.

Schenck (27) proposes that nearly all energy transfer occurs by the addition - elimination mechanism in which the excited sensitizer adds to the acceptor forming the intermediate diradical and this intermediate reacts with another molecule to produce a new compound or the biradical collapses to yield ground state sensitizer and excited state acceptor. For example, photochemical oxidation can be represented by following scheme:

$$\begin{array}{lllllll}
 & S & + & h\nu & \longrightarrow & \cdot S\cdot & & \\
 & \cdot S\cdot & + & AH & \longrightarrow & \cdot SH & + & \cdot A \\
 & A\cdot & + & O_2 & \longrightarrow & AO_2\cdot & & \\
 & AO_2\cdot & + & AH & \longrightarrow & AO_2H & + & A\cdot \\
 & AO_2\cdot & + & \cdot SH & \longrightarrow & AO_2H & + & S \\
\text{or} & \cdot S\cdot & + & O_2 & \longrightarrow & \cdot SOO\cdot & & \\
 & \cdot SOO\cdot & + & A & \longrightarrow & AO_2 & + & S
\end{array}$$

However, the photosensitized cycloaddition of maleic anhydride to benzene (28) and a study of the direct and sensitized photodimerization of coumarin by Hammond *et al*. (29) make this mechanism very questionable to apply in general photosensitized reactions. The same product, *trans* - head - to - head dimer, was obtained from the sensitized photoreaction by benzophenone and also from direct photoreaction at highly dilute solution in which intersystem crossing in coumarin can compete with self - quenching. This fact demonstrates that benzophenone is not a necessary agent in the formation of *trans* - head - to - head dimer and also implies that energy transfer, rather than addition and elimination, is responsible for the photosensitized reaction.

Specially the Schenck mechanism is not likely to fit to the *cis* $\rightleftarrows$ *trans* isomerization of olefins since such close coupling of sensitizer and substrate might be permanent and lead to formation of a sensitizer - olefin addition compound. But for some low energy sensitizers like quinones and terphenyl, a mechanism similar to Schenck mechanism seems to work (26).

Hammond et al. have considered the mechanism of the sensitized process in terms of extensive quantitative spectroscopic, chemical and kinetic evidence on the stilbenes, ethyl maleate - ethyl fumarate, and the piperylenes (16). They interprete the photosensitized cis ⇄ trans isomerization of olefins in terms of a simple energy transfer mechanism in which the sensitizer remains unchanged at the end of the reaction. In this mechanism, the photostationary cis / trans ratio is a complicated function of the nature of the photosensitizers. In the case of stilbene isomerization as well as other reactions (16, 25, 30 - 32), the photostationary ratio of isomers or products can be predicted from the stilbene triplet decay (substrate triplet decay) ratio and the sensitizer quenching constants obtained from flash spectroscopy.

$$(c/t)_{p.s.s.} = (k_{T \to c} / k_{T \to t}) \cdot (k_{qt} / k_{qc})$$

where T is a single or an equilibrated mixture of triplet intermediates, k_q's are first order quenching constants of triplet - triplet absorption of the excited sensitizer by stilbene.

From the studies of stilbene system, Hammond and his co - workers demonstrated that:

1. With sensitizers whose triplet energy is 3 - 5 kcal greater than the acceptor triplet energy, the energy transfer is diffusion controlled (16, 41 - 43).

2. Low energy sensitizers having less triplet energy than trans - stilbenes were capable of reversibly transferring energy back and forth with trans - stilbene triplets but the cis -stilbene triplet was always formed irreversibly.

3. Certain low energy sensitizers whose triplet energy is less than that of cis stilbene (57 kcal) are capable of transferring energy to cis stilbene with moderate efficiency.

4. The cis -triplet converts rapidly to a phantom triplet which is in equilibrium with trans - triplet.

A Saltiel plot, a plot of the cis / trans ratio versus sensitizer triplet energy, E_T, at the photostationary state is shown in Figure 2 and 3. To explain the behavior of low energy sensitizers, Saltiel and Hammond (23) proposed the " nonvertical " transitions because the Franck - Condon restrictions do not obtain for this system. According to this mechanism, energy transfer can be synchronous with substantial distortion of the geometry of the ground state of the acceptor. This type of electronic transition is well documented if not fully understood (35 - 40). The potential curves versus the angle of twist about the central bond for stilbene and methylstilbene is shown in Figure 4 and 5.

To account for the facts mentioned above and data in Figure 2 and Figure 3, the following mechanism was proposed by Hammond et al. (16).

Excitation

$$S \xrightarrow{h\nu} S^1_x \longrightarrow S^1$$

$$S^1 \xrightarrow{k_2} S^3$$

Classical energy transfer

$$S^3 + t \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} S + t^3$$

$$S^3 + c \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} S + c^3$$

$$t^3 + Q \xrightarrow{k_5} t + Q^3$$

$$c^3 + Q \xrightarrow{k_6} c + Q^3$$

Transfer with nonvertical excitation

$$S^3 + t \xrightarrow{k_7} S + c^3$$
$$S^3 + c \xrightarrow{k_8} S + t^3$$
$$S^3 + t \xrightarrow{k_9} S + p^3$$
$$S^3 + c \xrightarrow{k_{10}} S + p^3$$

Interconversion of excited states

$$t^3 \underset{k_{-11}}{\overset{k_{11}}{\rightleftharpoons}} c^3$$
$$t^3 \underset{k_{-12}}{\overset{k_{12}}{\rightleftharpoons}} p^3$$
$$c^3 \xrightarrow{k_{13}} p^3$$

Decay process

$$t^3 \xrightarrow{k_{14}} t$$
$$t^3 \xrightarrow{k_{15}} c$$
$$c^3 \xrightarrow{k_{16}} c$$
$$c^3 \xrightarrow{k_{17}} t$$
$$p^3 \xrightarrow{k_{18}} t$$
$$p^3 \xrightarrow{k_{19}} c$$
$$t^3 + t \xrightarrow{k_{20}} 2t$$

where S is sensitizers, c and t represent cis and trans stilbenes, Q is quenchers, p represents phantom triplets and numbers in superscription represent spin multiplicity in excited states. k's are rate constants.

The steric hindrance of sensitization and asymmetric induction

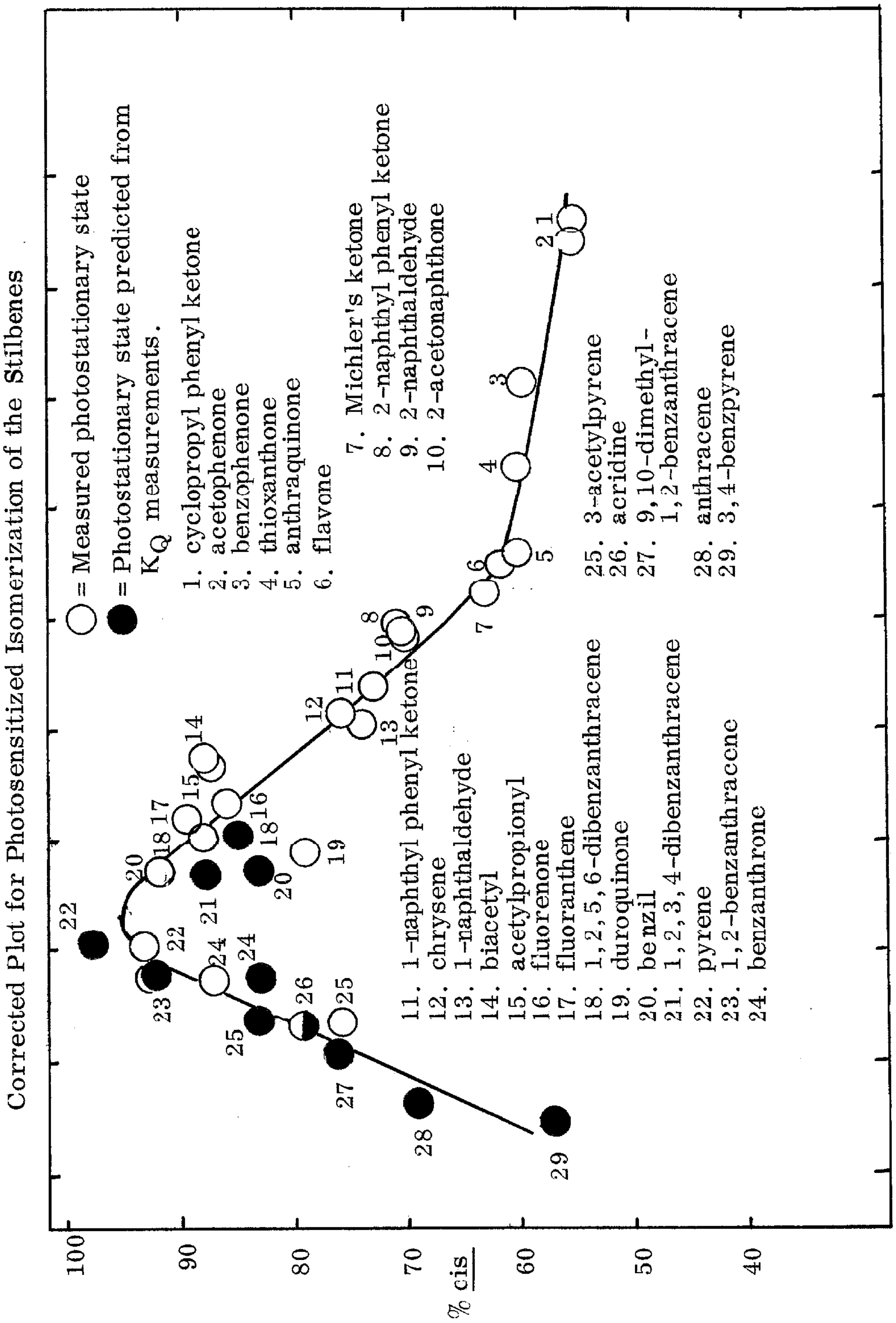

Corrected Plot for Photosensitized Isomerization of the Stilbenes
○ = Measured photostationary state
● = Photostationary state predicted from K_Q measurements.
1. cyclopropyl phenyl ketone
2. acetophenone
3. benzophenone
4. thioxanthone
5. anthraquinone
6. flavone
7. Michler's ketone
8. 2-naphthyl phenyl ketone
9. 2-naphthaldehyde
10. 2-acetonaphthone
11. 1-naphthyl phenyl ketone
12. chrysene
13. 1-naphthaldehyde
14. biacetyl
15. acetylpropionyl
16. fluorenone
17. fluoranthene
18. 1, 2, 5, 6-dibenzanthracene
19. duroquinone
20. benzil
21. 1, 2, 3, 4-dibenzanthracene
22. pyrene
23. 1, 2-benzanthracene
24. benzanthrone
25. 3-acetylpyrene
26. acridine
27. 9, 10-dimethyl-1, 2-benzanthracene
28. anthracene
29. 3, 4-benzpyrene
% cis
100
90
80
70
60
50
40
E_T (kcal/mole)
40
44
48
52
56
60
64
68
72
76

Figure 2.

Corrected Plot for Photosensitized Isomerization of the 1, 2-Diphenylpropenes

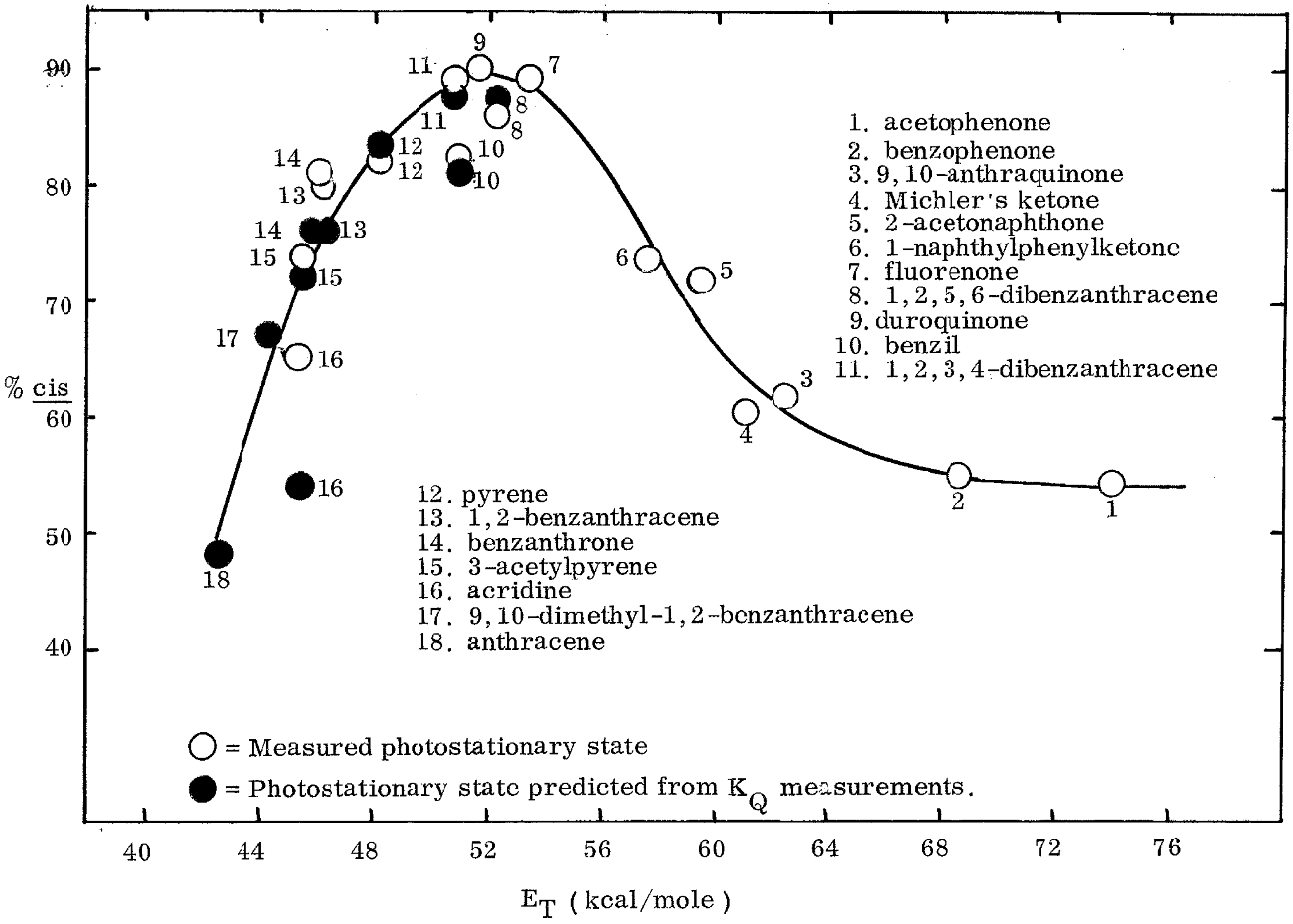
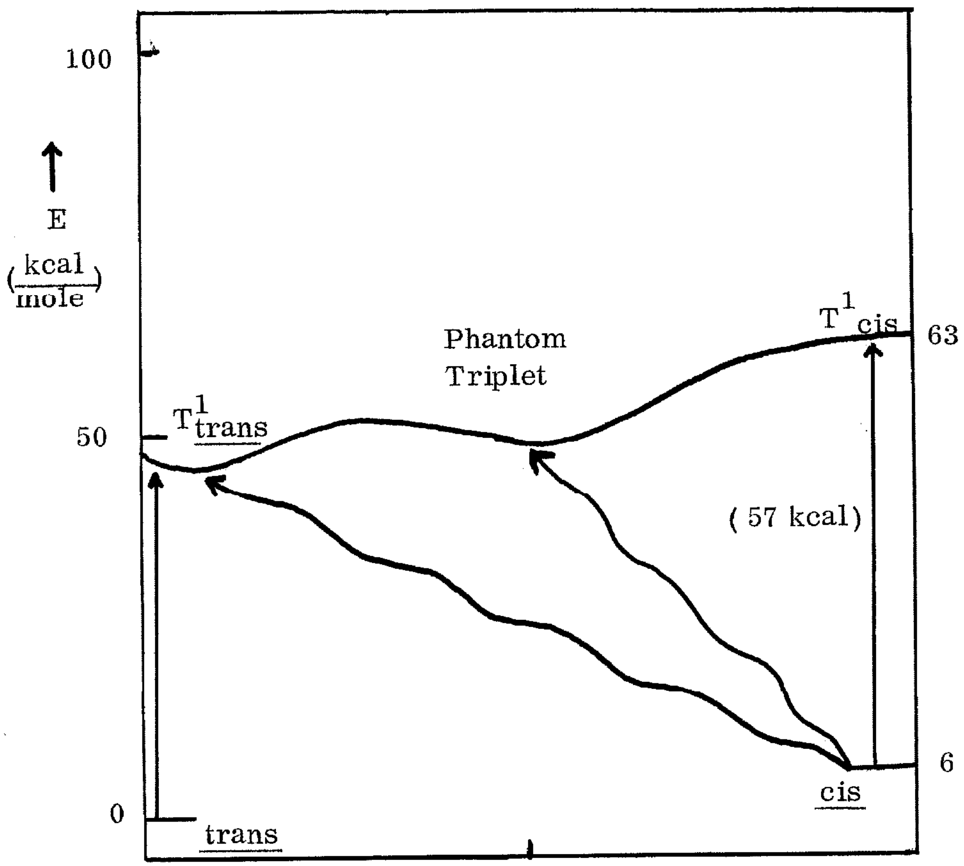


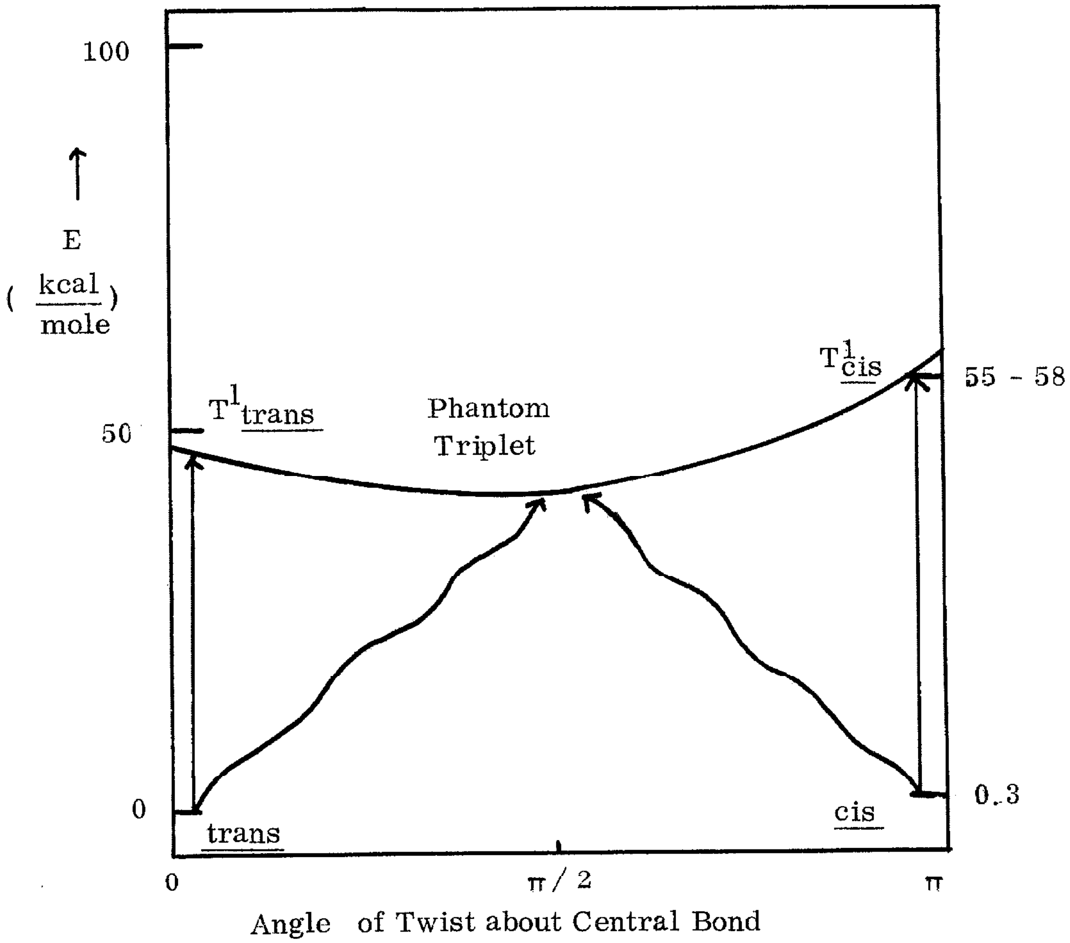
Figure 3.

Figure 4 Potential Function for Rotation in Stilbene Triplet States .



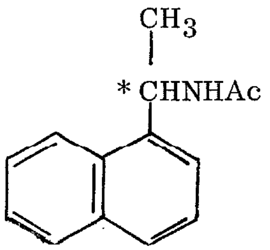
Angle of Twist about Central Bond

Figure 5 Possible Potential Function for Rotation in 1,2-Diphenylpropene Triplet State.

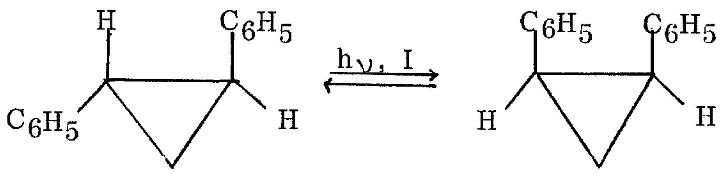


with optically active sensitizer stress the evidence that transfer of triplet excitation requires molecular contact between donor and acceptor (33 - 35). DeBoer (40) suggests from his study of photostationary state of the <u>cis</u>- and <u>trans</u> - 1, 2 - diphenylcyclopropane system that sensitizers used in his reactions prefer to react with the <u>trans</u> isomer rather than the <u>cis</u> because of the steric hindrance in the <u>cis</u> isomer.

The optically active amide, I, was used as a sensitizer to effect the stereoisomerization of <u>trans</u> - 1, 2 - diphenylcyclopropane.



I



d , l - II

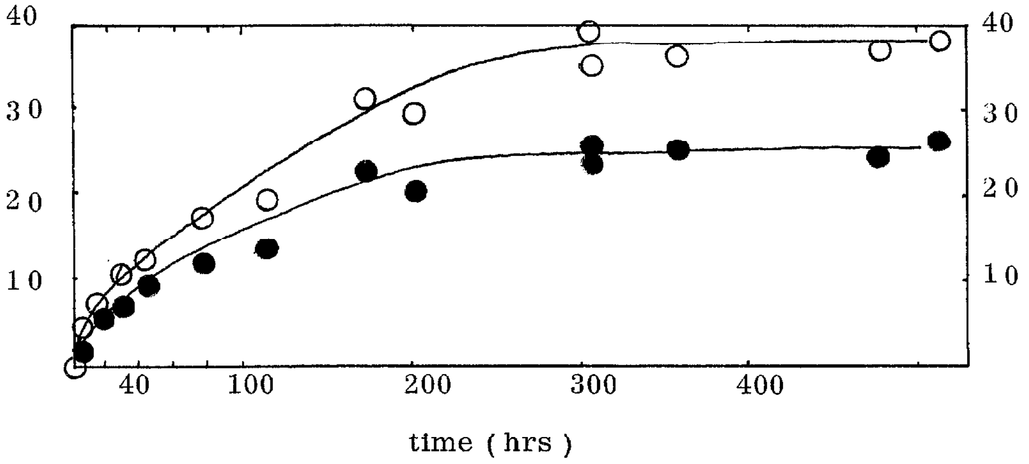


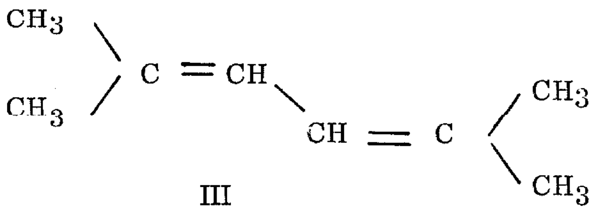
Figure 6. Development of Optical Activity, ○ ; percent <u>cis</u> isomer, ● .

As shown in Figure 6, the extent of asymmetric induction is large indicating that energy transfer requires very intimate interaction between donor and acceptor. The same isomerization of cis - 1, 2 - diphenylcyclopropane resulted in optically inactive trans isomer. This suggests that products are not formed by decay of an excited sensitizer - substrate complex since the cis isomer is sterically less hindered than the trans isomer. Various optically active derivatives of naphthalene other than I was used and it was suggested that the extent of asymmetric induction is no simple function of bulk or polarity of the substituents attached to the asymmetric center of the sensitizer.

The excited triplets of optically active naphthalene derivatives were quenched by 1, 1, 4, 4 - tetramethylbutadiene (III). However, the quantum yield of stereoisomerization of trans - 1, 2 - diphenylcyclopropane was not changed significantly. Furthermore, it is observed that

$$I / I^{\circ} = F / F^{\circ}$$

where I and I° are quantum yields of isomerization with or without quenchers respectively and F and F° are relative fluorescence quantum yields with or without quenchers. In other words, the quantum yields of isomerization decreased in an exact ratio as the fluorescence was quenched by III. This clearly indicates that the stereoisomerization and asymmetric induction of trans - 1, 2 - diphenylcyclopropane go through singlet intermediates and it seems that even singlet energy transfer occurs with very intimate interaction between donor and acceptor.



III

It will be very interesting to study whether or not nonvertical transition in β - styrylnaphthalene will be as efficient as in stilbenes. Because of localization of excitation in the naphthalene ring, it is expected that a rather small fraction of β - styrylnaphthalene would get nonvertical excitation because it would maintain largely the ground state planar configuration around the ethylenic bond in the excited states. Also it will be worth while to study whether the sensitizers prefer <u>trans</u> - β - styrylnaphthalene to the <u>cis</u> isomer because of steric crowding in the <u>cis</u> isomer.

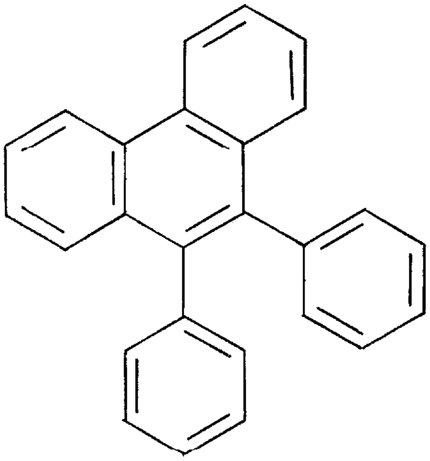
RESULTS AND DISCUSSIONS

Quantum Yields by Direct Irradiation

The quantum yields for the direct isomerization of β - styrylnaphthalene were measured at three different wavelengths, 3660, 3130 and 2537 Å, with various concentration in benzene and n - hexane solutions. They are shown in Tables I - IV. The measurements were made with carefully filtered light and the ferrioxalate actinometry was used.

No corrections were made for the back reactions because of side reactions causing inaccurate photostationary states. However, the error is not very serious since the measurements were carried out with a small percentage of conversions.

As shown in Table IV, the sum of the quantum yields of isomerization, from cis to trans and from trans to cis, is less than 0.5 at all wavelengths used, thus indicating that much of the energy is wasted as we predicted. We believe that in the lowest excited singlet states, localization of excitation in the naphthalene chromophore makes these states preferentially planar and introduces a significant barrier to interconversion of cis and trans forms. This kind of localization of excitation is not unusual. For example, Mallory et al. showed that in 9, 10 - diphenylphenanthrene (I) the excitation in the excited singlet state is confined largely to the phenanthrene system with little involvement of the two phenyl groups. This notion is supported by the ultraviolet absorption spectrum of I which bears strong resemblance to that of phenanthrene and is not closely similar to that of cis - stilbene (48). The absorption spectrum of cis - β - styrylnaphthalene is very similar to that of 2 - vinylnaphthalene and bears no similarity to that of cis - stilbene. The absorption spectra of trans - β - styrylnaphthalene are closer to those of naphthalene and 2 - vinylnaphthalene than to that of trans - stilbene specially at the short wavelengths.



I

As shown in Table V, some substituted stilbenes also give low quantum yields of isomerization. However, these compounds are quite different from β - styrylnaphthalene. For example, the last four substituted stilbenes in Table V are probably the example of strong coupling of the substituent groups through the entire system in the excited states and consequently the entire molecule should maintain the planar structure which would give poor isomerization. It is possible that 4, 4' - dinitrostilbene is somewhat similar to β - styrylnaphthalene in a sense that the excitation can be localized. Otherwise it is also different from our compound since there are nonbonding electrons in 4, 4' - dinitrostilbene and perhaps different type of excitations, like $n - \pi^*$ transitions, are involved rather than the simple $\pi - \pi^*$ transitions and consequently the fate of the excited states is quite different from that of pure hydrocarbons like stilbene and β - styrylnaphthalene where we get only $\pi - \pi^*$ transitions. In other words, a different mechanism may be involved in isomerization.

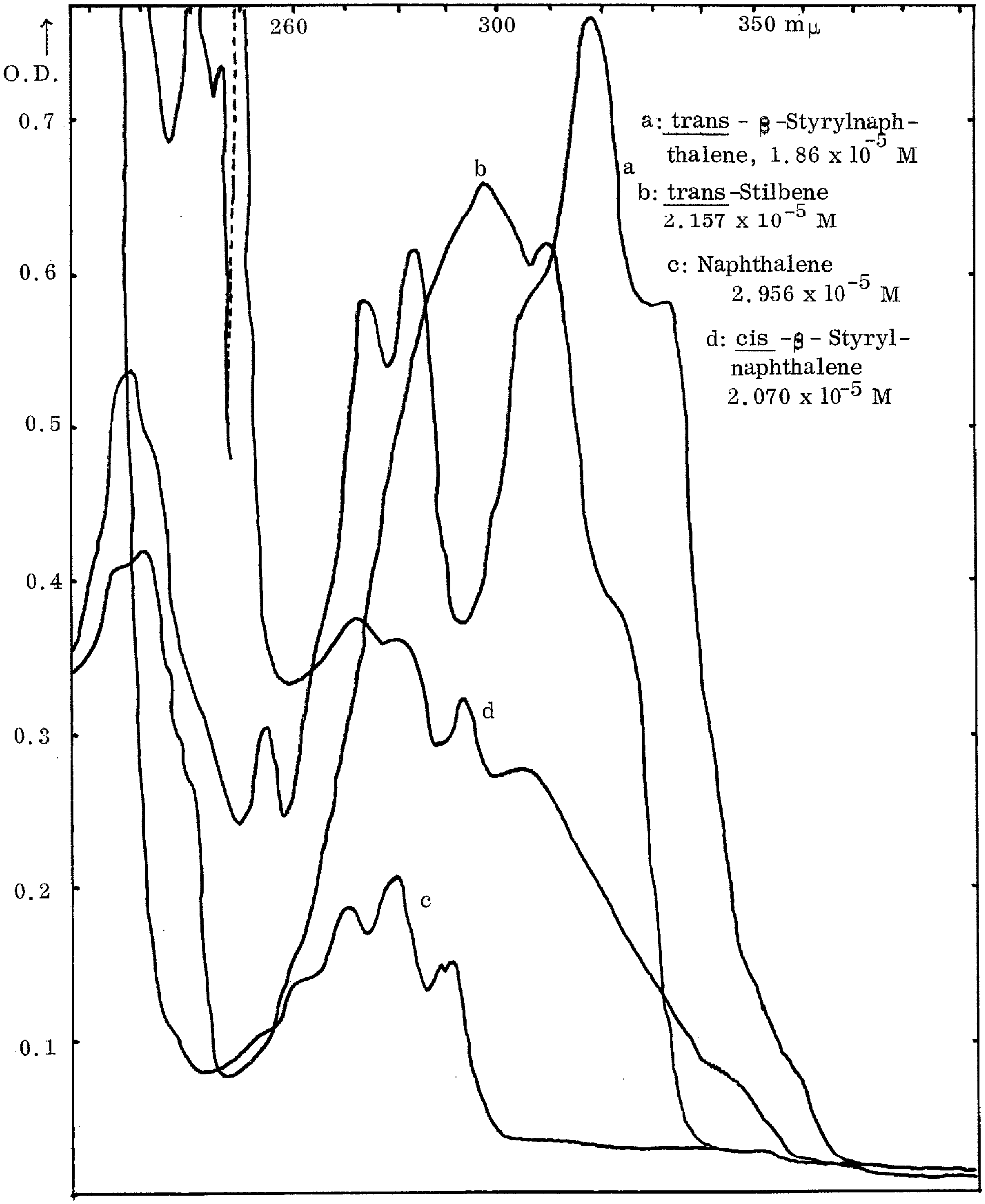


Figure 7 UV Absorption Spectra in n-Hexane

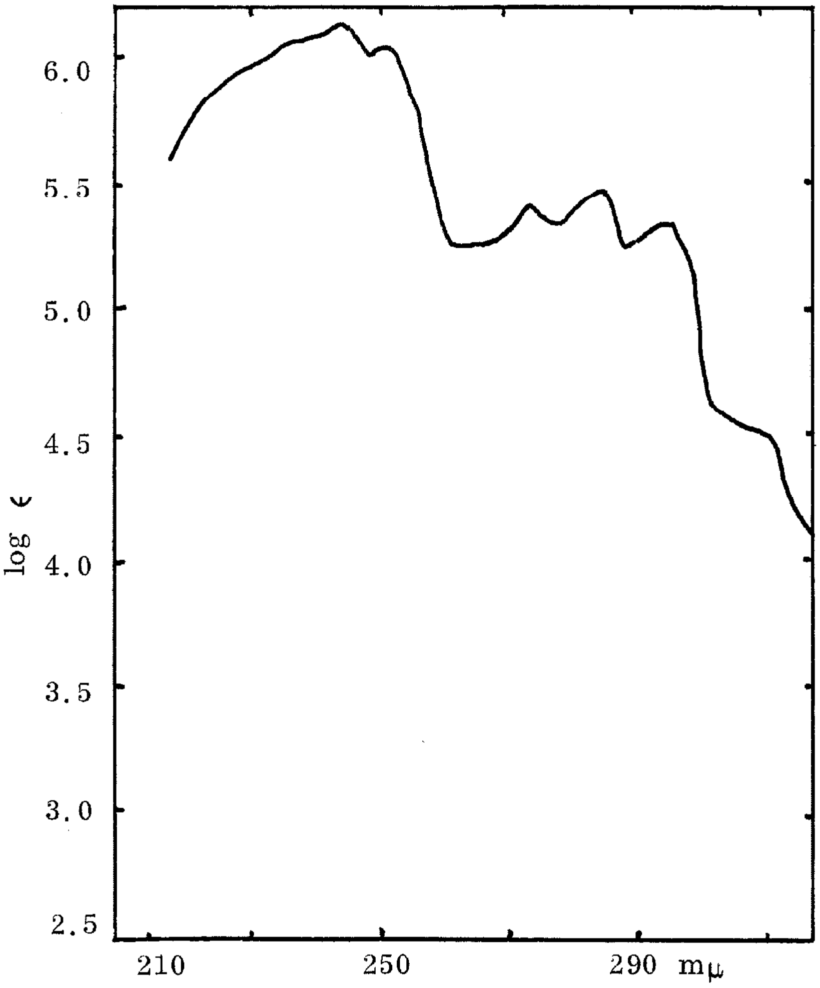


Figure 8 UV Absorption Spectra of 2-Vinylnaphthalene in Cyclohexane.

TABLE I

Quantum Yields for Direct Isomerization at 3660 Å

	Conc. (M)	I	% Conversion	Quantum Yields (Φ)	1 / Φ
<u>Cis</u>	2.293×10^{-2}	b	4.15 ± 0.19	0.048 ± 0.002	20.41
	3.539×10^{-2}	b	3.38 ± 0.06	0.061 ± 0.001	16.39
	4.881×10^{-2}	b	2.87 ± 0.11	0.071 ± 0.002	14.09
	6.391×10^{-2}	b	1.96 ± 0.003	0.063 ± 0.001	15.88
	6.153×10^{-2}*	b	0.96 ± 0.25	0.030 ± 0.008	33.33
<u>Trans</u>	2.318×10^{-2}	a	16.98 ± 2.51	0.131 ± 0.26	7.64
	3.074×10^{-2}	b	7.02 ± 1.08	0.109 ± 0.017	9.18
	3.947×10^{-2}	a	7.95 ± 0.39	0.104 ± 0.005	9.61
	4.636×10^{-2}	b	3.22 ± 0.07	0.075 ± 0.001	13.32
	5.132×10^{-2}	b	2.86 ± 0.07	0.074 ± 0.002	13.50
	5.263×10^{-2}	a	5.16 ± 0.47	0.090 ± 0.008	11.11
	5.291×10^{-2}	c	1.62 ± 0.08	0.091 ± 0.006	10.99
	11.78×10^{-2}	b	1.00 ± 0.10	0.059 ± 0.009	16.94
	6.51×10^{-3}*	c	6.96 ± 1.45	0.049 ± 0.011	20.40
	9.30×10^{-3}*	c	7.10 ± 0.54	0.071 ± 0.007	14.09

Table I (continued)

* n-Hexane solution

I = a: (2.86 ± 0.33) x 10^{-7} E/min. for 210 min. = 6.01 x 10^{-5} E/210 min.

b: (4.948 ± 0.035) x 10^{-7} E/min. for 120 min. = 5.938 x 10^{-5} E/120 min.

c: (3.116 ± 0.107) x 10^{-7} E/min. for 90 min. = 2.804 x 10^{-5} E/90 min.

TABLE II

Quantum Yields for Direct Isomerization at 3130 Å

	Conc. (M)	I	% Conversion	$\Phi_{c \to t,\ t \to c}$	1 / Φ
Cis	2.293 x 10^{-2}	b	19.18 ± 0.68	0.168 ± 0.005	5.95
	3.539 x 10^{-2}	b	15.55 ± 0.81	0.209 ± 0.009	4.79
	6.391 x 10^{-2}	b	5.68 ± 0.01	0.139 ± 0.001	7.20
	1.846 x 10^{-2}*	c	2.56 ± 0.25	0.140 ± 0.010	7.15
Trans	2.318 x 10^{-2}	a	8.45 ± 0.41	0.056 ± 0.003	17.85
	3.074 x 10^{-2}	b	5.38 ± 0.43	0.063 ± 0.005	15.88
	3.938 x 10^{-2}	a	5.21 ± 0.24	0.057 ± 0.001	17.54
	4.927 x 10^{-2}	b	3.01 ± 0.06	0.057 ± 0.001	17.54
	5.132 x 10^{-2}	b	2.85 ± 0.18	0.056 ± 0.004	17.85

Table II (continued)

Conc. (M)	I	% Conversion	$\Phi_{c \to t,\ t \to c}$	1 / Φ
5.263×10^{-2}	a	3.66 ± 0.13	0.055 ± 0.002	18.18
5.291×10^{-2}	c	0.374 ± 0.006	0.059 ± 0.001	16.95
6.153×10^{-2}*	c	1.52 ± 0.04	0.278 ± 0.008	4.40
7.016×10^{-2}	b	2.04 ± 0.31	0.055 ± 0.008	18.18
6.51×10^{-3}*	c	2.67 ± 0.09	0.052 ± 0.002	19.22
9.30×10^{-3}*	c	1.70 ± 0.05	0.047 ± 0.001	21.28

* n-Hexane solution

I = a: (3.34 ± 0.31) x 10^{-7} E/min. for 210 min. = 7.014 x 10^{-5} E/210 min.

b: (4.36 ± 0.35) x 10^{-7} E/min. for 180 min. = 7.85 x 10^{-5} E/180 min.

c: 1.01 x 10^{-5} E/total

TABLE III

Quantum Yields for Direct Isomerization at 2537 Å

	Conc. (M)	I	% Conversion	$\Phi_{c \to t,\ t \to c}$	1 / Φ
Trans	4.65×10^{-3}	a	15.30 ± 2.49	0.044 ± 0.007	22.75
		b	19.12 ± 1.02	0.049 ± 0.003	22.00
		c	3.3 ± 0.42	0.041 ± 0.005	24.40
	6.510×10^{-3}	a	10.46 ± 0.50	0.043 ± 0.002	23.22
		b	10.35 ± 0.09	0.037	27.10
		c	3.05 ± 0.05	0.052 ± 0.001	19.22
	9.300×10^{-3}	a	7.17 ± 0.42	0.042 ± 0.002	23.80
		b	7.12 ± 0.49	0.036 ± 0.003	27.80
		c	1.45 ± 0.07	0.036 ± 0.002	27.80
Cis	1.846×10^{-2}	b	18.44	0.280	3.57
	3.692×10^{-2}	b	11.67	0.354	2.82
		c	3.11 ± 0.08	0.294 ± 0.002	3.40
	6.153×10^{-2}	b	6.83	0.345	2.90

Table III (continued)

All in n-Hexane solution

I = a: (1.453 ± 0.209) x 10^{-7} E/min. for 330 min. = 4.795 x 10^{-5} E/330 min.

b: (1.090 ± 0.130) x 10^{-7} E/min. for 335 min. = 3.652 x 10^{-5} E/335 min.

c: (6.369 ± 0.270) x 10^{-8} E/min. for 180 min. = 1.146 x 10^{-5} E/180 min.

TABLE IV

The Sum of Quantum Yields

Wavelength	Approx. Conc.	$\Phi_{c \to t}$	$\Phi_{t \to c}$	$\Phi_{c \to t}/\Phi_{t \to c}$	$\Phi_{c \to t} + \Phi_{t \to c}$
3660 Å	2.3 x 10^{-2} M	0.048	0.131	0.37	0.179
3660 Å	3.5 x 10^{-2} M	0.061	0.109	0.56	0.170
3660 Å	5.0 x 10^{-2} M	0.071	0.074	0.96	0.145
3130 Å	2.3 x 10^{-2} M	0.168	0.056	2.90	0.224
3130 Å	3.5 x 10^{-2} M	0.209	0.057	3.67	0.266
3130 Å	5.7 x 10^{-2} M	0.139	0.055	2.53	0.194

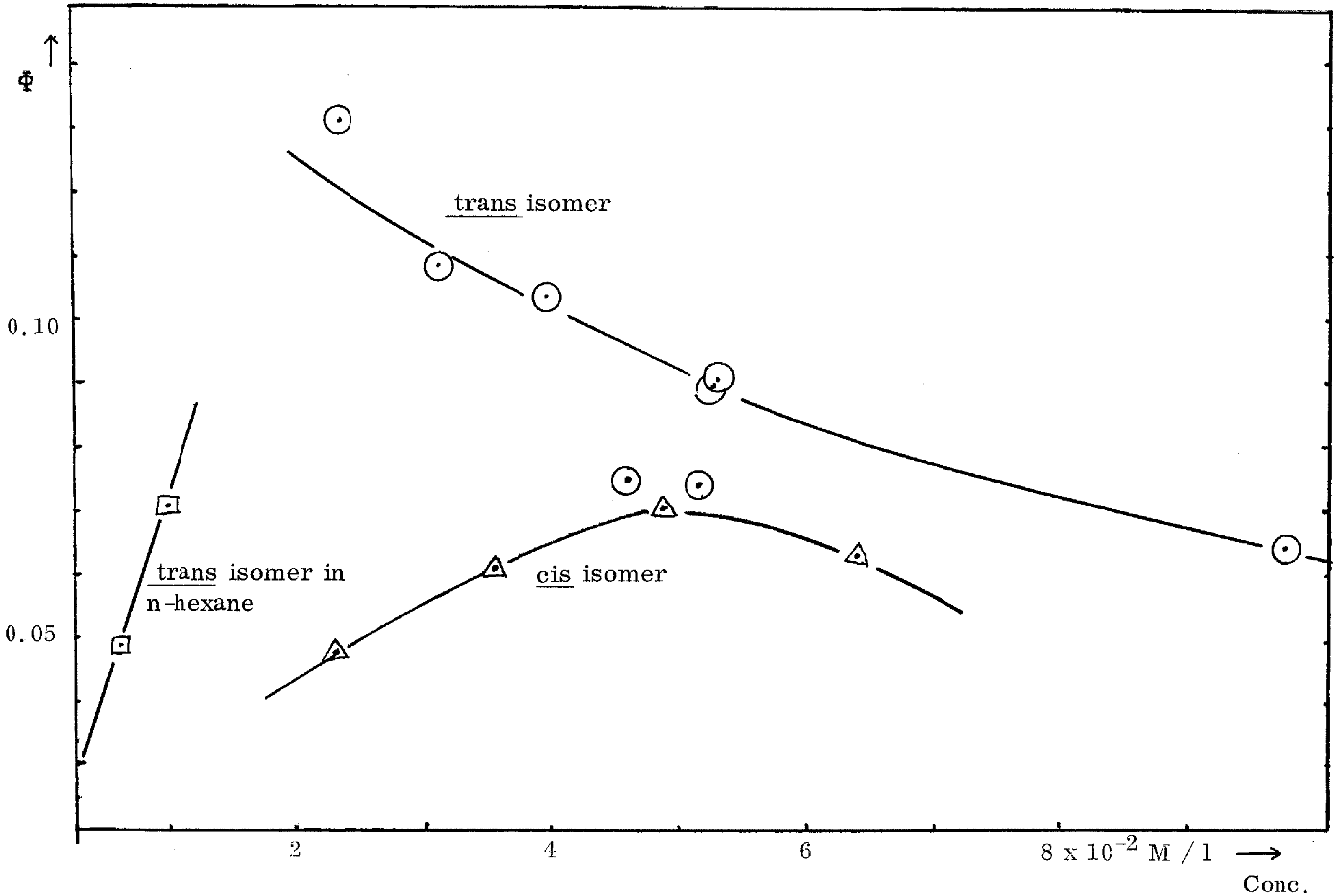


Figure 9 Quantum Yields at 3660 Å

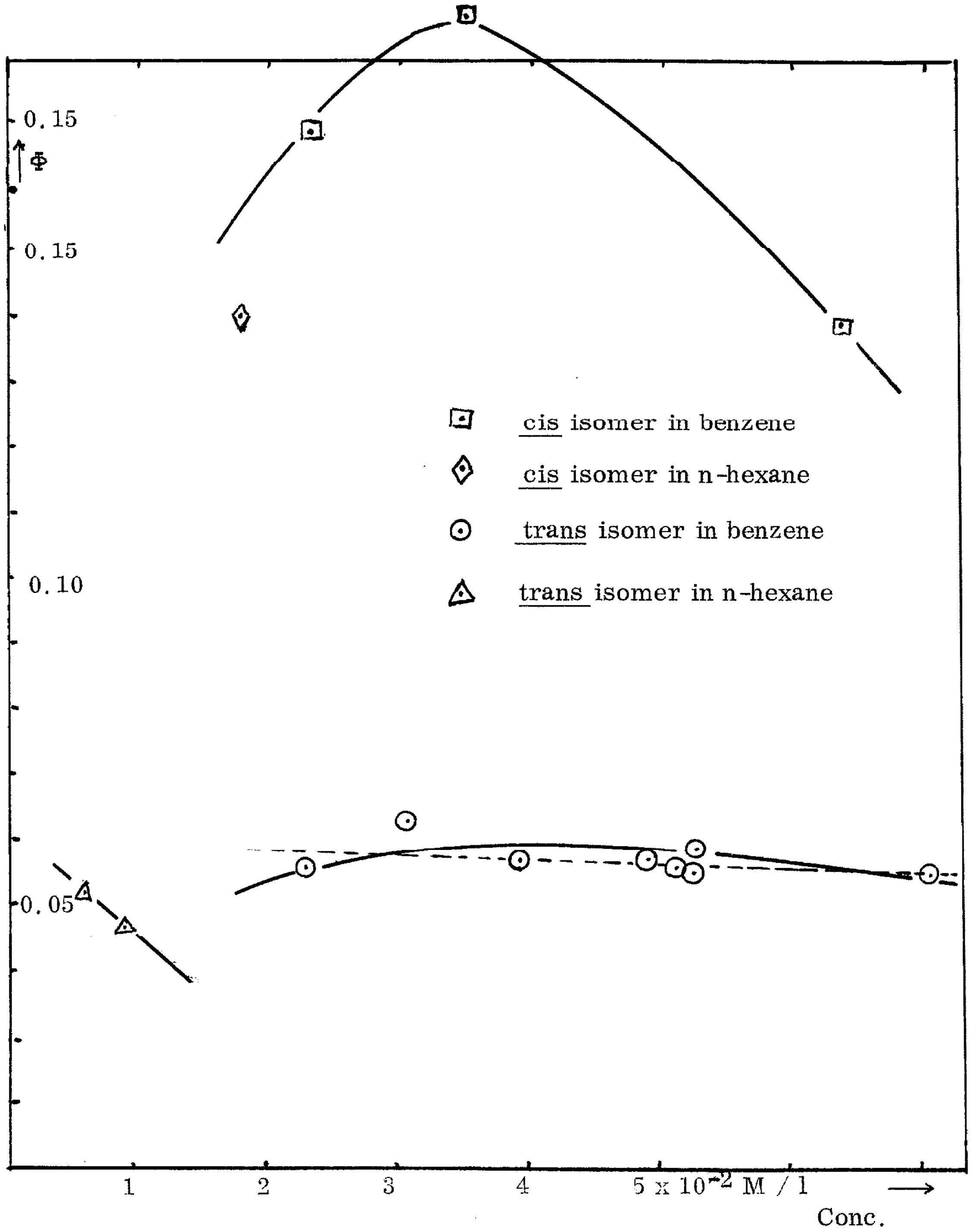


Figure 10 Quantum Yields at 3130 Å

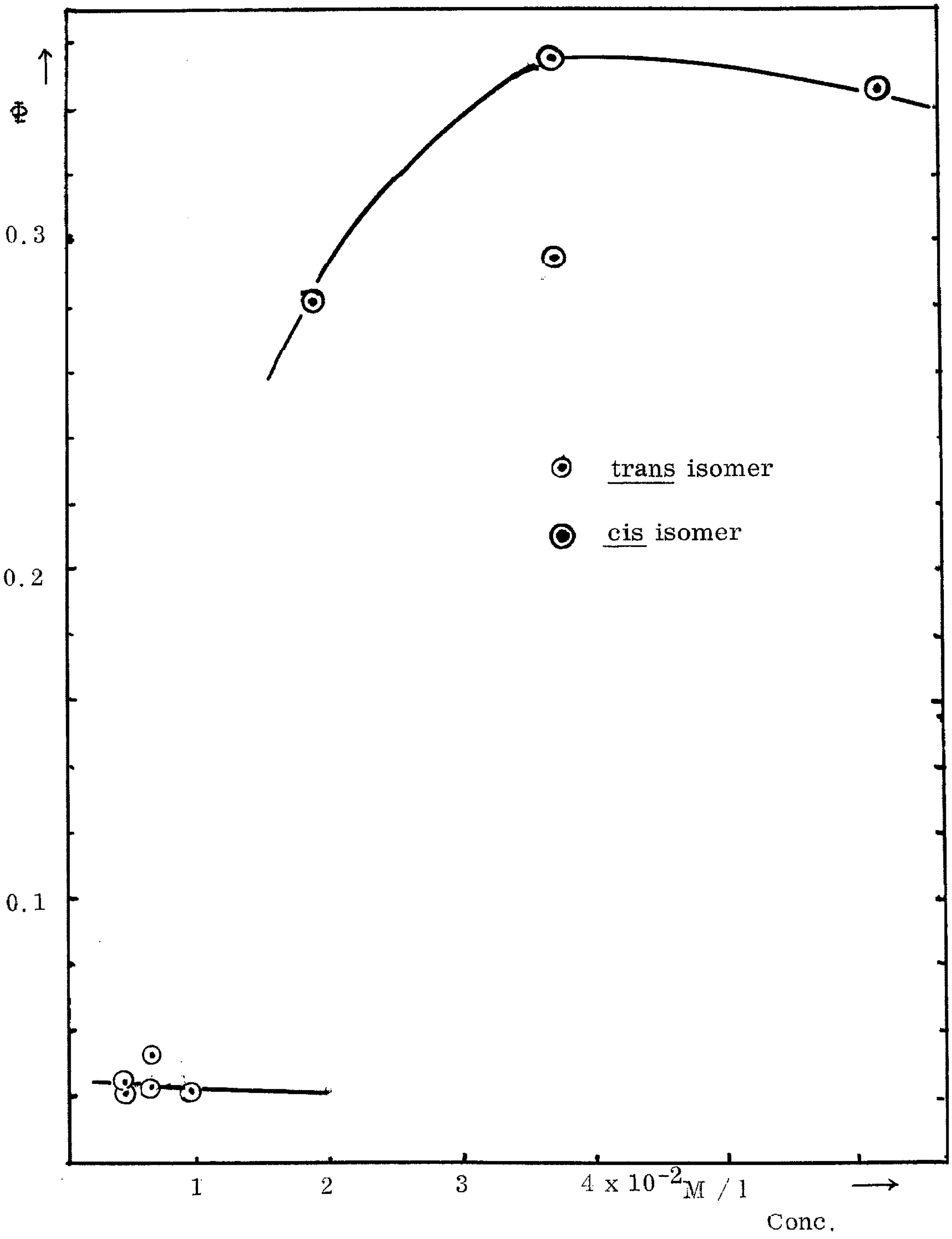


Figure 11 Quantum Yields at 2537 Å

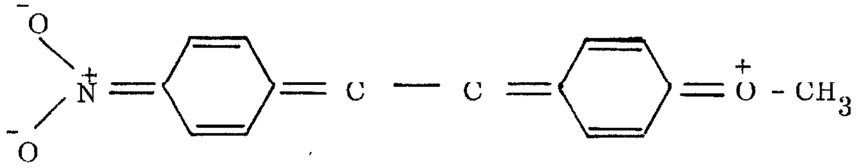
TABLE V

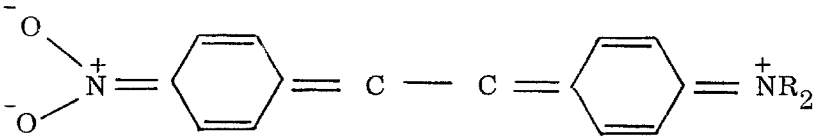
Quantum Yields of Stilbenes

Compounds	Solvent	Conc.	Wavelength (Å)	Temp.	$\Phi_{c \rightarrow t}$	$\Phi_{t \rightarrow c}$	$\Phi_{c \rightarrow t} + \Phi_{t \rightarrow c}$	x_t	Ref.
p-Bromostilbene	Methylcyclohexane-isohexane	0.62×10^{-5} M	3130	25° C	0.17	0.35	0.52	-	15
p-Chlorostilbene	Methylcyclohexane - isohexane	0.85×10^{-5} M	3130	25° C	0.4-0.5	0.60	1.0-1.10	-	15
Stilbene	Methylcyclohexane - isohexane	0.8×10^{-5} M	3130	25° C	0.30	0.50	0.80	-	15
Stilbene	n-Hexane	0.8×10^{-5} M	2537	25° C	0.28	0.67	0.95	0.424	14
Stilbene	n-Hexane	0.8×10^{-5} M	3130	25° C	0.32	0.59	0.91	0.070	14
4,4'-Dinitrostilbene	Benzene	-	3660	25° C	0.34	0.27	0.61	0.20	13
4-Nitro-3'-methoxystilbene	Benzene	-	3660	25° C	0.40	0.38	0.78	0.14	13

Table V (continued)

Compounds	Solvent	Conc.	Wavelength (Å)	Temp.	$\Phi_{c \to t}$	$\Phi_{t \to c}$	$\Phi_{c \to t} + \Phi_{t \to c}$	x_t	Ref.
4-Nitro-4'-methoxy-stilbene	Benzene	-	3660	25° C	0.43	0.40	0.83	0.27	13
4-Nitro-4'-amino-stilbene	Benzene	-	3660	25° C	0.44	0.10	0.54	0.66	13
4-Nitro-4'-dimcthyl-amino-stilbene	Benzene	-	3660	-	0.40	0.016	0.42	0.93	13





(R = H, CH_3)

Wavelength Effect

The wavelength of the absorbed light is an important variable unique to photochemical systems. One can alter the energy of the excited intermediate by precisely known amounts and study the effect on primary and secondary processes. In certain photochemical systems, the quantum yields of secondary processes are a function of light intensity which is liable to be misinterpreted as a wavelength effect.

The implications from the wavelength effects can be varied and significant in character. If within a given absorption band a wavelength dependence of the primary quantum yields is observed, then usually vibrational equilibration has not been achieved in the electronically excited state, i.e., the reaction probably proceeds from a short-lived ($\tau < 10^{-11}$ sec.) vibrationally and electronically excited singlet state. The less likely possibilities also exist: When internal conversion ($S_1^{v} \longrightarrow S_1^{v'}$) occurs more quickly after absorption than vibrational cascade ($v' \longrightarrow v = 0$), and the primary process occurs from a vibrationally excited ground state $S_1^{v'}$, then wavelength effect will be observed if : (a) The efficiency of internal conversion depends on the vibrational level v' of the excited state S_1^v . (b) The quantum yield of primary process is dependent on the vibrational level v' of the ground state $S_0^{v'}$. A similar argument could be made if one assumed that intersystem crossing from S_1 to $T_1^{v'}$ is faster than the vibrational equilibration of S_1 and the reaction occurs from the vibrationally excited triplet state T_1^v before it is vibrationally equilibrated (48).

In stilbene and most substituted stilbenes, no wavelength effect was observed (13). If the wavelength variation has no effect on the quantum yield of a given photochemical primary process, one of the two reaction mechanisms seems likely (48): (a) the excited state or states produced are very short-lived and completely rearrange, dissociate, fluoresce, or react by some other single path at all wavelengths of absorbed light; or (b) the initially formed species S_1^v is vibrationally equilibrated to S_1^o and from this state it decomposes or undergoes radiational or non-radiational transitions to lower excited states from which it reacts. The latter situation is often encountered in solution-phase photochemistry. The stilbene case is interpreted like the case of (b) shown above.

As shown in Figure 13, there are positive wavelength effects for the cis - β - styrylnaphthalene, i.e., the quantum yields, $\Phi_{c \rightarrow t}$, increase as the exciting wavelength becomes shorter. This is not unexpected even though this kind of phenomenon is rarely observed. A shift toward the shorter wavelengths or higher energies usually results in a higher efficiency of primary photodecompositions, assuming that the molecule does not already decompose efficiently at the longer wavelengths. The shorter the wavelength of the light absorbed by a molecule the higher is the vibrational level to which the molecule is carried in the primary act and thus the lifetime is shorter, since the rate constant for the unimolecular decomposition or other reactions is larger as the rate constant for a given excited molecule of energy E^* is given by (49 - 56):

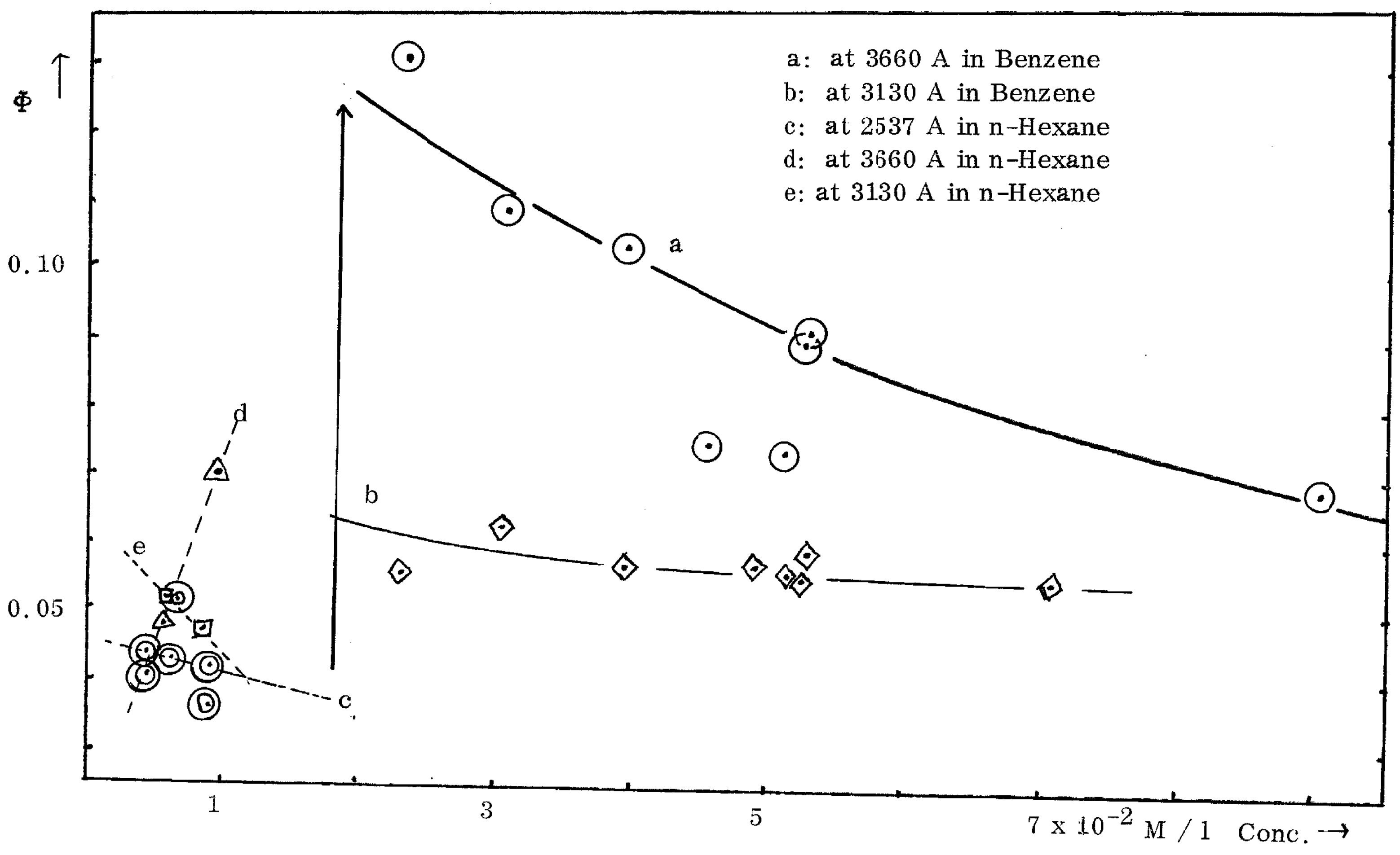


Figure 12 Wavelength Effect on Quantum Yields of Trans Isomer

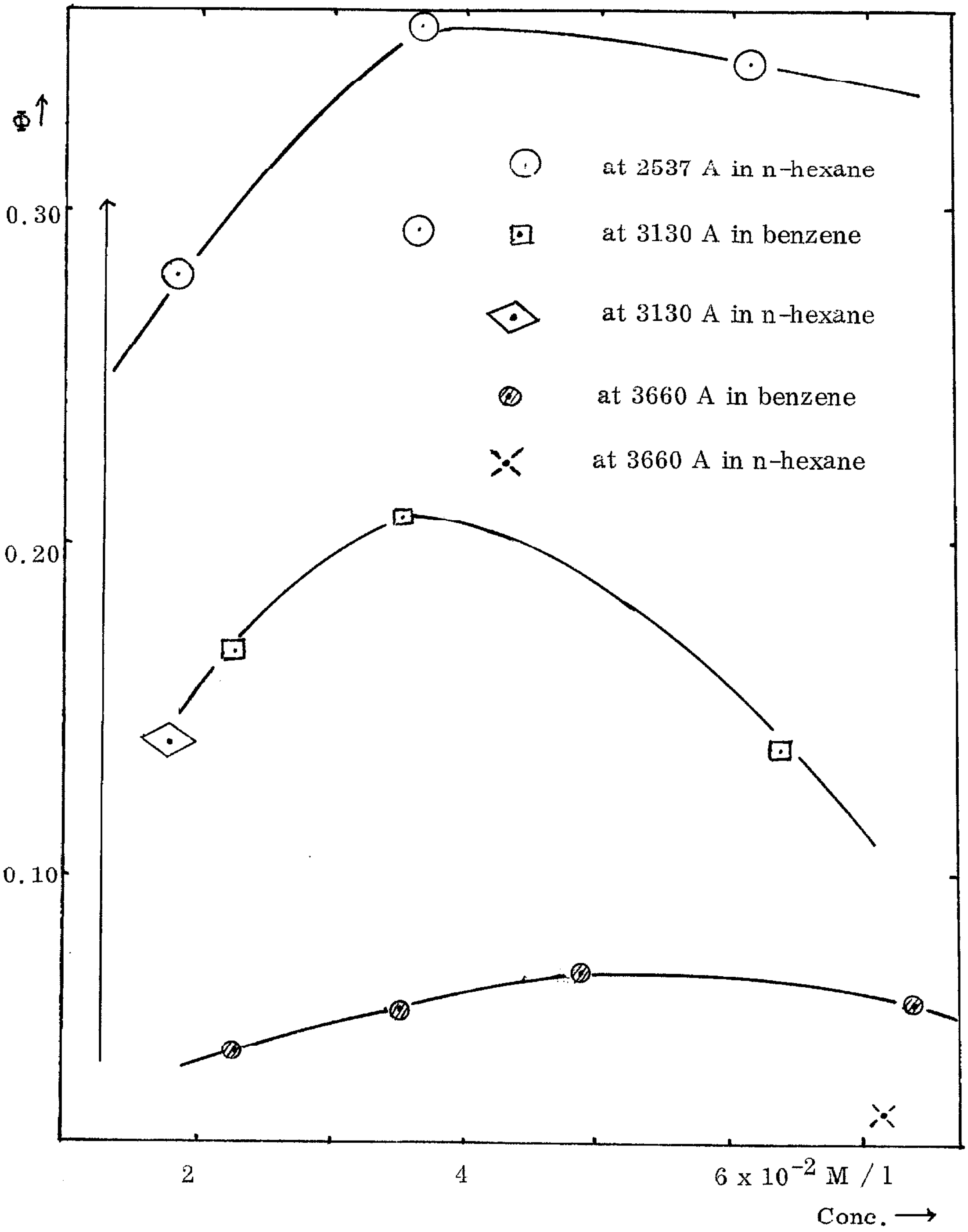


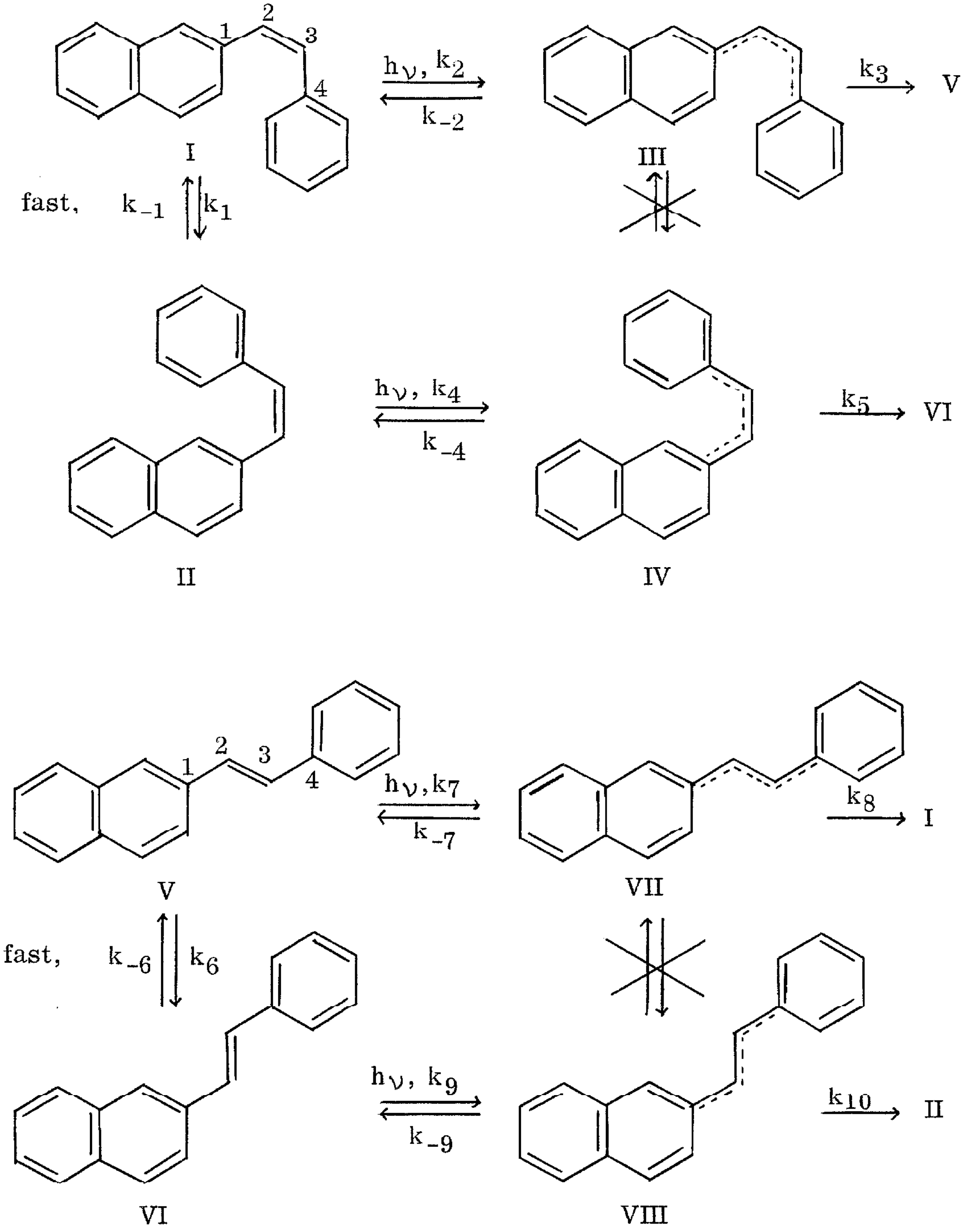
Figure 13 Wavelength Effect on Quantum Yields of Cis Isomer

$$k_{E*} = \gamma (1 - E / E^{*})^{s-1}$$

where γ is a proportionality factor, E is minimum energy from which the unimolecular reaction can occur, and s is vibrational degrees of freedom. Accordingly, fluorescence efficiencies are commonly lower in these systems, and the unimolecular reactions are much more extensive at the short wavelengths. However, a lot better explanation is given in the next paragraph for the cis - β - styrylnaphthalene as well as for the trans isomer which shows surprising negative wavelength effect.

Very unusual and unexpected results are obtained from trans - β - styrylnaphthalene as shown in Figure 12. The quantum yields, $\Phi_{t \rightarrow c}$, decrease as the exciting wavelengths getting shorter, i.e., a "negative" wavelength effect is observed. This kind of phenomenon has not been observed so far in other systems. We believe that two or more different species of electronically excited states from which the isomerization occurs are involved. This is shown in Figure 14.

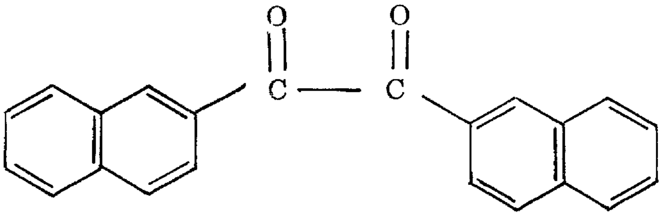
In the electronic ground states at room temperature, both cis- and trans - β - styrylnaphthalenes exist in two forms in the ground state vibrational level as shown in Figure 14, and I and II are in rapid equilibrium by the fast rotation around the bond 1 - 2. The same thing happens between V and VI. However, the 1 - 2 and 3 - 4 bonds develop more double bond character and a significant rotational barrier should prevent rapid equilibration reactions, III ⇌ IV and VII ⇌ VIII. This kind of phenomenon is observed in aliphatic conjugated dienes (57). The trans- and cis - butadiene are in rapid equilibrium at room temperature but in the lowest excited states, a large barrier to rotation about the central bond develops since the excitation promotes an electron from an orbital that is antibonding to one that is bonding in that region (58). The rate of interconversion of cis and trans excited states should be enormously slow in comparison with decay times of excited



1
2
3
4
I
hν, k_2
k_{-2}
III
k_3
V
fast,
k_{-1}
k_1
II
hν, k_4
k_{-4}
IV
k_5
VI
1
2
3
4
V
hν, k_7
k_{-7}
VII
k_8
I
fast,
k_{-6}
k_6
VI
hν, k_9
k_{-9}
VIII
k_{10}
II

Figure 14

states. Consequently, the stereoisomeric excited species should each undergo characteristic chemical reactions as shown in butadiene cis and trans triplets. In the photosensitized reactions of aliphatic conjugated dienes, the lowest triplet excited states are shown to exist in cis and trans isomeric modifications (59). Also Hammond et al. (60) suggested that two different triplets, cis and trans isomeric triplets, exist in the α- diketones. They investigated the phosphorescence spectrum of β - naphthil (I) in an ether (5 parts) -isopentane (5 parts) - ethanol (2 parts) (EPA) glass at 77° K and in a glass



I

prepared from methylcyclohexane (5 parts) and isopentane (1 part) (MCIP). They obtained the two different phosphorescence spectra from EPA and MCIP and presumed that the emission from EPA solution arises essentially exclusively from cis triplets and the emission from MCIP solution arises from trans triplets when the fast sector speed is used.

By the same token as in the conjugated dienes and α-diketones, the excited states of β - styrylnaphthalene, III, IV, VII and VIII, should exist and the interconversions of III $\rightleftharpoons$ IV and VII $\rightleftharpoons$ VIII should be very inefficient. The comparison of models of III and IV indicates that IV has more steric hindrance than III since the whole naphthyl group interacts with the phenyl ring. Consequently IV will be in higher energy state than III. Furthermore, the decay of IV to II may be less efficient than decay of III to I because of steric influences. Thus, the isomerization of IV to VI may be more efficient than that of III to V. As shown in Tables I - III, the quantum yields from *cis* to *trans* increase steadily as the exciting wavelength shortens. This leads to the thought that we get more excited state IV as we go to shorter wavelengths. In the *trans* isomer the argument is more convincing. As shown in Figure 14, VII has lower energy than VIII since the transition moment through the bond 2 - 3 will be bigger in VII than in VIII. Consequently at the longer wavelength we will get more VII than VIII and vice versa. Also it may be harder to get *cis* isomer II from VIII, than to get I from VII because of steric hindrance in II compared to I. This explains the negative wavelength effect for the *trans* isomer very nicely as well as the positive wavelength effect for the *cis* isomer. This can be expressed by rate constants as:

$$\begin{array}{lcccl} & k_{-2} & > & k_{-4} & \\ & k_5 & > & k_3 & \\ & k_7 & > & k_9 & \text{at long wavelengths} \\ \text{and} & & & & \\ & k_8 & > & k_{10} & \end{array}$$

One may be suspicious about the difference of V and VI in UV absorption. This can be explained by the examination of UV absorption spectra of several compounds and the study of the fluorescence of β - styrylnaphthalene.

There are quite big differences between the ionization potentials of "acenes" and "phenes" with the same number of six membered rings in polycyclic hydrocarbons (61).

There are also big differences in UV absorptions, between "phenes" and "acenes" because of different symmetry. For example, the spectra of 1,2-benzphenanthrene and 1,2-benzanthracene, whose geometric relationship is very close to that of between I and II or III and IV, are shown (62) in Figure 15. As expected 1,2-benzanthracene absorbs the light

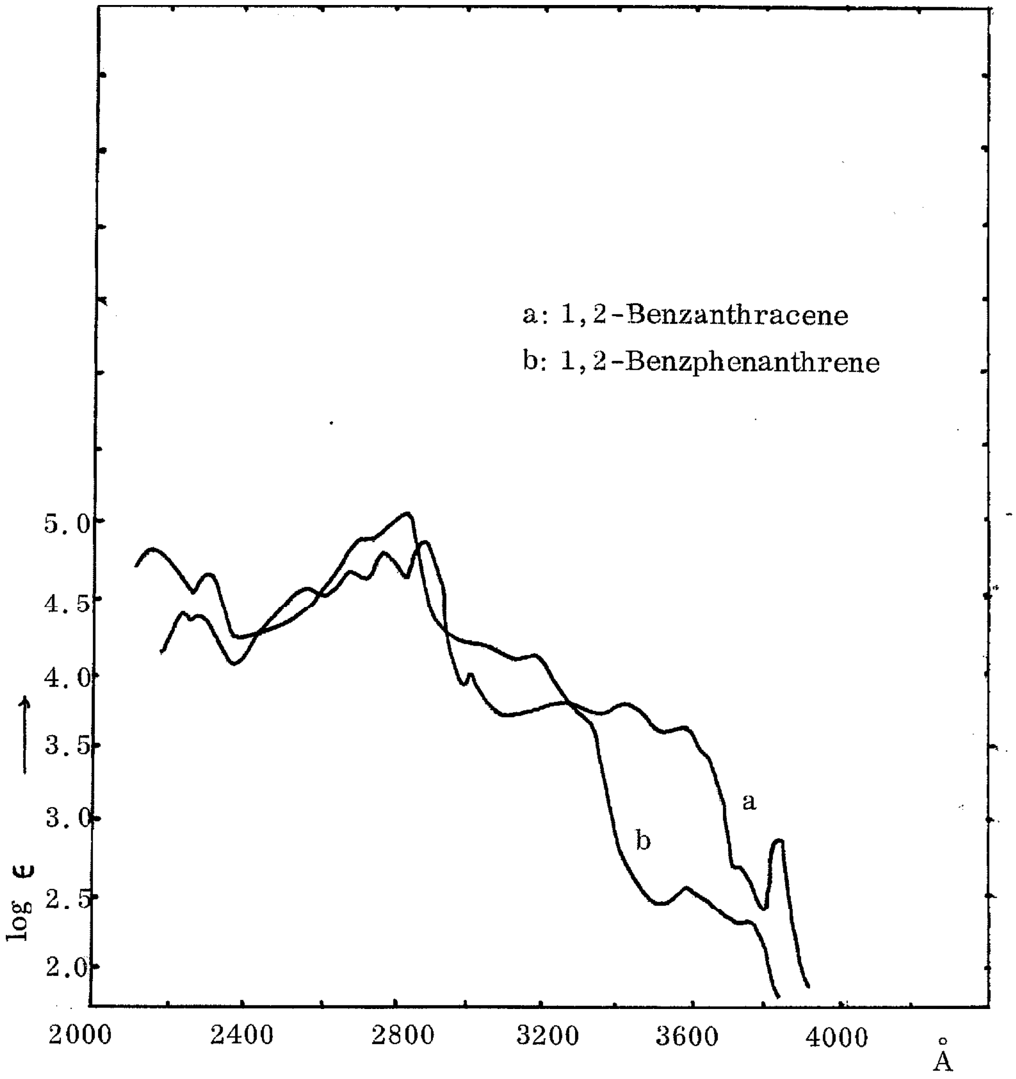


Figure 15. Absorption Spectra of 1,2-Benzanthracene and 1,2-Benzphenanthrene

TABLE VI

Ionization Potentials of Polycyclic Hydrocarbons

Compounds	Ionization Potential in	Energy of Highest Occupied Orbital in
Naphthacene	6.64	0.295
1,2-Benzanthracene	7.42	0.452
Anthracene	7.23	0.414
Phenanthrene	8.02	0.605

a lot more strongly at the long wavelengths but less efficiently at the short wavelengths than 1,2-benzphenanthrene. The same kinds of phenomena are expected for I and II, and V and VI which agrees with quantum yield results.

Fluorescence Study

The fluorescence study is very interesting. Both cis and trans isomers fluoresce in contrast to the stilbenes where cis stilbene does not fluoresce at room temperature. This shows that the excited cis singlet state of β - styrylnaphthalene has a significantly long lifetime.

The fluorescence spectra of the cis- and trans- β -styrylnaphthalene were taken with various activating wavelengths and are shown in Figure 16 - 18. The cis isomer has an extra maximum at 3650 Å . This was suspected to be the fluorescence of a dihydrobenzphenanthracene which is formed by cyclization of cis compound. However, the degassed solutions of cis isomer, in which the cyclization is very inefficient, also give this peak in their fluorescence spectra and the peak does not change as irradiation period is pro-

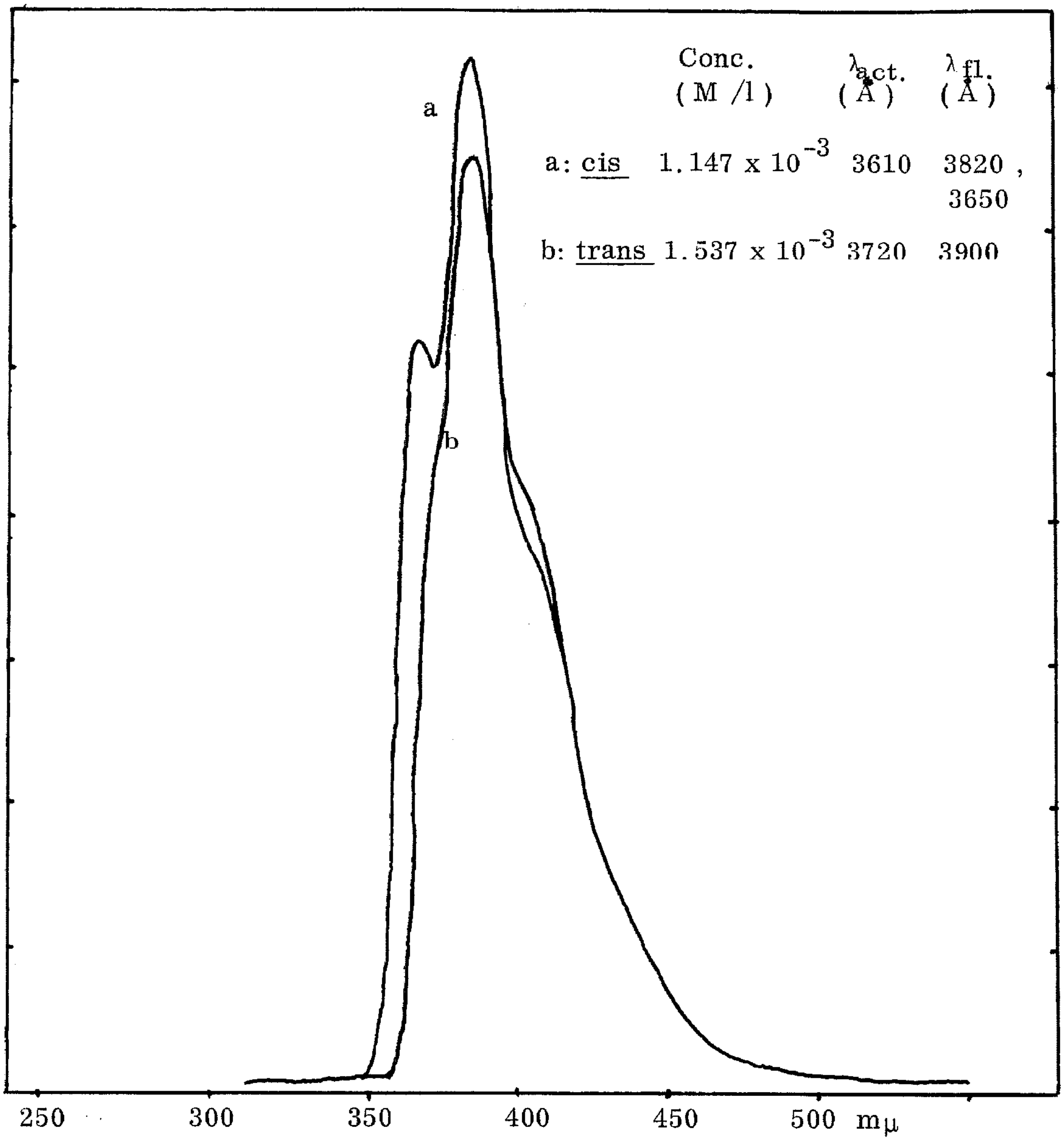


Figure 16 Fluorescence Spectra of β-Styrylnaphthalene in Benzene

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* These samples were not degassed and the spectra were taken at room temperature

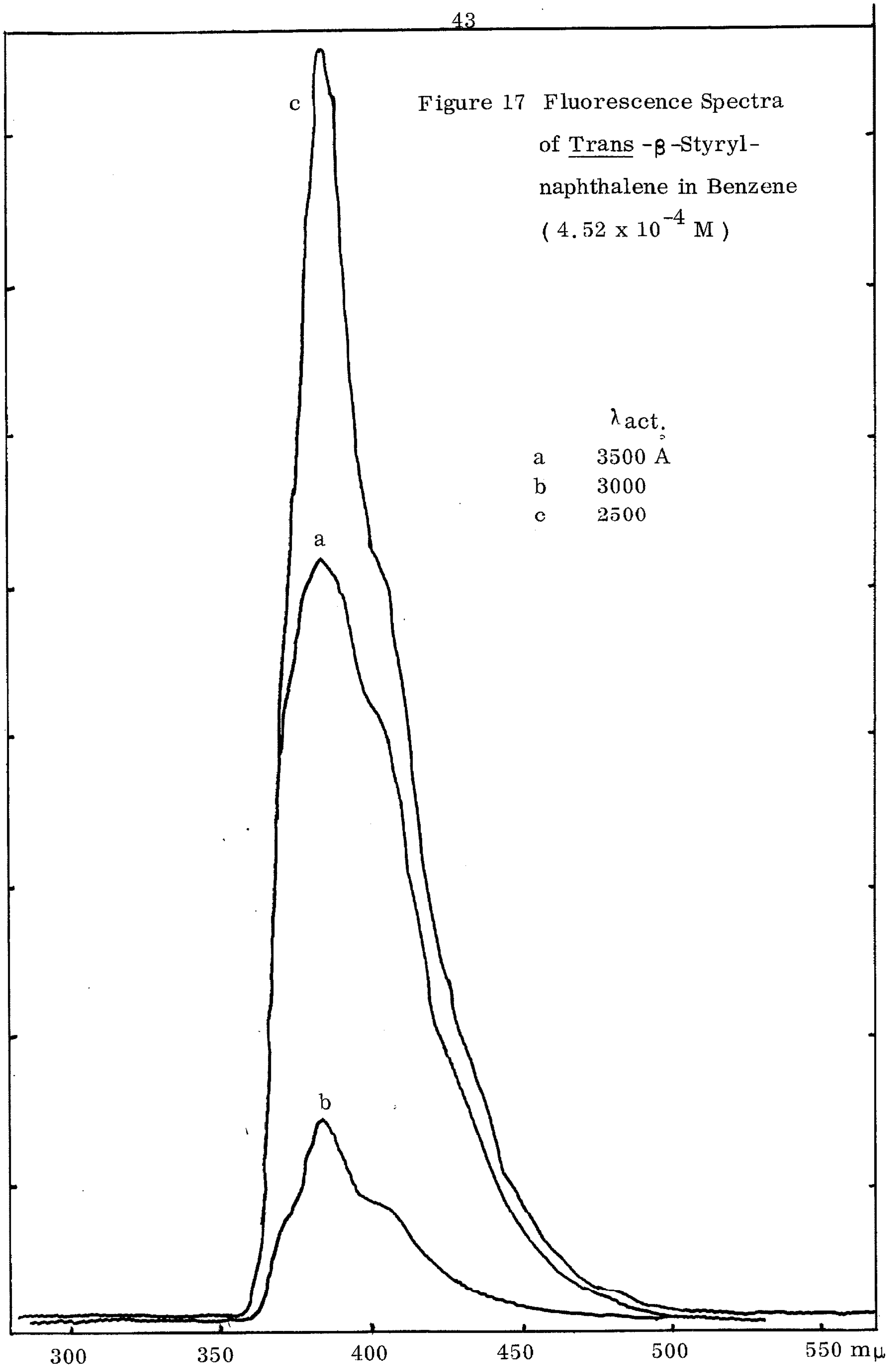

Figure 17 Fluorescence Spectra of Trans -β-Styryl- naphthalene in Benzene (4.52 x 10^{-4} M)

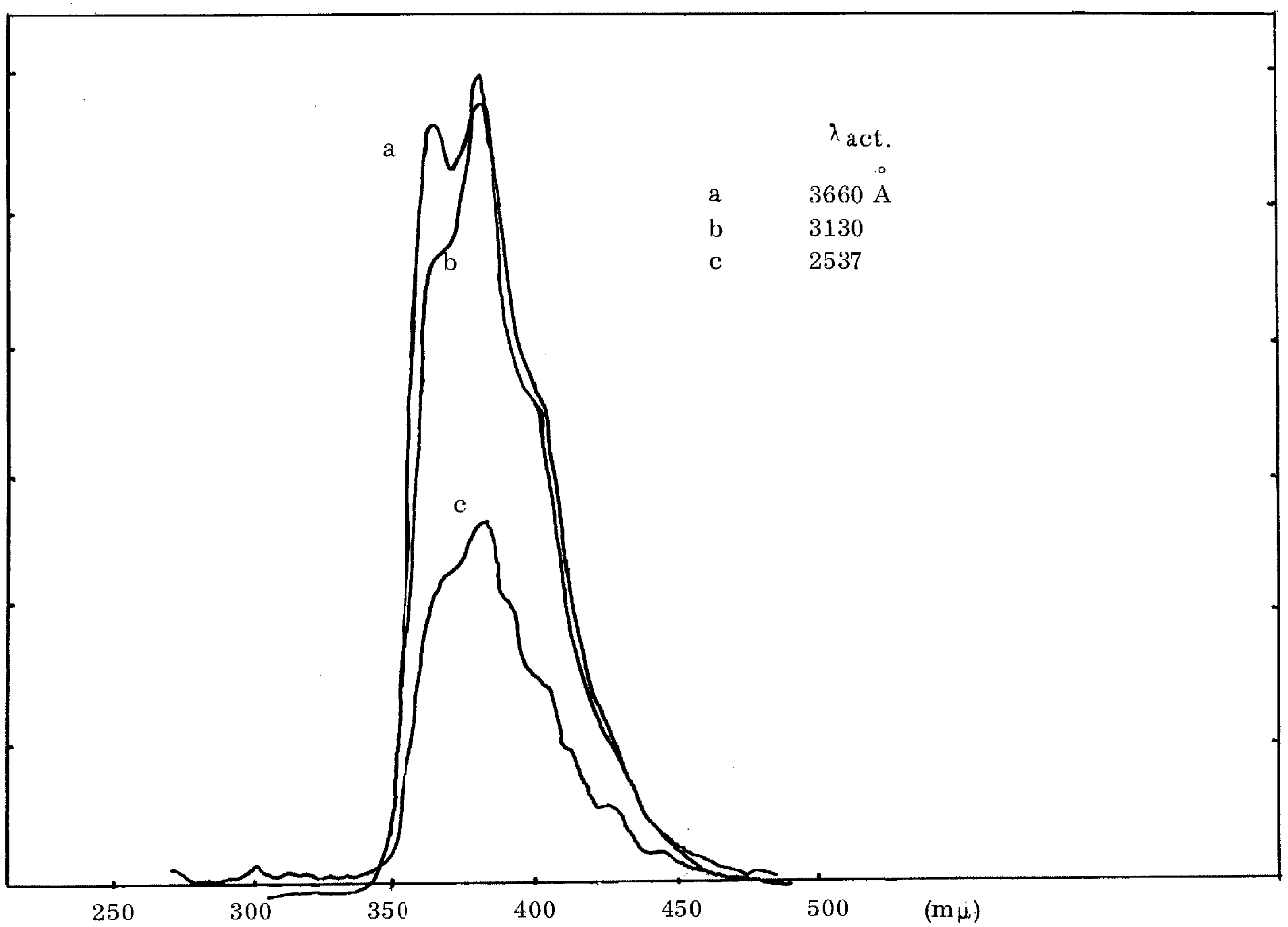

Figure 18 Fluorescence Spectra of Cis-β-Styrylnaphthalene in Benzene(5.18×10^{-4}M)

longed. So this maximum is a genuine part of the fluorescence of the _cis_-isomer. As shown in Table VII, in both _cis_ and _trans_ isomer the ratio of

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TABLE VII

The Comparison of Intensities of Fluorescence

Trans- β -styrylnaphthalene

	$\lambda_{fl.}$ (Å)		
$\lambda_{act.}$ (Å)	3700	3820	4000
2500	6.7 (46.5)	6.3 (85.0)	7.4 (51.5)
3000	1.0 (7.0)	1.0 (13.4)	1.0 (7.0)
3500	5.7 (40.0)	3.8 (51.0)	5.8 (40.6)

Cis- β - styrylnaphthalene

	$\lambda_{fl.}$ (Å)		
$\lambda_{act.}$ (Å)	3650	3820	4000
2537	1.0 (42.0)	1.0 (53.0)	1.0 (30.5)
3130	2.26 (95.0)	2.22 (117.5)	2.23 (71.0)
3660	2.67 (114.0)	2.28 (122.0)	2.40 (73.0)

fluorescence intensities at three different wavelengths of the activating light varies. In other words the fluorescence spectra are different as the wavelength of the activating light varies. Consequently this means we get different excited singlet states as we excite the compound with different wavelengths since in general the fluorescence spectrum is the mirror image of UV absorption spectra. This phenomena agree very well with the argument we used in the quantum yield measurements.

Fluorescence Quenching Experiments

Both cis and trans isomer fluorescence were quenched very efficiently by piperylene. In fact, fluorescence of the cis compound was completely quenched. They are shown in Figure 19 and 20.

Again we compared the efficiency of quenching at different wavelengths in fluorescence spectra. This is shown in Table VIII.

TABLE VIII

Fluorescence Quenching by Piperylene

(1.537 x 10^{-3}M solution of trans- β-styrylnaphthalene in benzene)

	Intensity of Fluorescence at		
Conc. of Piperylene (M)	375 mμ	390 mμ	415 mμ
0	6.08 (73)	7.54 (128)	7.67 (69)
1.002	3.16 (38)	3.70 (63)	3.78 (34)
2.505	1.83 (22)	2.06 (35)	2.11 (19)
8.016	1.0 (12)	1.0 (17)	1.0 (9)

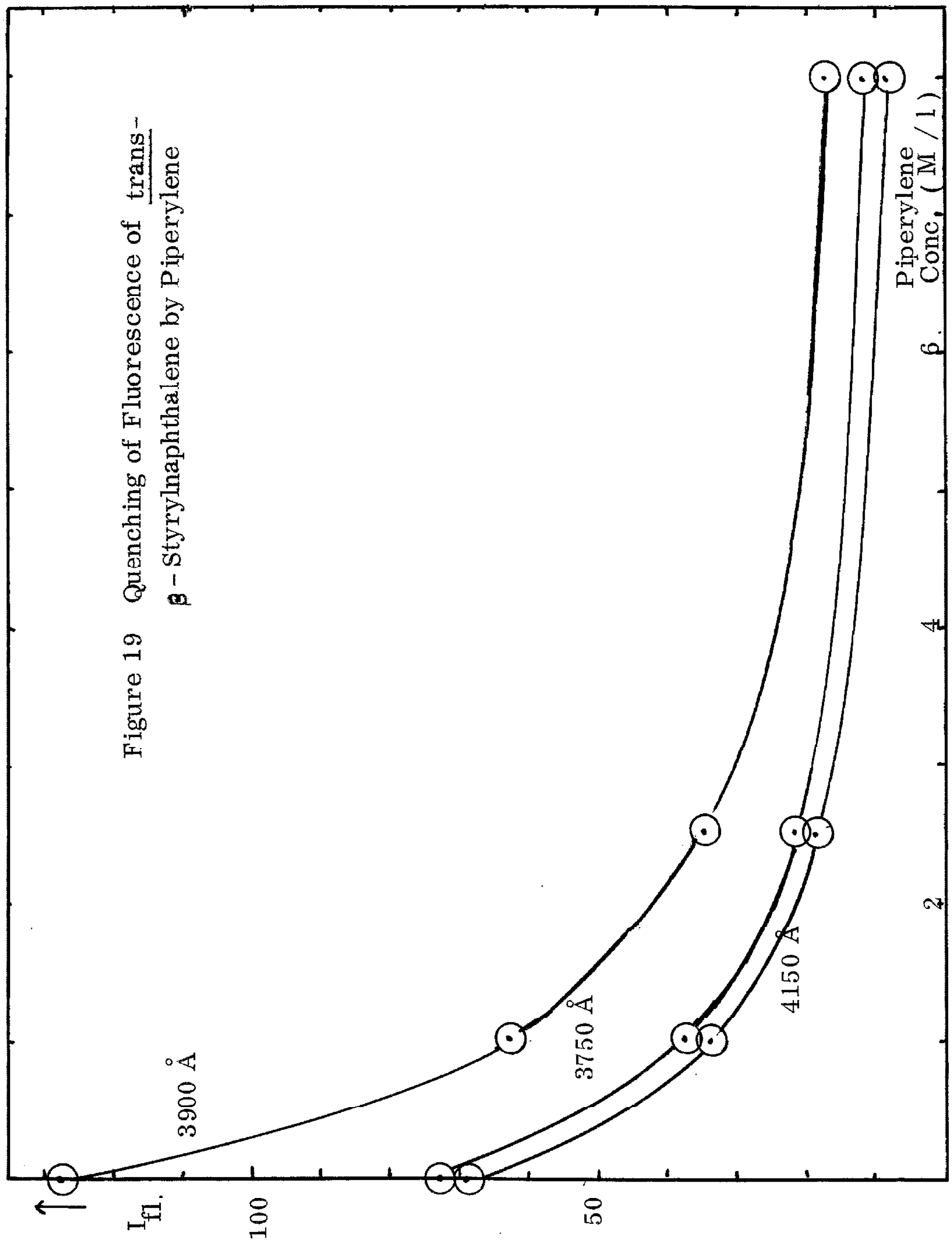
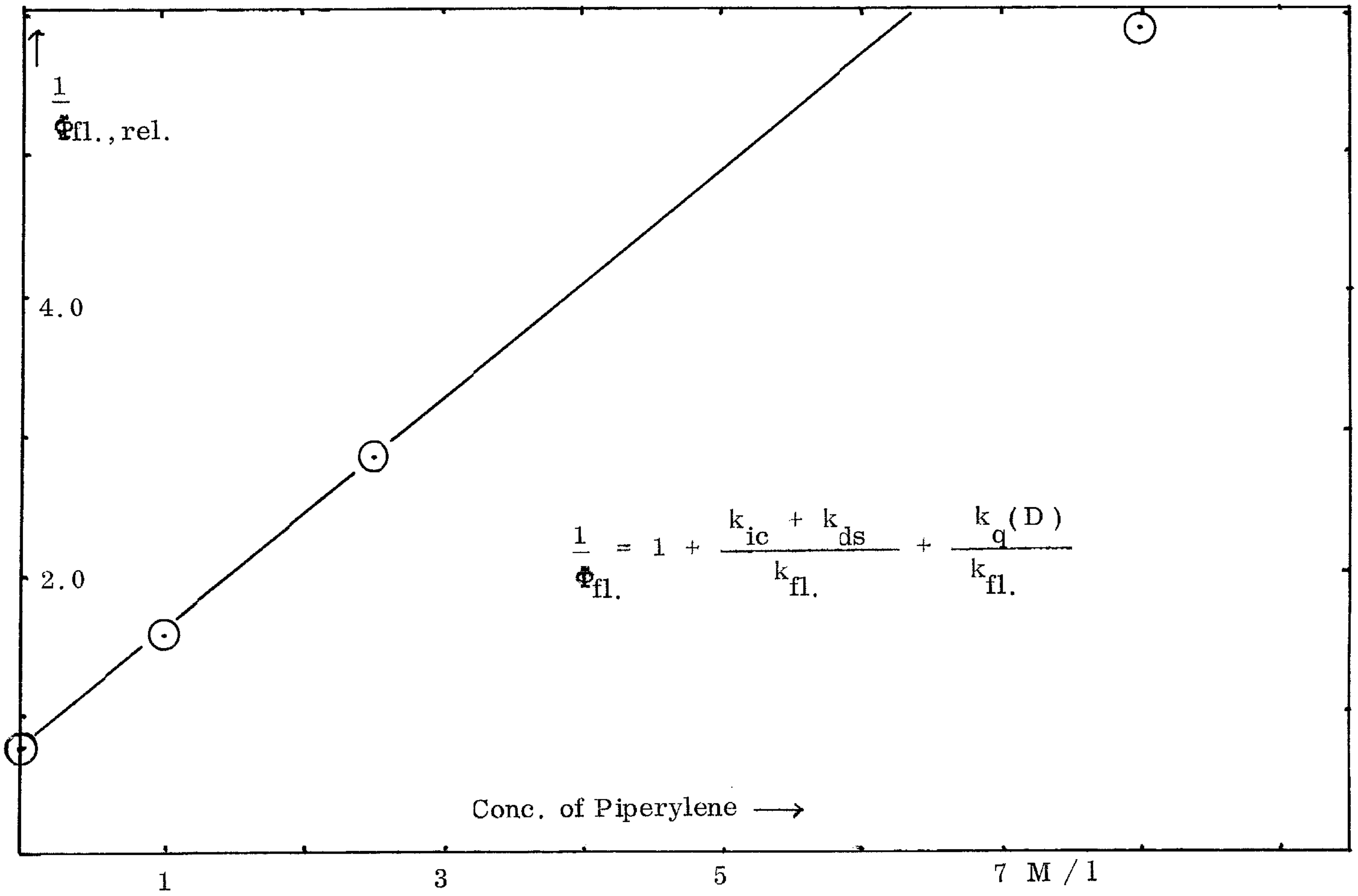
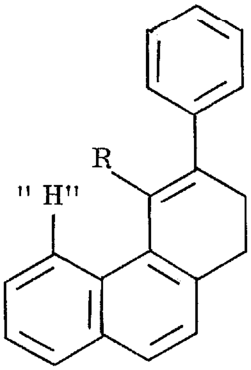


Figure 19 Quenching of Fluorescence of *trans*-β-Styrylnaphthalene by Piperylene

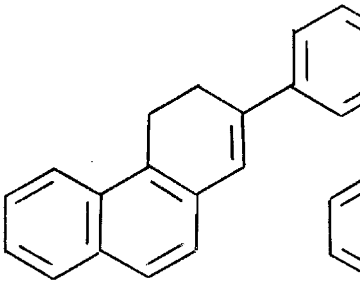
Figure 20 Quenching of Fluorescence of β - Styrylnaphthalene by Piperylene



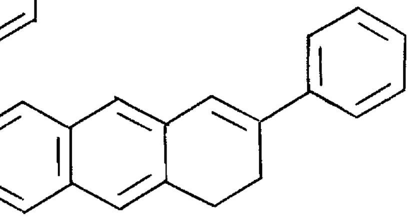
The efficiency of quenching is different at the different wavelengths which means the fluorescence is not from single excited singlet state but two or more different excited singlet states are involved. The mechanism of fluorescence quenching of aromatic hydrocarbons by dienes is discussed elsewhere (63). It is very interesting to compare ultra violet absorption spectra and fluorescent emission spectra of 1,2-dihydro-3-phenylphenanthrene (I) and 3,4-dihydro-2-phenylphenanthrene (II) (64 - 66).



I , R = H
IV, R = CH_3



II



III

It will be very interesting to compare absorption and emission spectra of II and 3,4-dihydro-2-phenylanthracene (III) but very unfortunately III is not available at the moment. The fluorescence $\lambda_{max.}$ and relative intensities of I and IV are shown in Table X (66). This indicates how steric crowding effects the fluorescence of the molecule. In IV, the methyl substituent can effectively twist the adjacent phenyl substituent out of the plane of the rest of the molecule just like phenyl group in cis- β-styrylnaphthalene. The hydrogen atom labeled "H" in IV clearly provides a buttressing effect on the steric requirements of the methyl group in this compound.

TABLE IX

UV Absorption and Fluorescence of I, II, and _trans_ - β -Styrylnaphthalene

	I	II	_trans_ - β - styrylnaphthalene	
$\lambda_{max., abs.}$ (mμ) and log ϵ	351 (4.46)	345 (4.265)	332 (4.46)	318 (4.59)
	248 (4.70)	287 (4.52)	282 (4.51)	272 (4.48)
	208 (4.84)	278 (4.53)	252 (4.19)	226 (4.42)
		225 (4.45)		
$\lambda_{max., fl.}$ (mμ)	405	400	390	

TABLE X

Fluorescence of I and IV

	I	IV
$\lambda_{max.}$ (in mμ)	405	395
Relative Intensity	0.8	0.1

Scintillation Study

It is shown (67) that a number of solutions bombarded with high energy radiation exhibit strong fluorescence when only a small amount of "fluorescent molecules" are added to the solvent. The same amount of fluorescent substance alone would give only about 0.01 of the observed light emission in the solution. The large emission in the solution is explained by a transfer of excitation energy from the solvent to the fluorescent molecule. These processes of energy transfer trapping the excitation energy, and of light emission compete with other processes: (a) an internal quenching of the excitation energy of the solvent molecule in the solvent itself, i.e., internal conversion of solvent molecules. (b) self quenching among similar fluorescent molecules which is dependent on the concentration of fluorescent molecule. (c) internal conversion of fluorescent molecules.

The fluorescence of naphthalene, trans-stilbene, and trans-β-styrylnaphthalene was induced with the irradiation by β-rays in benzene-^{14}C as solvent and β-ray source. A liquid scintillation counting method was used to evaluate the intensity of fluorescence. The results are shown in Table XI. As shown in the Table, trans-β-styrylnaphthalene is a lot more efficient liquid scintillator solute than trans-stilbene and naphthalene. In other words, the singlet energy transfer from excited benzene singlet to ground state β-styrylnaphthalene is more efficient than that between excited benzene singlet and ground state trans-stilbene or naphthalene. It is also likely that the lifetime of the excited singlet state of β-styrylnaphthalene is long enough to allow the fluorescence to compete with the internal conversion or the relaxation of the solvent cage. In other words, the lifetime of the excited singlet state of β-styrylnaphthalene is longer than that of stilbene or naphthalene.

TABLE XI

Scintillation Experiments

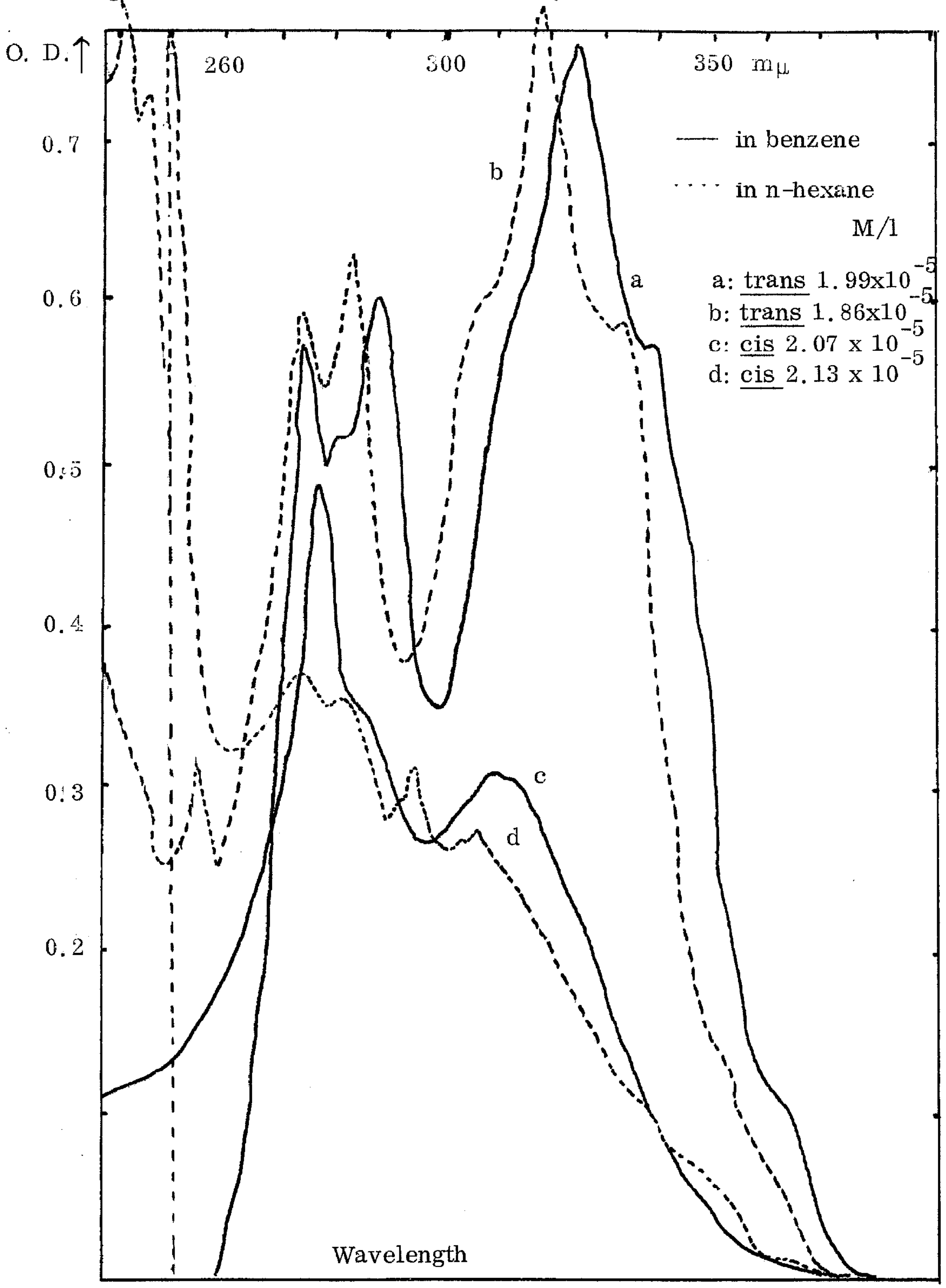
Compound	Counts					
Naphthalene	175	135	173	131	118	135
trans-Stilbene	1751	152	2040	1961	130	1452
trans-β-Styryl-naphthalene	29115	9674	26037	27499	6313	28921

Solvent Effect

The quantum yields of cis ⇄ trans isomerization of β-styrylnaphthalene were measured in benzene and n-hexane. As shown in Table I and II, a substantial solvent effect is observed at 3660 and 3130 Å. The quantum yields, $\Phi_{c \to t}$, and $\Phi_{t \to c}$, decrease considerably in n-hexane except $\Phi_{t \to c}$ at 3130 Å which is not significantly different in both solutions.

Both absorption spectra of cis- and trans-β-styrylnaphthalene are red shifted a little in benzene solution as shown in Figure 21. Bayliss and McRae (68) pointed out that, because of the Franck - Condon effect, excitation from a solvated ground state leads, not to the energetically most stable solvated conformation of the excited state, but to a conformation geometrically identical to the solvated ground state and necessarily having an energy higher than the equilibrium conformation of the solvated excited state. A number of factors are involved in the solvation of the ground and excited states. Nonpolar solutes can interact with nonpolar solvents through London dispersion forces and polar solutes can interact with nonpolar solvents through the dipole-induced dipole forces which are in general stronger than the London dispersion forces. In general, solutions in the least polar sol-

Figure 21 UV Absorption Spectra of β - Styrylnaphthalene



vents with the lowest solvating power, have the least effect on spectra effective in inhibitting vibrational structure. Jaffé and Orchin (7) suggested that the rapid relaxation of the solvent cage in polar solvents prevents establishment of vibrational quantization of the solvent cage, and leads to the blurring of vibrational structure of the spectra of polar solutes. The most general interaction is due to polarization forces (London dispersion forces) and Bayliss (69) obtained the expression for the frequency shift, $\Delta\nu$, relative to the vapor spectrum by the quantum-mechanical method:

$$\Delta\nu = (e^2Q^2 / \underline{a}^3hc) \cdot (\epsilon - 1) / (2\epsilon + 1)$$

where e is the charge on the electron, Q the transition moment, a the radius of the cavity in the solvent in which the solvent molecule is located, h Planck's constant, c the velocity of light, and ϵ the dielectric constant of the medium. This relation is similar to:

$$\Delta\nu = 10.71 \times 10^9 \; \frac{f}{\nu a^3} \cdot \frac{n^2 - 1}{2n^2 + 1}$$

where f is the oscillator strength, ν the frequency, and n the refractive index of the solvent. This effect always leads to a red shift due to solvation, the larger the more polar the solvent.

As shown in Figure 21, the vibrational structure of cis- β-styrylnaphthalene is blurred out in benzene compared to that in n-hexane solution. Also both cis- and trans- β-styrylnaphthalenes give red shift in benzene solvent as expected, since benzene is more polarizable than n-hexane.

The quantum yields of isomerization, $\Phi_{c \rightarrow t}$ and $\Phi_{t \rightarrow c}$, are higher in benzene solvent than that of n-hexane solution at 3660 and 3130 Å. This phenomenon is not observed in stilbenes and 4,4'-dinitrostilbenes but substitution of one of nitro groups in 4,4'-dinitrostilbene by an electron

TABLE XII

Average Frequency Shifts between Aliphatic and Benzene Solvent (70)

Compound	cm $^{-1}$		
	^1L_a	^1L_b	^1B_b
Phenanthrene	295	118	310
Anthracene	275	. . .	. . .
1, 2-Benzanthracene	312	155	570
9, 10-Dimethylanthracene	313	. . .	470
1, 2, 5, 6-Dibenzanthracene	297	150	440
Methylcholanthrene	340	210	470
Naphthacene	323	120	. . .

donating group results in the dependence of the trans $\rightleftarrows$ cis quantum yields upon the polarity of solvents (13). They suggested that the dependence of $\Phi_{t \rightarrow c}$ on solvent can be explained by solvation of the excited singlet state and consequently the trans → cis isomerization is hindered. But it is doubtful since the quantum yield, $\Phi_{t \rightarrow c}$, of 4-nitro-4'-aminostilbene is bigger in benzene (0.44) than that in cyclohexane (0.36) even though solvation would be more efficient in benzene solvent. The extinction coefficients of cis- and trans- isomers are shown in Table XIII.

As shown in Table XIII, benzene solutions of both cis- and trans-isomers absorb the light more efficiently at 3660 and 3130 Å than n-hexane solutions do and consequently give better quantum yields in benzene solution. β - Styrylnaphthalene is more polar than stilbene and a bigger solvent effect is expected since solute-solvent interaction will be stronger than stilbene case.

TABLE XIII

The Extinction Coefficients of cis- and trans- β-Styrylnaphthalene in Benzene and n-Hexane

Solvent	Molar Extinction Coefficient at 3130 Å		3660 Å	
	cis	trans	cis	trans
Benzene	1.362×10^4	3.154×10^4	96.6	392.7
n-Hexane	1.08×10^4	3.715×10^4	78.5	273.9

At any rate, the lifetime of excited intermediate which is responsible for the isomerization of β-styrylnaphthalene is long enough for the isomerization to compete with the relaxation of the solvent cages. In other words, the arrangement of orientation polarization of the solvent can compete with the isomerization in β-styrylnaphthalene. The long lifetime of the excited reaction intermediate was also shown in fluorescence studies of both cis- and trans-β-styrylnaphthalene.

Concentration Effect

The quantum yields of cis ⇄ trans isomerization of β-styrylnaphthalene, $\Phi_{c \to t}$ and $\Phi_{t \to c}$, were measured with various concentrations and are shown in Tables I - III. Both cis and trans isomers show certain concentration optimum in contrast to the stilbene cases where the quantum yield of isomerization from trans to cis, $\Phi_{t \to c}$, decreases steadily as the concentration of stilbene increases (14, 18).

TABLE XIV

Concentration Effect of Photoisomerization of Stilbene in n-Hexane at 25° C

Wavelength (Å)	Conc. (Mol/1.)	$\Phi_{t \rightarrow c}$	$\Phi_{c \rightarrow t}$	$\sum \Phi$	$(x_t)_{p.s.s.}$	Ref.
3130	1×10^{-5}	0.59	0.32	0.91	0.070	14
3130	4×10^{-5}	0.44	0.37	0.81	...	18
3130	5×10^{-2}	0.34	0.19	0.53	...	18
2537	1×10^{-5}	0.67	0.28	0.95	...	14

Schulte - Frohlinde et al. (13) also observed a big concentration effect in the photochemical stereoisomerization of 4-nitro-3'-methoxystilbene. These were explained by assuming the interaction between excited and non-excited molecules of stilbenes, i.e., the self quenching at high concentrations of stilbenes.

TABLE XV

Quantum Yields of trans → cis Isomerization of 4-Nitro-3'-Methoxystilbene in 1-Methylnaphthalene at Different Concentrations (3660 Å)

Conc. (Mol/1)	$\Phi_{t \to c}$	$(x_c)_{p.s.s.}$
1.0×10^{-5}	0.32	0.805
1.0×10^{-4}	0.31	0.810
5.0×10^{-4}	0.30	0.775
5.0×10^{-3}	0.29	0.775
1.0×10^{-2}	0.25	0.775
5.0×10^{-2}	0.22	0.585
1.0×10^{-1}	0.18	0.410
5.0×10^{-1}	0.13	0.220
7.5×10^{-1}	0.04	0.040
1.0×10^{0}	0.00	0.000

However, the self quenching can not be the only factor contributing to the concentration effect with β-styrylnaphthalene since the quantum yields pass through maxima as the concentrations are increased. The plots of 1/ Φ versus concentration of β-styrylnaphthalene are shown in Figures

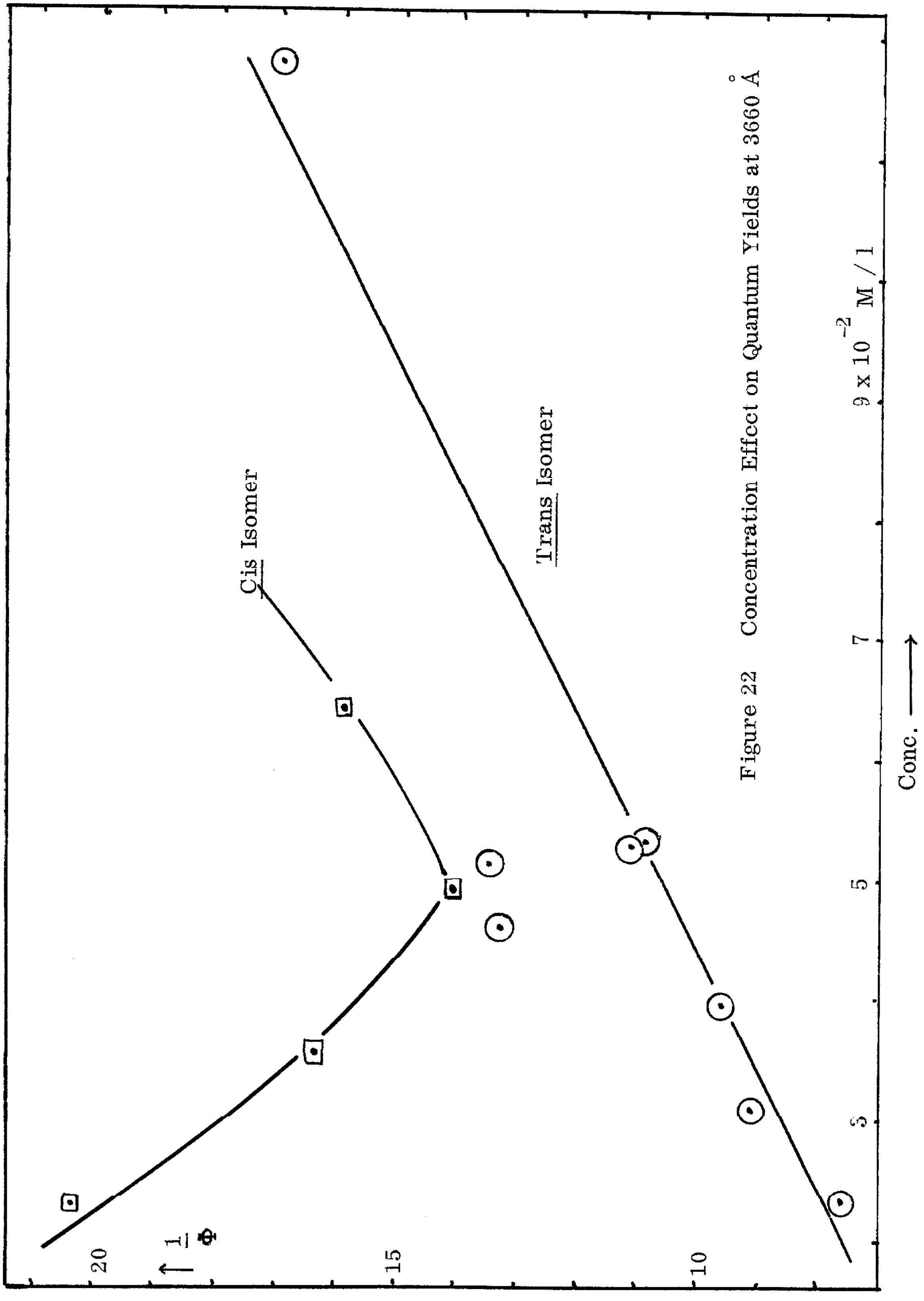


Figure 22 Concentration Effect on Quantum Yields at 3660 Å

Figure 23 Concentration Effect on Quantum Yields at 3130 Å

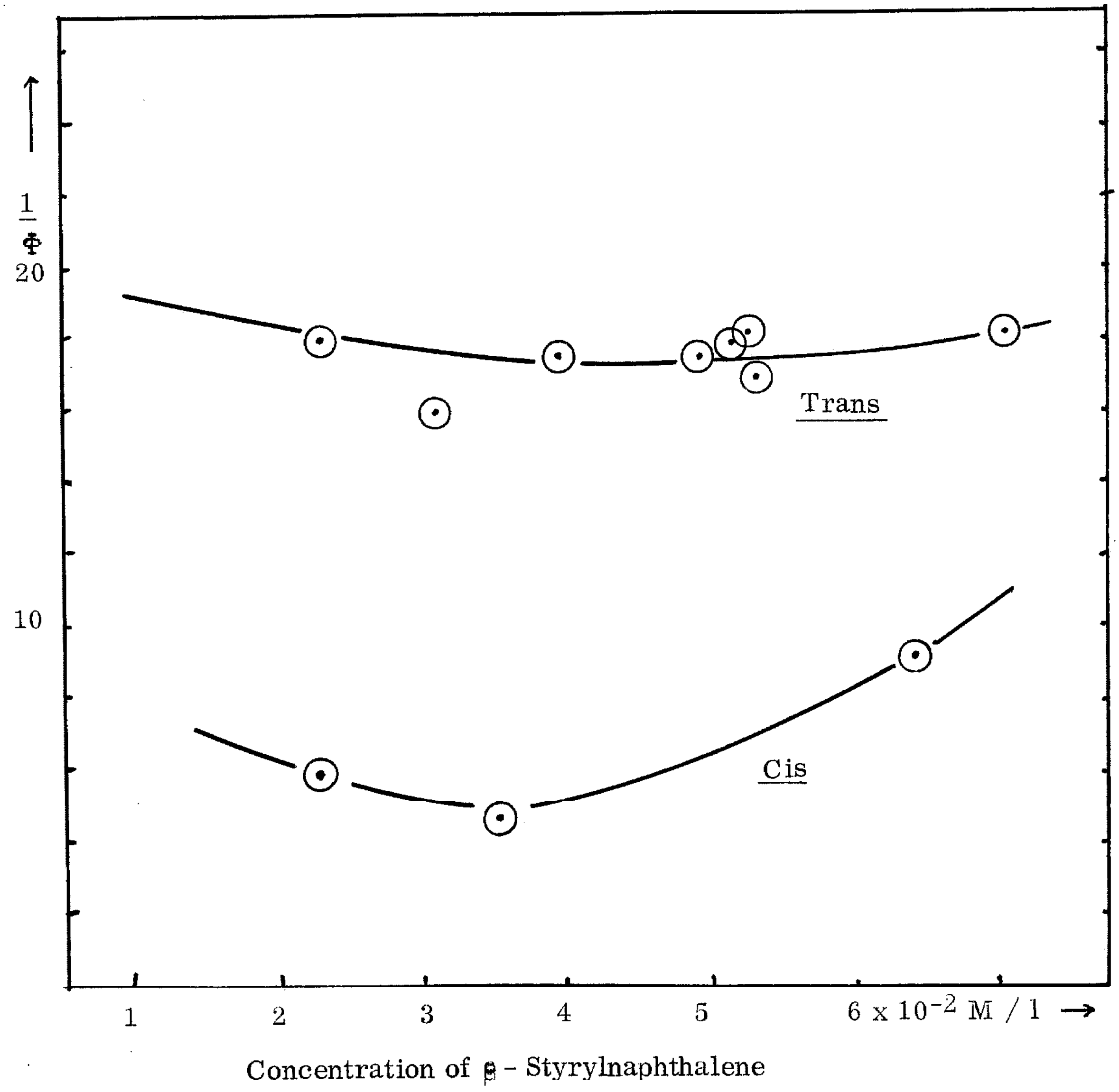
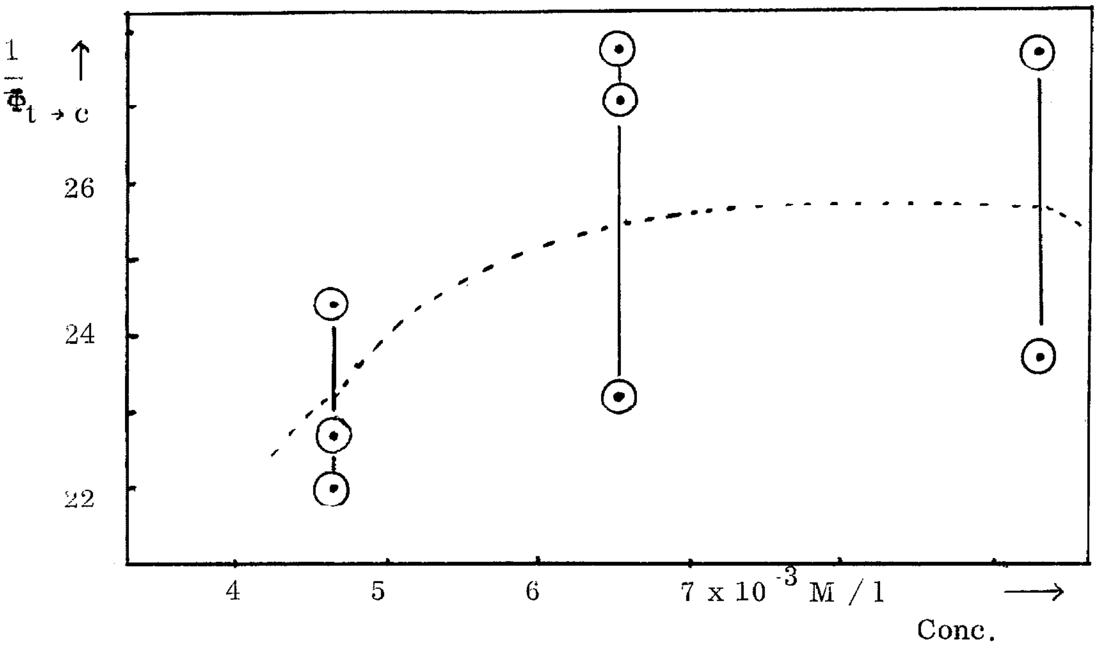
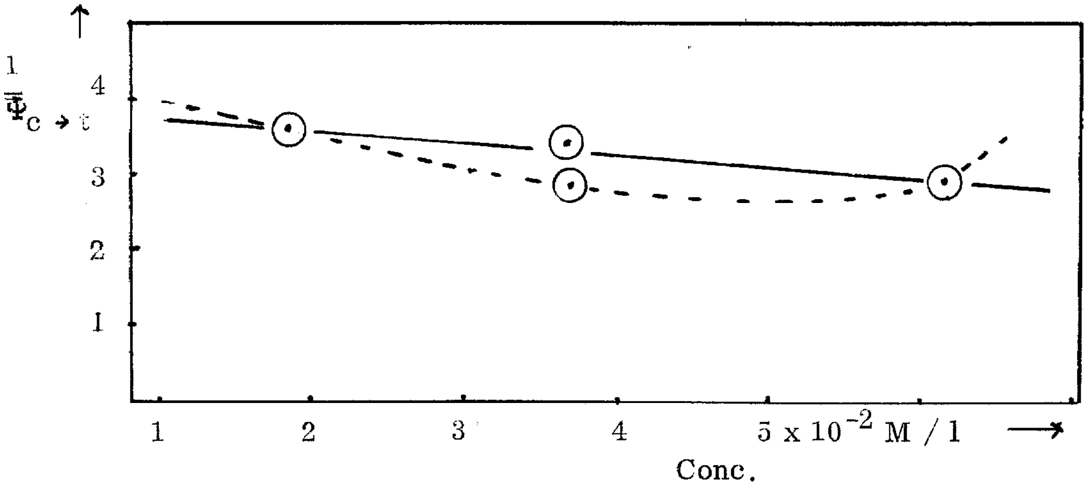


Figure 24 Concentration Effect on Quantum Yields at 2537 Å



Trans Isomer



Cis Isomer

22 - 24. In general, they are not straight lines as would be expected if self quenching were the only factor. It seems that internal conversion or the vibrational relaxation through solvent cage competes with isomerization efficiently at lower concentration giving low quantum yields and the self quenching becomes effective at the higher concentrations creating a concentration maximum.

$$c^* + c \longrightarrow (c_2)^* \longrightarrow 2c$$
$$t^* + t \longrightarrow (t_2)^* \longrightarrow 2t$$

where c^* and t^* are excited singlet or triplet states of cis- and trans- β-styrylnaphthalene.

It is also probable that the energy transfer is involved between the excited and ground states of the β-styrylnaphthalenes. A hypothetical energy level scheme for the β-styrylnaphthalene is shown in Figure 25.

The following energy transfer may occur in concentrated solutions. When the energy transfer from IV to I occurs, the quantum yield,

$$\mathrm{IV} + \mathrm{I} \longrightarrow \mathrm{III} + \mathrm{II}$$
$$\mathrm{VIII} + \mathrm{V} \longrightarrow \mathrm{VII} + \mathrm{VI}$$

$\Phi_{c \to t}$, would be decreased if the decay of III to I is more efficient than that of IV to II, as suggested by the effect of variation of excitation wavelength on quantum yields, and if the isomerization of III to VII is not more efficient than that of IV to VIII. Consequently, the quantum yield, $\Phi_{c \to t}$, should decrease as the concentration of β-styrylnaphthalene increases. On the other hand, energy transfer from VIII to V should enhance the isomerization of β-styrylnaphthalene since the isomerization of VII to I should be more efficient than that of VIII to II, while the decay of VII to V, and VIII to VI should not be much different. The combination of internal conver-

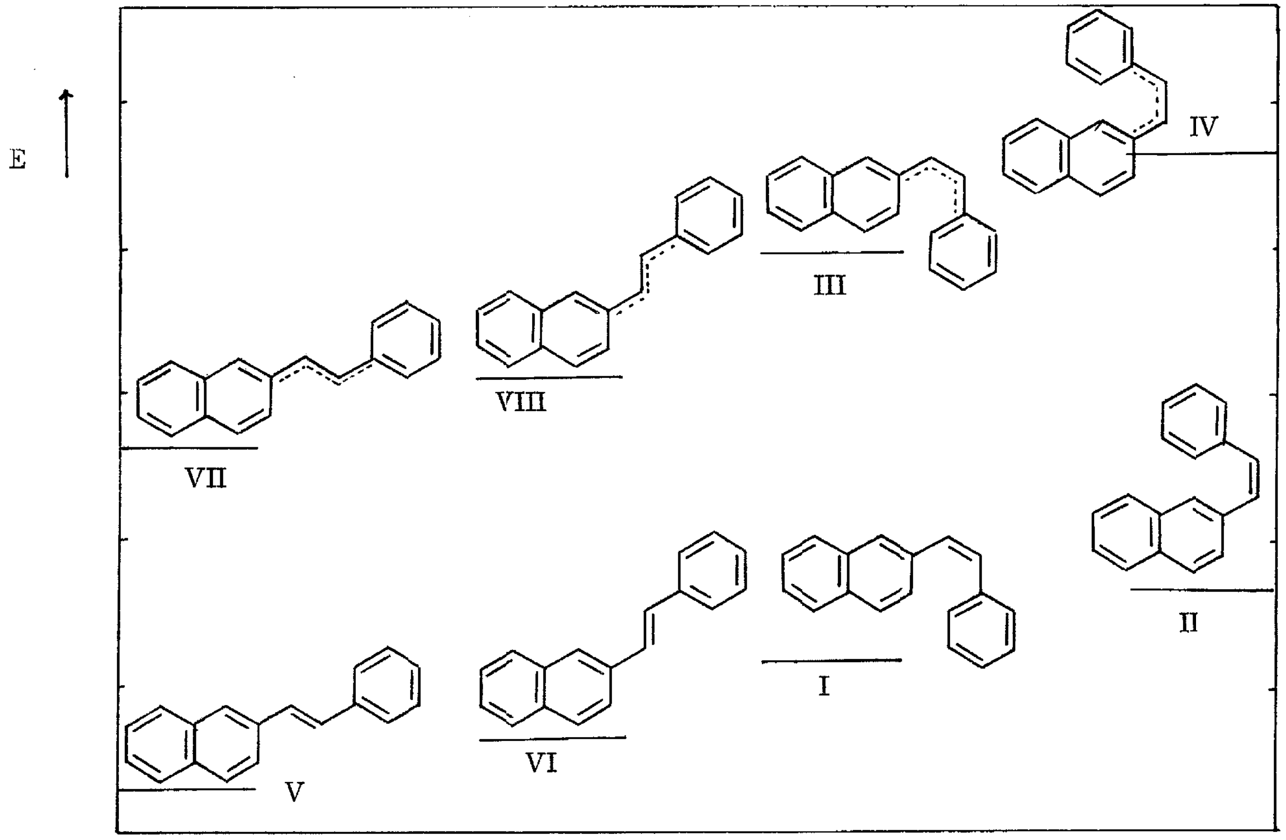


Figure 25 A Hypothetical Energy Level Scheme for β - Styrylnaphthalene

sion efficiency, self quenching, and the energy transfer should explain the concentration maximum of quantum yields of cis ⇌ trans isomerization of β-styrylnaphthalene. This can be shown by following scheme.

$$\mathrm{IV} \xrightarrow{k_1} \mathrm{II}$$

$$\mathrm{IV} \xrightarrow{k_2} \mathrm{VI}$$

$$\mathrm{III} \xrightarrow{k_3} \mathrm{I}$$

$$\mathrm{III} \xrightarrow{k_4} \mathrm{V}$$

$$\frac{k_3}{k_3 + k_4} > \frac{k_1}{k_1 + k_2}$$

and

$$\mathrm{VII} \xrightarrow{k_5} \mathrm{I}$$

$$\mathrm{VII} \xrightarrow{k_6} \mathrm{V}$$

$$\mathrm{VIII} \xrightarrow{k_7} \mathrm{II}$$

$$\mathrm{VIII} \xrightarrow{k_8} \mathrm{VI}$$

$$\frac{k_5}{k_5 + k_6} > \frac{k_7}{k_7 + k_8}$$

Photostationary States

The attempts were made to reach photostationary states at 3660, 3130 and 2537 Å with direct irradiation of β-styrylnaphthalene solutions in benzene or in n-hexane for a long period of time. The results are shown in Table XVI - XVIII.

The samples were degassed thoroughly on the vacuum line

(5.0×10^{-4} mm Hg) but cyclization and dehydrogenation products were observed. It is well known that cis-stilbene and its derivatives are converted photochemically in good yields to the corresponding phenanthrene derivatives in presence of oxidants such as dissolved oxygen or iodine (24, 71 - 73). In absence of oxidants, cis-stilbene forms an orange transient but not phenanthrene when irradiated. In photosensitized isomerization, this transient was not observed. Thus this transient is formed from cis-stilbene singlet state. The transient is postulated to be 4a,4b-dihydrophenanthrene.

In degassed solution, photochemical cis ⇄ trans isomerization of stilbene takes place with essentially no net loss in total amount of stilbene and thus it was suggested that the dihydrophenanthrene must undergo ring opening under the irradiation conditions to regenerate cis-stilbene at such a rate that the steady-state concentration of this intermediate is low relative to the concentration of stilbene. The thermal ring opening of the dihydrophenanthrene has been found to occur with a half-life on the order of 2 hours at 30° C (24). Also it has been found that the ring opening can be accomplished photochemically (24). Cis- β-styrylnaphthalene also forms an orange transient which decays thermally to cis- β-styrylnaphthalene at room temperature. But we observed that not only photocyclization but also dehydrogenation follows cyclization with prolonged irradiation in degassed solution of β-styrylnaphthalene. Malkin and Fischer also observed that in 1,2-di-(α-naphthyl) ethylene, irreversible photoreactions (cyclization) predominate over photoisomerization and suggested that the substitution of the naphthyl groups in the β-positions would probably prevent such cyclization (15). Also it is observed that a small amount of phenanthrene is formed when degassed benzene solutions are irradiated for a long time with ^{60}Co- γ-ray (24).As shown in Table XVI-XVIII, some unknown compounds were formed with prolonged irradiation. One of them was identified by v.p.c. as 1,2-benzanthracene (I) and the other is presumed to be

TABLE XVI

Photostationary States at 3660 Å

Starting Material	Irradiation Time (hour)	% <u>Cis</u>	%<u>Trans</u>	Unknown I	Unknown II
a	91.2	43.7	45.4	3.2	7.6
a	112.5	42.1	47.1	3.6	7.2
a	146	22.2	31.6	0.0	46.2
a	161.2	30.1	51.8	9.7	8.6
a	188.8	16.5	29.4	0.0	54.1
b	28	5.6	94.4		
b	76.8	19.8	80.2		
b	96.1	19.3	80.7		
b	120.5	33.1	66.9		
b	144	40.9	59.1		
b	179	41.2	58.8		
b	351	26.1	<u>trans</u> isomer and other products		

a: 6.56 x 10^{-2} M <u>trans</u>- β-styrylnaphthalene in benzene.

b: 5.252 x 10^{-2} M <u>trans</u>- β-styrylnaphthalene in benzene.

All numbers are mean averages of 3 measurements and all solutions were degassed carefully. The <u>cis</u> isomer gave side products long before reaching stationary states.

TABLE XVII

Photostationary States at 3130 Å

Starting Material	Irradiation Time (days)	% Products with Retention Time (Min.)					
		7	9 (*Cis*)	17 (*Trans*)	20	14	28
a	4	5.2	29.1	57.5	8.0		
b	5	4.5	30.2	42.6	18.4	4.1	
a	6	5.9	28.2	56.7	6.7	0.6	2.2
c	6		22.2	77.0	0.8		
c	11		24.2	74.0	1.8		
d	4.3		26.2	73.8			
d	6		23.29				
d	12		24.29				
d	13		25.57				
d	14		23.43				
d	16		26.92				
d	18		26.36				

Table XVII (continued)

a: 2.59×10^{-2} M *cis* - β - styrylnaphthalene in benzene

b: 1.698×10^{-2}M *cis*- β - styrylnaphthalene in benzene

c: 4.927×10^{-2}M *trans*- β -styrylnaphthalene in benzene

d: 5.263×10^{-2}M *trans*- β -styrylnaphthalene in benzene

All measurements are mean averages of three measurements.

TABLE XVIII

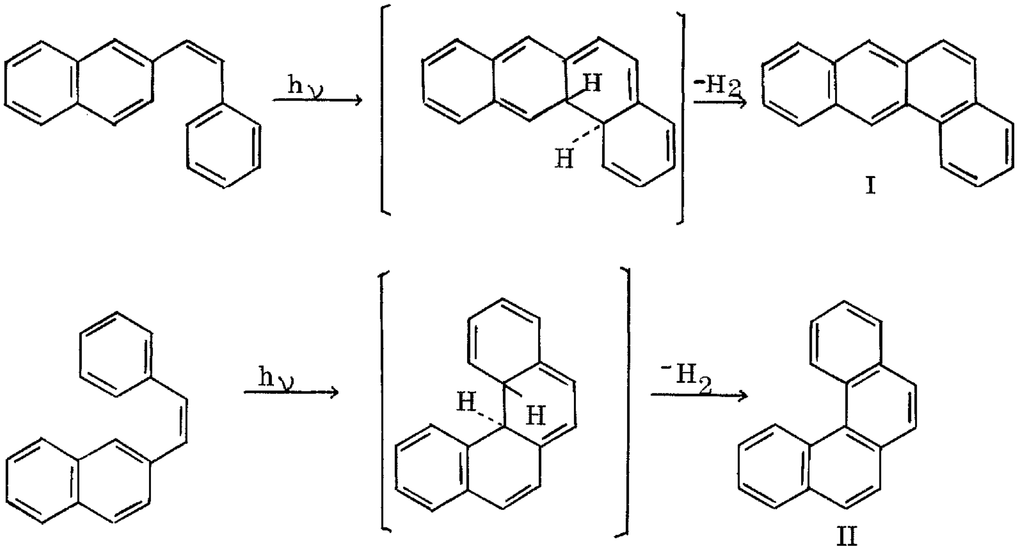
Photostationary States at 2537 Å

Starting Material	% *Cis*
Trans- β -styrylnaphthalene 9.30×10^{-3}M in n-hexane	40.8

With prolonged irradiation resulted in net loss of β -styrylnaphthalene with increasing side products.

With *cis* isomer, side products appear even with 6 hours of irradiation. Even though the concentration of β -styrylnaphthalene were higher than the *trans* isomer case, the conversions were only 7 - 18 % when the side products were observed.

1,2-benzphenanthrene (II).



With prolonged irradiation, β - styrylnaphthalene eventually disappears and irreversible photoreactions, presumably dimerization and polymerization as well as cyclizations and formation of I and II, predominate. The attempts to reach photostationary states are made from both directions, from the cis and trans isomers. But other irreversible reactions start to interfere before reaching the photostationary states. It is very interesting to know that photostationary states of stilbenes are heavily dependent on concentration (13). This was explained by the self quenching between excited and ground state of trans-stilbenes. If the excimer is formed in β - styrylnaphthalene, it is very probable that dimerization through naphthalene rings occurs. Even though no precipitate is observed, some unknown compounds of high molecular weight are observed in v. p. c. analyses of products indicating polymerization occurs. It is also possible that some addition compounds between benzene solvent ground state and excited state of β - styrylnaphthalene are formed.

TABLE XIX

Concentration Effect on Photostationary States of 4-Nitro-3'-methoxystilbene in 1-Methylnaphthalene

Conc.	% Cis at Stationary State
1.0×10^{-5}	80.5
1.0×10^{-4}	81.0
5.0×10^{-4}	77.5
5.0×10^{-3}	77.5
1.0×10^{-2}	75.5
5.0×10^{-2}	58.5
1.0×10^{-1}	41.0
5.0×10^{-1}	22.0
7.5×10^{-1}	4.0
1.0×10^{0}	0.0

PHOTOSENSITIZED ISOMERIZATION

Most photosensitized reactions involve transfer of electronic excitation, either singlet or triplet, from the sensitizer to an acceptor. In general, triplet excitation is more probable in transfer of excitations especially in photosensitized isomerization of olefins since the triplets are generally much longer-lived than singlets. In all cases, sensitizers absorb the light and most of the sensitizers absorb the light of long wavelengths which are out of the lowest optical transitions of the acceptors. Usually carbonyl compounds are good sensitizers since the intersystem crossing from singlet to triplet in these compounds is very efficient (71). The success of photosensitized reactions is largely due to the fact that the splitting between the lowest singlet and triplet states varies widely in organic compounds (21). Thus, it is feasible to excite a sensitizer using light of a wavelength longer than any absorbed by the acceptor. As mentioned in the introduction, the photostationary states cis/trans ratio in photosensitized isomerization of olefins is a complicated function of the nature of the photosensitizers. The triplet energies of both sensitizers and acceptors are very important as well as their chemical structure.

Phosphorescence Spectra

An attempt has been made to see the phosporescence spectra by taking total emission spectra of trans- β-styrylnaphthalene in methylcyclopentane - isopentane glass but the strong fluorescence interfered to make it impossible to see the phosphorescence. Thus we were unable to evaluate the accurate value of triplet energy of both cis- and trans- β-styrylnaphthalene.

Singlet-Triplet Absorption Spectra

Intramolecular or intermolecular heavy atoms enhance the spin-orbital coupling or spin decoupling thus enabling singlet-triplet transitions (71).

$$S_0 \quad + \quad h\nu \longrightarrow T_1$$

The singlet-triplet absorption spectrum of trans- β -styrylnaphthalene was taken in purified ethyl iodide to evaluate approximate triplet energy of the compound. The spectrum is shown in Figure 26. As shown in Figure 26, it has a long tail without giving a clear maximum or a clear point where it starts to absorb the light even though highly concentrated solution (ca. 0.4 mol/l) was used. Approximately 5690 Å is the starting wavelength where trans - β - styrylnaphthalene absorbs the light indicating that the triplet energy of trans- β -styrylnaphthalene is in the vicinity of 50 kcal/mol.

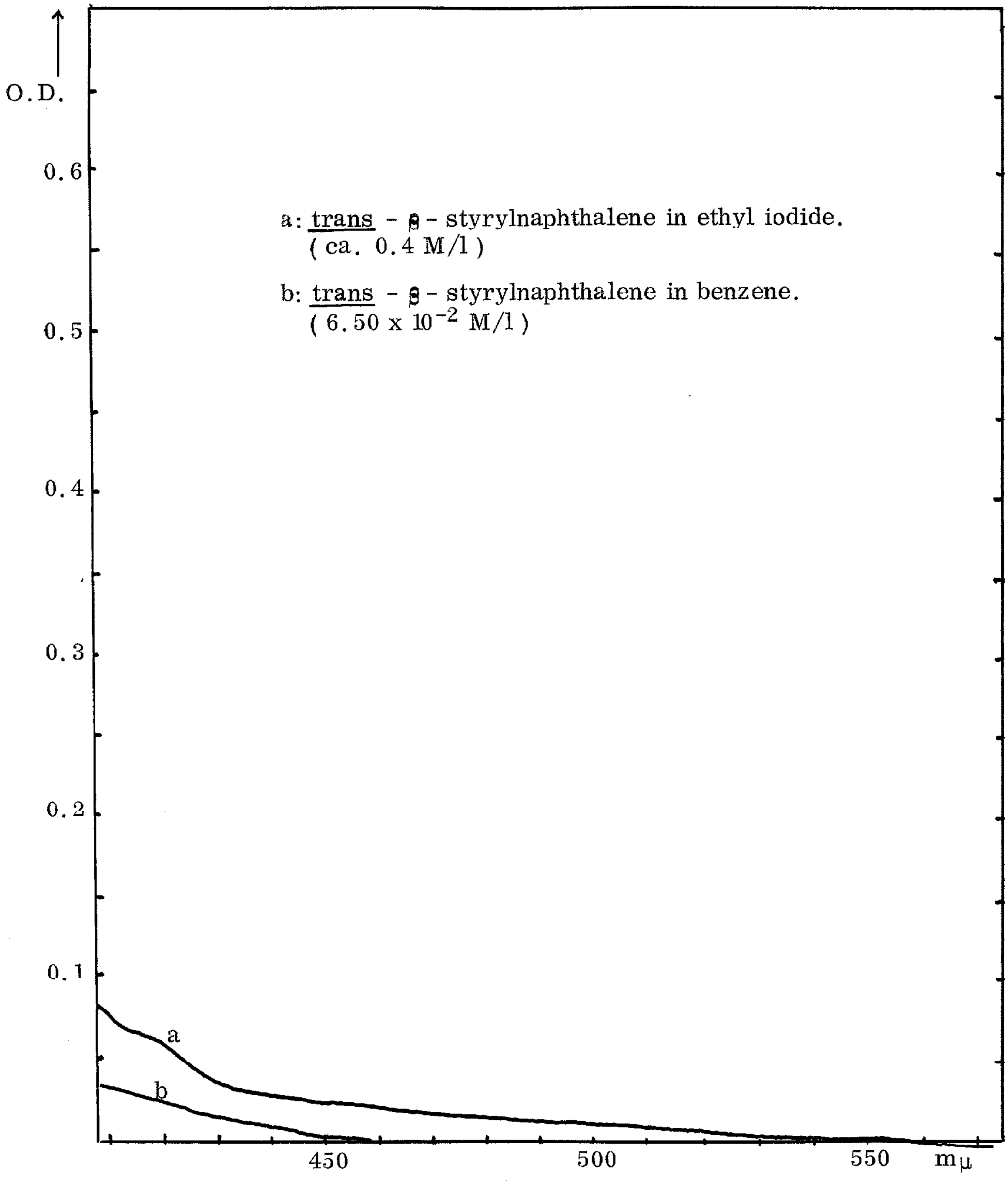
$$E = E_2 - E_1 = \frac{2.86 \times 10^5}{\lambda \text{ (in Å)}} \text{ kcal/mol} = \frac{2.86 \times 10^5}{5690} = 50.3 \text{ kcal/mol}$$

Photostationary States for Sensitized Isomerization

The ratio of the compositions of photostationary mixture is very important to figure out the nature of reactions. The quantitative measurements can be obtained if the stationary states can be reached without any side reactions. The ratio of reactions in the stationary states must become time - independent and the same result must be obtained when the stationary state is approached from either side.

It is not easy to find appropriate sensitizers for β -styrylnaphthalene since it absorbs light of long wavelengths. Very dilute solutions of acceptor

Figure 26 Singlet - Triplet Absorption Spectra of β - Styrylnaphthalene in Ethyl Iodide.



and highly concentrated solutions of high energy sensitizers were used. Otherwise, rather unusual sensitizers such as quinones, α-diketones, fluorenone, and 9, 10-dibromoanthracene were used with 1 cm thick solution filter of 0.1 M trans- β-styrylnaphthalene in benzene (absorbs all the light of wavelengths shorter than 3800 Å).

For the high energy sensitizers such as benzophenone, the ordinary 3660 Å Corning glass filter was used. The solutions were made up so that more than 99 % of the light should be absorbed by the sensitizers.

When benzene is used as a sensitizer, a 2537 Å solution filter was used. Most of the light was absorbed by benzene. However singlet reaction should interfere with the triplet reaction in this case since the lifetime of benzene singlet state is long and thus the singlet energy transfer is very probable. An addition reaction of benzene is also observed but not to great extent.

Irradiation of degassed solutions of β-styrylnaphthalene and various sensitizers in benzene solution resulted in cis ⇌ trans isomerization of β-styrylnaphthalene and yielded various cis/trans ratios in the photostationary mixture depending on the triplet energy of sensitizers. They are shown in Figure 27 and Table XX.

The sensitizers such as triphenylene, the quinones, the α-diketones, and various halogen containing aromatic compounds behave abnormally in the energy transfer for the photosensitized isomerization of stilbenes. The simple energy transfer does not fit for this sensitizers. The mechanism involved in the photoisomerization of stilbenes by those sensitizers is discussed thoroughly by Coyne (26). She included the mechanisms of excited state complex of either a triplet or a singlet state, and of free radical reactions even though the conclusion was not decisive in the discussion of the nature of these sensitized reactions.

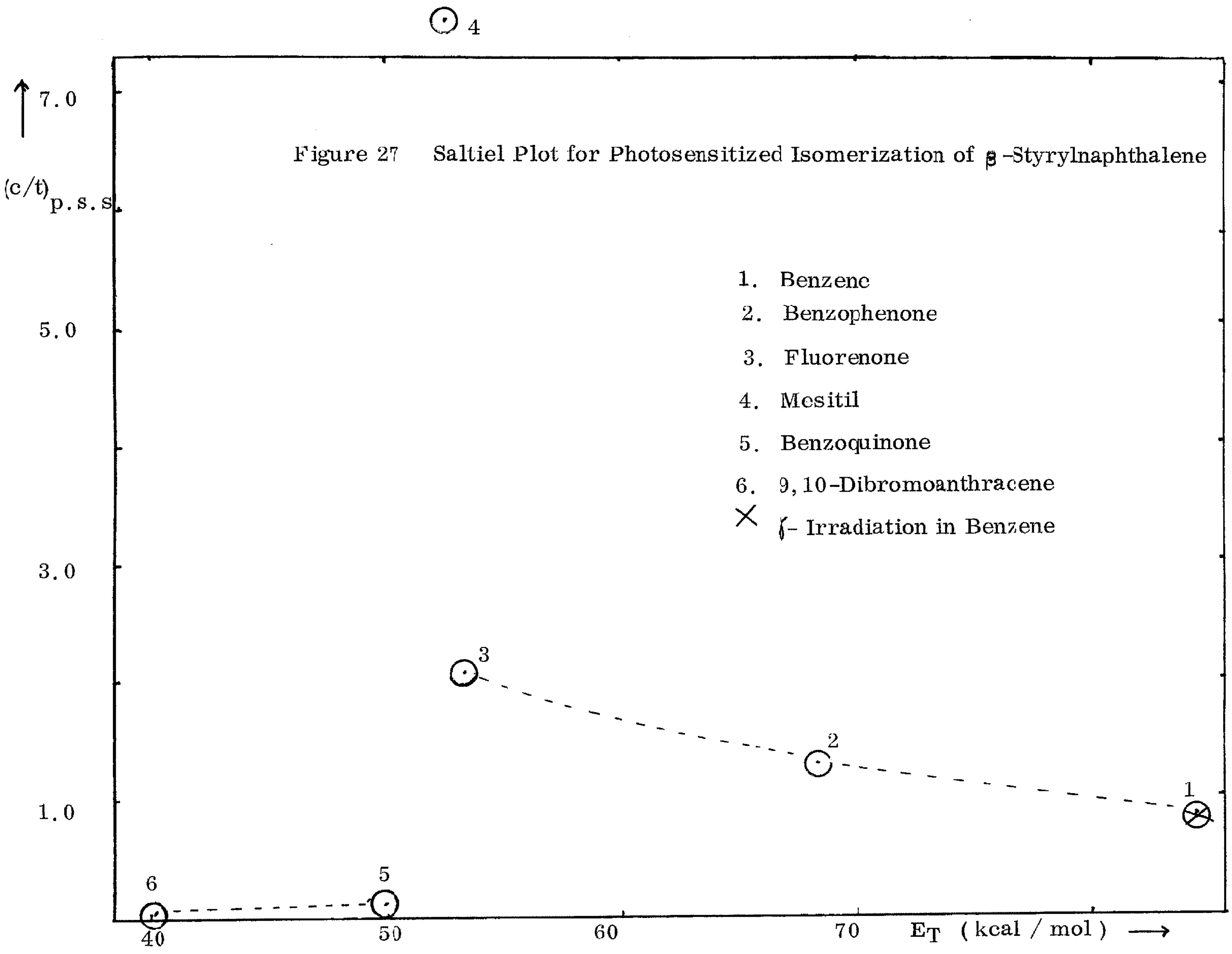


Figure 27 Saltiel Plot for Photosensitized Isomerization of β-Styrylnaphthalene

TABLE XX

Photostationary States for Sensitized Isomerization of β-Styrylnaphthalene

Sensitizer	Conc. of Sensitizer (mol/l)	E_T of Sensitizer	Conc. of β-Styrylnaphthalene (mol/l)	Irradiation Time (days)	% Cis	(cis/trans) at p.s.s.
Azobenzene	0.05	...	trans 4.409×10^{-2}	17	0.45	0.005
9,10-Dibromo-anthracene	0.05	40.2	trans 4.409×10^{-2}	17	1.67	0.017
Benzoquinone	0.05	50.0	trans 4.409×10^{-2}	17	9.26	0.102
Mesitil	0.006	52.6	trans 8.82×10^{-3}	7	86.69	7.09
Mesitil	0.006	52.6	trans 8.82×10^{-3}	10	86.76 ± 0.48	7.20 ± 0.30
Mesitil	0.006	52.6	trans 2.318×10^{-2}	10	87.56 ± 0.29	7.56 ± 0.17
Mesitil	0.006	52.6	trans 2.318×10^{-2}	17	88.09	7.85
Mesitil	0.006	52.6	trans 2.646×10^{-2}	7	88.32 ± 0.33	7.80 ± 0.27
Mesitil	0.006	52.6	cis 9.23×10^{-3}	17	88.14 ± 0.25	8.13 ± 0.07
Mesitil	0.006	52.6	cis 1.508×10^{-2}	7	87.79 ± 0.26	7.68 ± 0.21
Mesitil	0.006	52.6	cis 1.508×10^{-2}	10	87.14 ± 0.21	7.21 ± 0.17

Table XX (continued)

Sensitizer	Conc. of Sensitizer (mol/l)	E_T of Sensitizer	Conc. of β-Styrylnaphthalene (mol/l)	Irradiation Time (days)	% Cis	(cis/trans) at p.s.s.
Fluorenone	0.05	53.3	trans 2.646×10^{-2}	7	70.71	2.41
Fluorenone	0.05	53.3	trans 2.646×10^{-2}	10	70.10	2.33 ± 0.01
Fluorenone	0.05	53.3	trans 5.076×10^{-2}	10	66.33 ± 0.80	1.97 ± 0.07
Fluorenone	0.05	53.3	trans 5.076×10^{-2}	17	66.78 ± 1.30	2.01 ± 0.12
Fluorenone	0.05	53.3	cis 7.537×10^{-3}	10	63.29 ± 0.01	1.72 ± 0.0
Fluorenone	0.05	53.3	cis 7.537×10^{-3}	17	62.87 ± 0.01	1.69 ± 0.0
Fluorenone	0.05	53.3	cis 1.508×10^{-2}	7	69.63 ± 0.08	2.23 ± 0.08
Fluorenone	0.05	53.3	cis 1.508×10^{-2}	10	69.37 ± 1.23	2.27 ± 0.13
Benzophenone	0.05	68.5	trans 1.764×10^{-4}	1/12 (hrs)	50.09 ± 0.25	1.00
Benzophenone	0.05	68.5	trans 1.764×10^{-4}	1/6 (hrs)	53.73 ± 1.72	1.16
Benzophenone	0.05	68.5	trans 1.764×10^{-4}	1/2 (hrs)	53.90 ± 0.73	1.17
Benzophenone	0.05	68.5	trans 1.764×10^{-4}	1 (hrs)	55.41 ± 1.95	1.24
Benzophenone	0.05	68.5	trans 3.528×10^{-4}	1/2 (hrs)	54.27 ± 1.58	1.18
Benzophenone	0.05	68.5	trans 3.528×10^{-4}	1 (hrs)	56.41 ± 0.64	1.29

Table XX (continued)

Sensitizer	Conc. of Sensitizer (mol/l)	E_T of Sensitizer	Conc. of β-Styrylnaphthalene (mol/l)	Irradiation Time (hours)	% Cis	(cis/trans) at p.s.s.
Benzophenone	0.05	68.5	trans 1.971×10^{-4}	48	47.3 ± 1.20	1.99 ± 0.03 b
Benzophenone	0.05	68.5	trans 1.971×10^{-4}	96	36.95 ± 0.90	1.89 ± 0.05
Benzophenone	0.05	68.5	cis 3.015×10^{-4}	1	63.31 ± 0.35	- c
Benzophenone	0.05	68.5	cis 6.030×10^{-4}	1	72.86 ± 0.40	-
Benzophenone	0.05	68.5	cis 5.176×10^{-4}	48	46.2	1.77 ± 0.15
Benzophenone	0.05	68.5	cis 5.176×10^{-4}	96	57.60 ± 0.30	1.93 ± 0.02
Benzene	11.2	84.4	cis 5.176×10^{-4}	30	45.17	0.824

a: A side product increased steadily as irradiation time prolonged.

b: A side product was observed when irradiated for 48 hours and it increased as irradiation time prolonged.

c: Even after 10 min. of irradiation, a side product appeared and it increased as irradiation prolonged.

As expected, the same phenomena are observed in photosensitized isomerization of β-styrylnaphthalene. 9,10-dibromoanthracene and benzoquinone yielded trans rich photostationary mixtures. The same kind of radical mechanisms used in the case of stilbenes by Coyne may be applied.

Herkstroeter's measurements of triplet quenching constants for a variety of sensitizers by stilbene show the expected monotonic decrease (41) of quenching rate with $E_{donor} - E_{acceptor}$ when simple ketones or aromatic hydrocarbons are used as sensitizers. However, the rate at which the rate drops off is less than expected for the low energy sensitizers. This is attributed to twisting of the stilbene molecule to a non-spectroscopic state during the transfer process, i.e., nonvertical excitation.

Unfortunately the lowest triplet energy of cis- β-styrylnaphthalene is not known. However, if we guess that the singlet and triplet splitting of β-styrylnaphthalene is similar to that of stilbene, then the triplet energy of cis isomer will be 5 - 7 kcal higher than that of trans isomer which is around 50 kcal/mol. Thus, if we assume the triplet energy of cis isomer to be around 55 - 57 kcal/mol, then it is expected that mesitil ($E_T = 52.6$ kcal/mol) and fluorenone ($E_T = 53.3$ kcal/mol) should not transfer triplet excitation to the cis isomer in the way of classical energy transfer. However, it is observed that both mesitil and fluorenone sensitized the isomerization of cis isomer indicating the triplet energy transfer. Mesitil gives exceptionally high cis rich stationary states, an observation that is hard to interprete since the compound has previously behaved "abnormally" as a sensitizer. For the fluorenone, the nonclassical energy transfer, i.e., nonvertical excitation, in which β-styrylnaphthalene is excited with significant change in geometry is probably involved. Thus, the localization of triplet excitation to the naphthalene chromophore may not prevent nonvertical excitation. It is also conceivable that the triplet energy of the cis isomer is exceptionally low (around 53 kcal/mol ?) since the most stable geometry of the cis isomer in its ground state is not planar and the most stable triplet state of cis isomer is expected to be nonplanar.

If we apply the same mechanism which Hammond et al. (16) applied for the sensitized photoisomerization of stilbenes (introduced in this thesis on p 9), the photostationary states can be expressed in absence of quenchers and self quenching as:

$$\left(\frac{c}{t}\right)_{p.s.s.} = \left(\frac{k_4 + k_{10}}{k_3 + k_9}\right) \left(\frac{k_{15} + k_{19}K_{12}}{k_{14} + k_{18}\,K_{12} + k_{-3}\,(S)}\right) \quad (1)$$

$$= (\text{ the excitation ratio }) \cdot (\text{ the decay ratio })$$

$$\left(\frac{t}{c}\right)_{p.s.s.} = \left(\frac{k_{qc}}{k_{qt}}\right) \cdot \left(A + \frac{k_{-3}(S)}{k_{15} + k_{19}}\right) \quad (2)$$

where $A = \dfrac{k_{14} + k_{18}K_{12}}{k_{15} + k_{19}K_{12}}$ = the natural decay ratio,

$k_{12} = (p^3) / (t^3)$, and k_{qc} and k_{qt} are sums respectively of the rates of all processes which transfer excitation to cis- and trans-β-styrylnaphthalene.

When the high energy sensitizers are used, both k_{qc} and k_{qt} are diffusion controlled and $k_{qt}/k_{qc} = 1$ and k_{-3} is too small to be detected. Then,

$$\left(\frac{t}{c}\right)_{p.s.s.} = \left(\frac{k_{qc}}{k_{qt}}\right) \cdot A = A = \text{the natural decay ratio.} \quad (3)$$

The value of A is 0.78 when benzophenone (0.05 M) is used at room temperature and the total concentration of β-styrylnaphthalene is 2 - 4 x 10^{-4}M.

The quantum yields of sensitized isomerization can be formulated as:

$$\Phi_{t \to c} = \underline{a} \left(\frac{k_{qt}(t)}{k_{qt}(t) + k_{21}} \right) \left(\frac{k_{19}K_{12} + k_{15}}{k_{14} + K_{12}(k_{18} + k_{19}) + k_{20}(t)} \right) \qquad (4)$$

$$\Phi_{c \to t} = \underline{a} \left(\frac{k_{qc}(c)}{k_{qc}(c) + k_{21}} \right) \left(\frac{k_{14} + k_{18}K_{12}}{k_{14} + K_{12}(k_{18} + k_{19}) + k_{20}(t)} \right) \qquad (5)$$

where $\underline{a}$ is the intersystem crossing yield of sensitizers and k_{21} is rate constant of radiationless decay of sensitizer triplets which is smaller than 10^6 sec^{-1} and negligible compared to other rate constants.

From the equation for the quantum yields, 4 and 5, we obtain the following expressions when the concentration of substrate is low enough so that the self quenching is insignificant:

$$\Phi_{t \to c} + \Phi_{c \to t} = \underline{a} = \text{the intersystem crossing yields of sensitizers.} \qquad (6)$$

and

$$\frac{\Phi_{c \to t}}{\Phi_{t \to c}} = \frac{k_{14} + k_{18}K_{12}}{k_{15} + k_{19}K_{12}} = \text{the natural decay ratio.} \qquad (7)$$

When the high energy sensitizers are used,

$$\left(\frac{c}{t} \right)_{\text{p.s.s.}} = \left(\frac{k_{qt}}{k_{qc}} \right) \cdot \left(\frac{\Phi_{t \to c}}{\Phi_{c \to t}} \right) \qquad (8)$$

The quantum yields were measured with benzophenone as a sensitizer and are shown in Table XXI. The values for cis isomer is not very accurate since it contained about 11 % of trans isomer as impurity. However, the values, $\Phi_{c \to t}$, are corrected for this impurity and the error should not be significant.

TABLE XXI

Quantum Yields for Photosensitized Isomerization of β-Styrylnaphthalene

Conc. of β-Styryl-naphthalene (mol/l)	Mol. of Starting Compound	Irradiation Time (min.)	Light Intensity (Einstein)	% Conversion (corrected)	Φ
trans 1.76×10^{-4}	5.29×10^{-7}	5	a	100.0	0.640
trans 3.53×10^{-4}	1.06×10^{-6}	3	b	34.8	0.741[=]
trans 3.53×10^{-4}	1.06×10^{-6}	5	a	50.4	0.645
cis 3.015×10^{-4}	8.39×10^{-7}	3	c	6.43	0.122
cis 3.015×10^{-4}	8.63×10^{-7}	5	d	14.42	0.169[=]
cis 3.015×10^{-4}	9.05×10^{-7}	10	e	20.03	0.123
cis 6.030×10^{-4}	1.67×10^{-6}	3	c	3.26	0.124
cis 6.030×10^{-4}	1.72×10^{-6}	10	e	8.54	0.118

Benzophenone (0.05 M, E_T = 68.5 kcal/mol) was used as a sensitizer and 3660 Å light was used.

Light intensities are: $a = 8.265 \times 10^{-7}$, $b = 4.959 \times 10^{-7}$, $c = 4.402 \times 10^{-7}$, $d = 7.336 \times 10^{-7}$, and $e = 1.469 \times 10^{-6}$.

[=] These values are off from other measurements and some experimental errors must be involved.

For benzophenone sensitizer, the sum $\Phi_{t \rightarrow c} + \Phi_{c \rightarrow t} = 0.764 \pm 0.003$ while the intersystem crossing yield of benzophenone is 1.00 ± 0.02. Thus a significant amount of quantum waste is observed. In stilbene, th sum $\Phi_{t \rightarrow c} + \Phi_{c \rightarrow t} = 0.93 - 0.95$ when benzophenone is used and 0.86 - 0.90 if acetophenone is used (18). In the photoisomerization of α-methylstilbene, the sum is 0.99 which agrees with the equation 6 (16). The explanation for the quantum waste in stilbene isomerization was not given but self quenching of trans - stilbene triplets and formation of a weak complex between sensitizer triplet and stilbene, which later breaks up to give stilbene triplets but not with full efficiency were suggested as contributing factors. Also reversible addition of sensitizer to stilbene is suggested. In the photosensitized isomerization of β- styrylnaphthalene, the quantum waste is significantly larger than that of stilbene case. Specially $\Phi_{c \rightarrow t}$ is very small compared to stilbene case. This may be attributed to localization of triplet excitation in the naphthalene chromophore. This is very probable since the geometry of the cis isomer, in either excited singlet or triplet states as well as ground state, is not planar and the localization of excitation is expected to be more efficient compared to the trans isomer. It should be also noted that some unknown side reactions are observed and these reactions are lot more efficient in cis isomers. It seems the cyclization and dehydrogenation of β- styrylnaphthalene occur.

If we compare the ratio $\Phi_{t \rightarrow c} / \Phi_{c \rightarrow t} = 0.642/0.122 = 5.26$ and $(c/t)_{p.s.s.} = 1.29$, the discrepancy from the equation 9 is too great to consider as an experimental error. For high energy sensitizers, (k_{qt} / k_{qc}) was considered to be one and

$$\left(\frac{c}{t}\right)_{p.s.s.} = \frac{\Phi_{t \rightarrow c}}{\Phi_{c \rightarrow t}} \qquad (9)$$

The calculated value of the ratio in photostationary mixture with this equation agreed excellently with the experimental value for α-methylstilbene (16) even though it was a little off from the observed value in stilbene case.

It is most interesting to observe such a big difference between $(c/t)_{p.s.s.}$ and $\Phi_{t \to c}/\Phi_{c \to t}$ in β-styrylnaphthalene when benzophenone is used as a sensitizer. This clearly indicates that benzophenone transfers its triplet excitation preferentially to cis isomer. In other words, k_{qc} and k_{qt} are not diffusion controlled even though they were expected to be. The same thing may be true for the stilbene case. In fact, the highest rate constants measured by Herkstroeter for the quenching of triplets by the stilbenes were lower by a factor of 2 - 3 than the calculated diffusion encounter rates.

If the unsensitized reaction at room temperature follows the triplet mechanism with quantitative intersystem crossing, the photostationary states should be given by :

$$\left(\frac{c}{t}\right)_{p.s.s.} = \left(\frac{\epsilon_t}{\epsilon_c}\right)\left(\frac{k_{15} + k_{19}K_{12}}{k_{14} + k_{18}K_{12}}\right)$$

$$= \left(\frac{\epsilon_t}{\epsilon_c}\right)\left(\frac{\Phi_{t \to c}}{\Phi_{c \to t}}\right)$$

In stilbene, the calculated and observed values of $(c/t)_{p.s.s.}$ agree very well with each other indicating the triplet mechanism also obtains for the direct isomerization (16).

When the intersystem crossing yield of trans and cis isomers is not same, the ratio $(c/t)_{p.s.s.}$ will be given by :

$$\left(\frac{c}{t}\right)_{p.s.s.} = \left(\frac{\epsilon_t}{\epsilon_c}\right)\left(\frac{\Phi_{i.c.,c}}{\Phi_{i.c.,t}}\right)\left(\frac{\Phi_{t \to c}}{\Phi_{c \to t}}\right)$$

where $\Phi_{i.c.}$ is the intersystem crossing yield of β-styrylnaphthalene. If

TABLE XXII

Photostationary States Established by Irradiation of Stilbene Solution with 3130 Å Light

Stilbene Conc. (mol/l)	Solvent	ϵ_t / ϵ_c	% Cis observed at p.s.s.	% Cis Calculated
1×10^{-5}	n-Hexane	7.2	93.0	92.0
1×10^{-5}	Isohexane	7.2	93.0	92.0
1×10^{-3}	Benzene	5.83	89.7	90.3

TABLE XXIII

Photostationary States Established by Irradiation of β-Styrylnaphthalene Solution with Light of Various Wavelengths

Wavelength Å	Solvent	ϵ_t / ϵ_c	% Cis observed at p.s.s.	% Cis Calculated
2537	n-Hexane	0.844	40.8	81.5
3130	Benzene	2.32	26.2	93.1
3660	Benzene	4.07	41.2	95.5

above equation is good for β-styrylnaphthalene, $\Phi_{i.c.}$ of cis isomer should be a few times bigger than that of trans isomer. We have no reason to believe $\Phi_{i.c.,c}$ should be larger than $\Phi_{i.c.,t}$ and it is rather opposite of what we expect since it is expected to get better intersystem crossing yield from the trans isomer. Thus, it is unlikely that the triplet mechanism alone can be responsible for direct isomerization of β-styrylnaphthalene. As discussed in the photostationary states for direct irradiation, more than one metastable intermediate and side reactions are involved making the photochemistry of β-styrylnaphthalene complicated and it is impossible to assign one single mechanism to explain all the data.

Saltiel (72) recently proposed that the direct isomerization of stilbene involves a common twisted singlet state, the phantom singlet state, from the study of isotope effect in the isomerization of perdeuteriostilbene. However, it is doubtful to observe any isotope effect in cis ⇄ trans isomerization of perdeuteriostilbene since the mode of vibrations of carbon deuterium bonds may have nothing to do with the isomerization. In β-styrylnaphthalene, the phantom singlet state is very unlikely to be responsible for the isomerization since we observe a strong wavelength effect for both the quantum yields and the ratio of photostationary states mixture. The wavelength effect is not expected if the phantom singlet state is solely responsible for the isomerization.

In conclusion with all the data obtained from direct and sensitized photoisomerization of β-styrylnaphthalene, many interesting and unusual results are obtained. (1) A few conformers of electronically excited states which are not interconvertible are involved in direct isomerization. This is very unusual but it is clearly indicated by the wavelength effect on both the quantum yields and on the fluorescence spectra. (2) A quite efficient triplet energy transfer from sensitizers to β-styrylnaphthalene is observed. However, most interestingly, benzophenone which is considered to be a high energy sensitizer, transfers triplet excitation preferentially to the cis isomer. Both k_{qt} and k_{qc} were expected to be diffusion controlled. However, the comparison of $(c/t)_{p.s.s.}$ and $(\Phi_{t \rightarrow c}/\Phi_{c \rightarrow t})$ indicates the opposite when benzophenone is used as a sensitizer. (3) A significant quantum waste is observed in both direct and sensitized photoisomerization as predicted because of localization of excitation in the naphthalene chromophore. The effect was far more pronounced in direct isomerization, perhaps because the excited singlets are shorter lived than triplets made by energy transfer. The sum of quantum yields in the direct isomerization, $\Phi_{t \rightarrow c} + \Phi_{c \rightarrow t}$, was less than 0.5. (4) Definitely a singlet mechanism is involved perhaps in conjunction with other mechanisms, in the direct isomerization. This may help to elucidate the mechanism of direct isomerization of stilbenes. (5) A solvent effect is observed in the direct isomerization and is attributed to solvation in the polarizable solvents. (6) A mild concentration effect was observed and explained in terms of self quenching at high concentrations and radiationless decay at low concentrations. Energy transfer was also included. (7) It seems that the nonvertical excitation is also effective in β-styrylnaphthalene as in stilbenes.

^{60}Co γ-ray Irradiation

It is known that aromatic compounds are generally relatively stable toward degradation by ionizing radiation such as ^{60}Co γ-rays. This stability was attributed to the availability of high electronic excited states having little probability of dissociation.

Radiation-induced cis ⇌ trans isomerization of stilbene and substituted stilbenes in benzene solution was investigated by Hammond and his co-workers (73). They concluded from the comparison of the radiostationary states and photostationary states established with high energy sensitizers that the radiation-induced isomerization involves formation and decay of excited triplet states of stilbenes. They believe from the studies of G values of triplets that a large fraction of the energy delivered to the system ultimately appears in the scavenging solutes as triplet excitation and the key step of kinetics is transfer of triplet excitation from solvent to solute. The proposed mechanism is as follows:

TABLE XXIV

Comparison of Radiostationary and Photostationary States

Starting Material	Radiostationary States in Benzene %	"High-energy" Photostationary States %
cis- and trans-Stilbene	58.79, cis	59.4, cis
cis- and trans-1,2-Diphenylpropane	54.65 , cis	54.75, cis
trans-Piperylene	57.5, trans	56.5, trans

$$C_6H_6 \rightsquigarrow (C_6H_6)^3$$

$$(C_6H_6)^3 + \textit{cis}\text{-olefin} \xrightarrow{k_2} C_6H_6 + (\text{olefin})^3$$

$$(C_6H_6)^3 + \textit{trans}\text{-olefin} \xrightarrow{k_3} C_6H_6 + (\text{olefin})^3$$

$$(C_6H_6)^3 \xrightarrow{k_4} C_6H_6$$

$$(\text{olefin})^3 \xrightarrow{k_5} \textit{cis}\text{-olefin}$$

$$(\text{olefin})^3 \xrightarrow{k_6} \textit{trans}\text{-olefin}$$

$$(C_6H_6)^3 + (C_6H_6)^3 \xrightarrow{k_7} (C_6H_6)^1 + (C_6H_6)^0$$

$$(C_6H_6)^3 + (C_6H_6)^3 \xrightarrow{k_8} (C_6H_6)^3 + (C_6H_6)^0$$

$$(C_6H_6)^3 + (C_6H_6)^3 \xrightarrow{k_9} 2(C_6H_6)^0$$

The crucial features of the mechanism are that $k_2 = k_3 = k$ (diffusion) and that the photochemically determined ratio of k_5 / k_6 gives the ratio of $G_{t \to c} / G_{c \to t}$. Meanwhile k_7, k_8 and k_9 are not important compared to k_2 and k_3.

The *cis* ⇌ *trans* isomerization reaction were carried out with β -styrylnaphthalene in benzene solution to low conversions (4~21 %) and the G values (100-ev yield) were obtained. These G values were corrected for the back reactions (74). The symbol G's are defined as follows: G_T = initial yield of substrate triplets, $G_{c \to t}$ = initial yield of *trans* from pure *cis* and $G_{t \to c}$ = initial yield of *cis* from pure *trans*. The results are shown in Table XXV.

Radiostationary states were also established by irradiating both *cis*- and *trans*- β-styrylnaphthalene solutions with various concentration in benzene for long periods of time and the results are shown in Table XXVI.

TABLE XXV

G Values of β-Styrylnaphthalene in Benzene

Starting Material	Conc. of Solute (mol/l)	% Conversion	$G_{t\to c}$ or $G_{c\to t}$	G_T	Dose Rate
trans- β-Styryl-naphthalene	2.626×10^{-2}	21.50 ± 0.79	1.58	3.58	a
trans- β-Styryl-naphthalene	2.631×10^{-2}	9.54 ± 0.38	1.63	3.70	b
trans- β-Styryl-naphthalene	3.938×10^{-2}	17.27 ± 0.37	1.76	4.00	a
trans- β-Styryl-naphthalene	3.947×10^{-2}	7.13 ± 0.24	1.77	4.02	b
trans- β-Styryl-naphthalene	5.250×10^{-2}	14.68 ± 0.54	1.92	4.36	a
trans- β-Styryl-naphthalene	5.263×10^{-2}	5.76 ± 0.12	1.87	4.25	b
trans- β-Styryl-naphthalene	1.178×10^{-1}	4.06 ± 0.09	2.21	5.01	c
cis- β-Styryl-naphthalene	3.539×10^{-2}	13.59 ± 0.25	2.40	4.17	c

Table XXV (continued)

a: Dose (benzene) = 6. 977 x 10^{19} cv/ ml/hr , tubes containing 2 ml of solutions were irradiated for 4 hours.

b: Same dose rate were used for 1 1/2 hours.

c: Dose = 27.272 x 10^{19} ev/2ml benzene/2hours

All values are means of three measurements.

TABLE XXVI

Radiostationary States of β - Styrylnaphthalene in Benzene

Starting Compound	Conc. of Starting Compound (mol/1)	% *Cis* at Stationary States	*(cis/trans)*$_{r.s.s.}$	Dose
trans- β -Styryl-naphthalene	1.764 x 10^{-2}	44.68	0.81	b
trans- β - Styryl - naphthalene	1.764 x 10^{-2}	44.30	0.80	c
trans- β - Styryl - naphthalene	2.626 x 10^{-2}	44.04	0.79	a

Table XXVI (continued)

Starting Compound	Conc. of Starting Compound (mol/l)	% Cis at Stationary States	$(\text{cis}/\text{trans})_{\text{r.s.s.}}$	Dose
trans - β - Styryl-naphthalene	3.527×10^{-2}	45.53	0.84	b
trans - β - Styryl-naphthalene	3.527×10^{-2}	44.57	0.81	c
trans - β - Styryl-naphthalene	5.291×10^{-2}	44.90	0.82	b
cis - β - Styryl-naphthalene	1.698×10^{-2}	43.27	0.76	b
cis - β - Styryl-naphthalene	1.698×10^{-2}	43.68	0.77	c
cis - β - Styryl-naphthalene	2.588×10^{-2}	43.68	0.77	c
cis - β - Styryl-naphthalene	2.588×10^{-2}	45.81	0.85	b
cis - β - Styryl-naphthalene	3.539×10^{-2}	43.92	0.78	c
cis - β - Styryl-naphthalene	3.539×10^{-2}	42.45	0.74 average 0.80 ± 0.03	d

Dose: $a = 6.80 \times 10^{21}$ ev, $b = 6.62 \times 10^{21}$ ev, $c = 1.66 \times 10^{22}$ ev, and $d = 6.022 \times 10^{21}$ ev.

The triplet energy of benzene is high enough (84.4 kcal/mol) to transfer the triplet excitation to cis- and trans- β-styrylnaphthalene with diffusion-controlled rate. A small amount of side products were observed. These are probably biphenyl, partially reduced biphenyl, hydrogen, and fulvene formed from bimolecular and unimolecular reactions of electrically excited states within spurs in benzene radiolysis. The cyclization and dehydrogenation of β-styrylnaphthalene were also observed to small extent. The formation of side products was far more efficient when the cis isomer was irradiated indicating that the side products are formed from cis isomer. The small difference between the $(c/t)_{r.s.s.}$ ratios of the cis and trans isomers as starting material may be attributed to these side reactions.

TABLE XXVII

Comparison of Radiostationary and Photostationary States of β - Styrylnaphthalene

Radiostationary State in Benzene % Cis	Photostationary States, % Cis			
	Direct Isomerization		Sensitized Isomerization	
	3660 Å in Benzene	2537 Å in n-Hexane	Benzophenone	Benzene
44.20	41.23	40.47	56.41	45.17

As shown in Table XXVII, there is good agreement between radiostationary state and photostationary state established with benzene as a sensitizer. However, there is a significant difference between radiostationary state and photostationary state when benzophenone is used as a sensitizer. Also, the photostationary states established with direct irradiation at

3660 and 2537 Å are very close to radiostationary states. As discussed in photosensitized reactions, there would be singlet reactions in photosensitized isomerization with benzene as a sensitizer. It seems there is also some singlet reaction in radiation-induced isomerization of β - styrylnaphthalene in benzene. This is not unexpected since we should get some excited benzene singlet which is long-lived. However, this singlet reaction was not serious in stilbene isomerization in benzene and is expected to be insignificant.

The similarity of radiostationary state and photostationary states with direct irradiation may be just a coincidence or singlet mechanism may be the dominating factor in determining radiostationary state. The latter is unlikely since some of the side products of the direct irradiation were not observed in radiation-induced reaction and even observed ones were formed in much smaller amounts than in the photoreactions.

The radiostationary *cis/trans* ratio in benzene should be determined by the ratio of triplet decay, k_5/k_6, if the mechanism proposed by Hammond *et al.* is applied. The decay ratio of β - styrylnaphthalene triplets was

$$(c/t)_{r.s.s.} = k_5/k_6 \qquad (11)$$

1.29 when benzophenone was used as a sensitizer. It also can be expressed by following equation :

$$\left(\frac{c}{t}\right)_{r.s.s.} = \frac{G_{t \to c}}{G_{c \to t}} \qquad (12)$$

and

$$(\% \underline{cis})_{r.s.s.} = \frac{G_{t \to c}}{G_{t \to c} + G_{c \to t}} \qquad (13)$$

The radiostationary *cis/trans* ratio is 0.80 ± 0.03 and $(G_{t \to c}/G_{c \to t})$ is 0.73 when 3.6×10^{-2} M solution of β - styrylnaphthalene is used. The agreement is good compared to benzophenone sensitized photoreactions. There is also excellent agreement between observed (44.2 %) and calculated (42.4 %) $(\% \underline{cis})_{r.s.s.}$. These observations strongly indicate that radiation-induced isomerization of β-styrylnaphthalene involves triplet mechanism and benzophenone shows some abnormality as a sensitizer for the β-styrylnaphthalene.

G_T values are plotted against the logarithm of the β-styrylnaphthalene concentration in Figure 28. These G_T values were determined by applying the decay ratio obtained from the stationary state measurements. This provides the measure of the number of β-styrylnaphthalene molecules that are excited to triplet states. As shown in Figure 28, G_T values of β-styrylnaphthalene agree excellently with those of stilbene and substituted stilbenes. This was expected since all acceptors are expected to quench the benzene triplets at the diffusion-controlled rate. Thus, all data obtained from γ-irradiation indicate the triplet mechanism for the isomerization of β-styrylnaphthalene in the radiolysis of benzene solution. It also indicates that the triplet energy of benzene is so high that k_5 and k_6 in radiolysis in benzene and k_{qc} and k_{qt} in photoisomerization with benzene sensitizer are diffusion-controlled or benzene triplet transfers excitation to both <u>cis</u> and <u>trans</u> isomers indiscriminately while benzophenone triplet prefers the <u>cis</u> isomer.

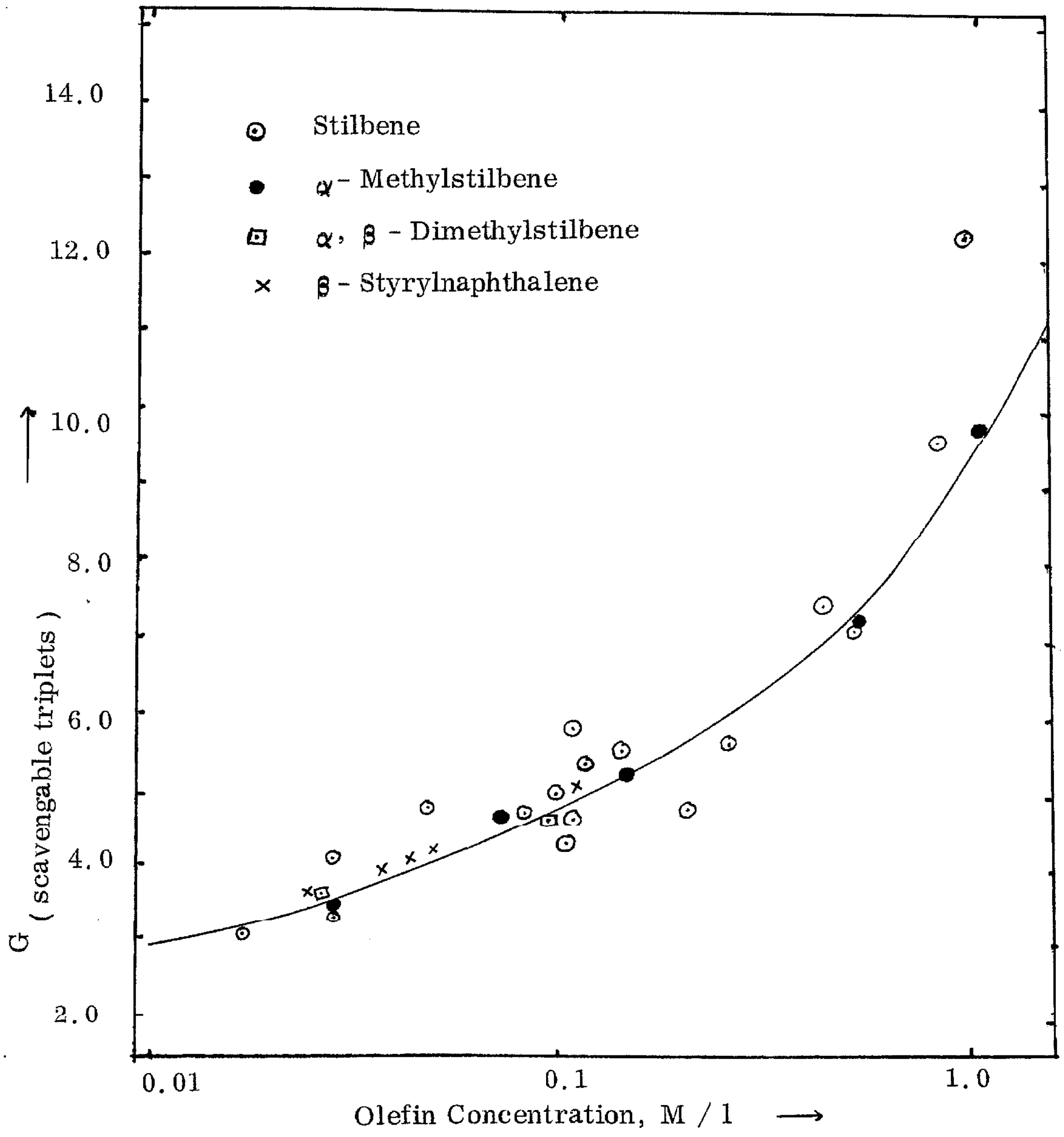


Figure 28 G Values for β - Styrylnaphthalene

EXPERIMENTAL

Syntheses

Benzyltriphenylphosphonium Bromide.- Triphenylphosphine (33.0 g) and benzylbromide (20.5 g) were dissolved in 300 ml of xylene (reagent grade) in a 500 ml round bottom flask and the mixture was refluxed for 26 hours with magnetic stirring. The mixture turned yellow at first then the white crystals were formed. The precipitate was filtered and washed with xylene and the product was dried under vacuum. The yield was almost 100 %.

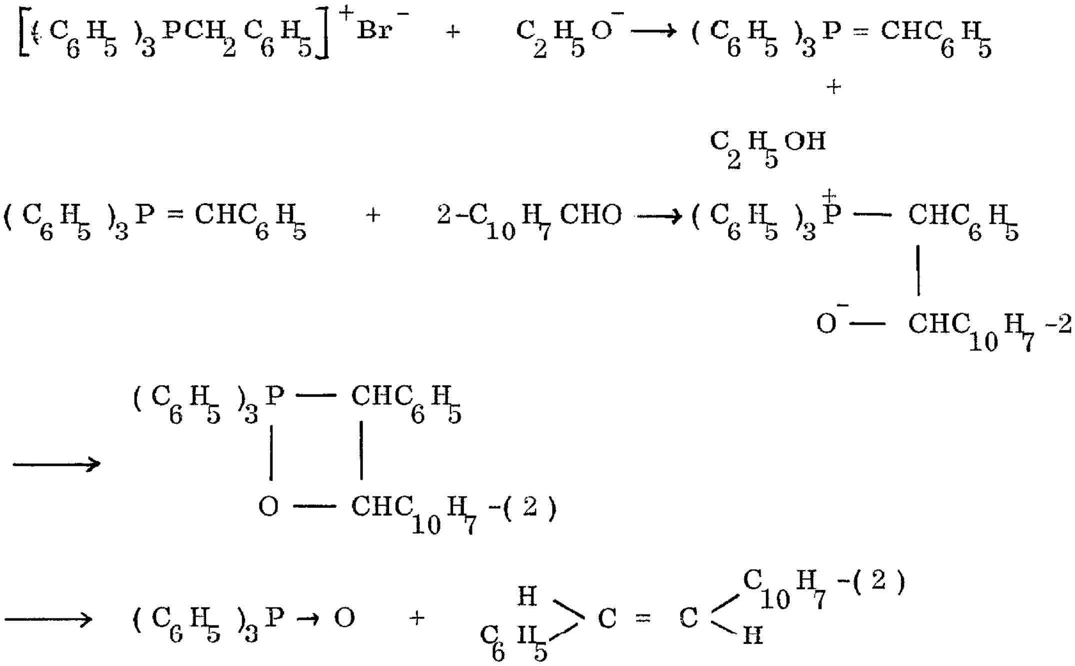
$$(C_6H_5)_3P \quad + \quad C_6H_5CH_2Br \longrightarrow \left[(C_6H_5)_3\overset{+}{P}C_6H_5CH_2\right] Br^-$$

trans- β - Styrylnaphthalene. - The Wittig reaction was used (44). Sodium ethoxide (5 g of sodium in 100 ml of absolute ethanol) was added slowly to the mixture of 2-naphthaldehyde (4.16 g) and benzyltriphenylphosphonium bromide (4.6 g) in 50 ml of absolute ethanol with magnetic stirring. The mixture was kept at room temperature for two days with stirring by magnetic bar. One hundred and fifty ml of water was added and the mixture was filtered to get a pale yellow residue. The residue was washed with 200 ml of 60 % ethanol and dried in vacuum at 56.5 °C over phosphorous pentoxide. The product was recrystallized from petroleum ether (60 - 70 °C b.p.) two or three times and chromatographed through the alumina column and finally recrystallized again from the purified n-hexane giving 1.43 g of pure trans- β -styrylnaphthalene (overall yield 23.3 %). m.p. 149.5 - 150 °C (Lit. 145 °C, 150 °C). The product was identified by m.p. , and IR, UV, and NMR spectra.

IR spectra were taken in chloroform and they show frequencies in cm^{-1}: 2950 (s), 2348 (m), 1575 (m), 1480 (s), 1390 (m), 1200 (vs), 1160 (vs), 945 (s), 900 (w), and 770 (vs).

UV spectra were taken in cyclohexane and they show absorption maximum wavelengths (in Å) as follows (the numbers in parentheses are log ϵ): 3324 (4.46), 3182 (4.58), 2823 (4.50), 2720 (4.48), 2521 (4.19), and 2258 (4.42).

NMR spectra were taken in carbon tetrachloride and shown in Figure 29. It shows a singlet at 7.13 p.p.m. , a multiplet at 7.40 p.p.m. , and a doublet at 7.65 p.p.m. .



$$[(C_6H_5)_3PCH_2C_6H_5]^+Br^- + C_2H_5O^- \longrightarrow (C_6H_5)_3P=CHC_6H_5 + C_2H_5OH$$

$$(C_6H_5)_3P=CHC_6H_5 + 2\text{-}C_{10}H_7CHO \longrightarrow \begin{array}{ll}(C_6H_5)_3\overset{+}{P} - & CHC_6H_5 \\ & | \\ O^- - & CHC_{10}H_7\text{-}2\end{array}$$

$$\longrightarrow \begin{array}{ll}(C_6H_5)_3P - & CHC_6H_5 \\ \quad | & | \\ \quad O - & CHC_{10}H_7\text{-}(2)\end{array}$$

$$\longrightarrow (C_6H_5)_3P \rightarrow O + \begin{array}{c}H \\ C_6H_5\end{array}\!\!> C = C <\!\!\begin{array}{c}C_{10}H_7\text{-}(2) \\ H\end{array}$$

+ Other products.

<u>cis</u>- β -Styrylnaphthalene. - (i) Photochemical Preparation. <u>trans</u>- β -Styrylnaphthalene in benzene solution was irradiated with Hanovia medium pressure mercury resonance lamp in Pyrex well with 3660 SF filter at room temperature. The <u>cis</u> isomer was isolated with Autoprep v.p.c. . The poor yield, various side products, and difficulty in separation made this method unsatisfactory. ^{60}Co γ-ray irradaition gave the same results.

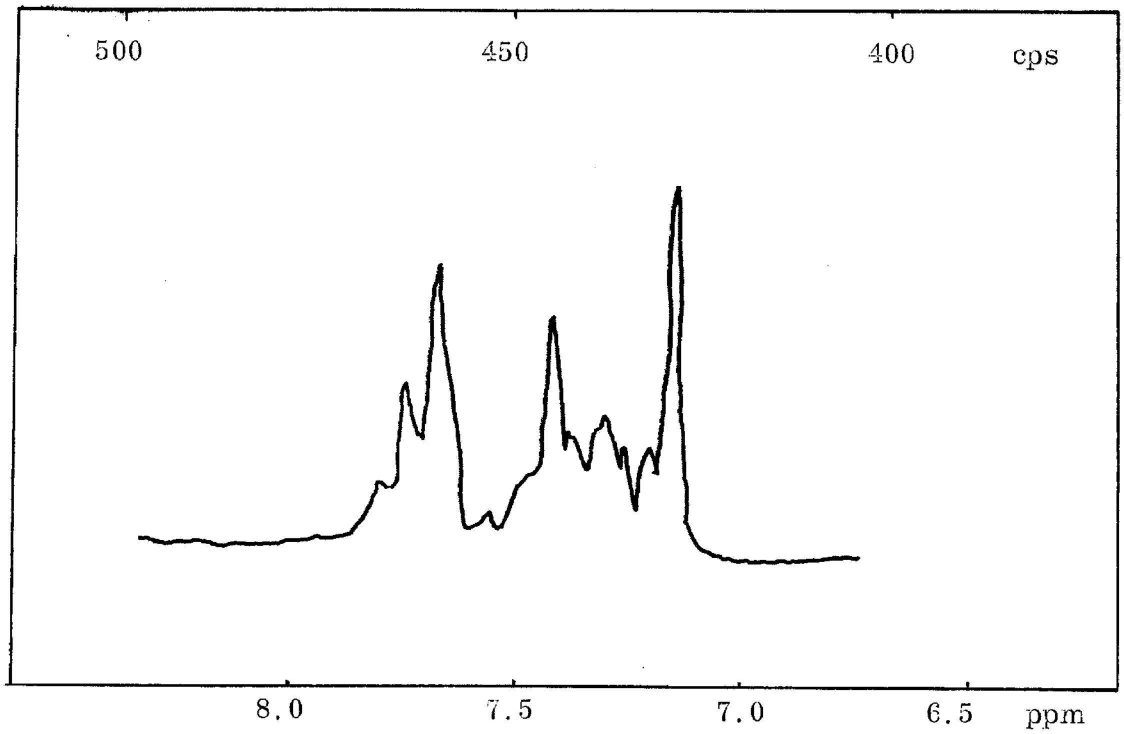
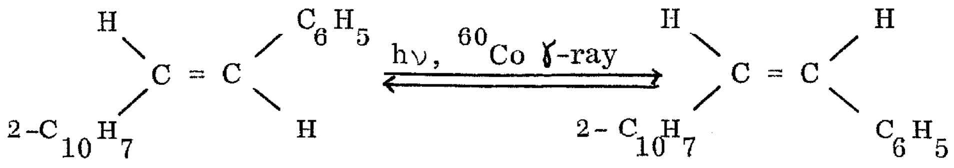
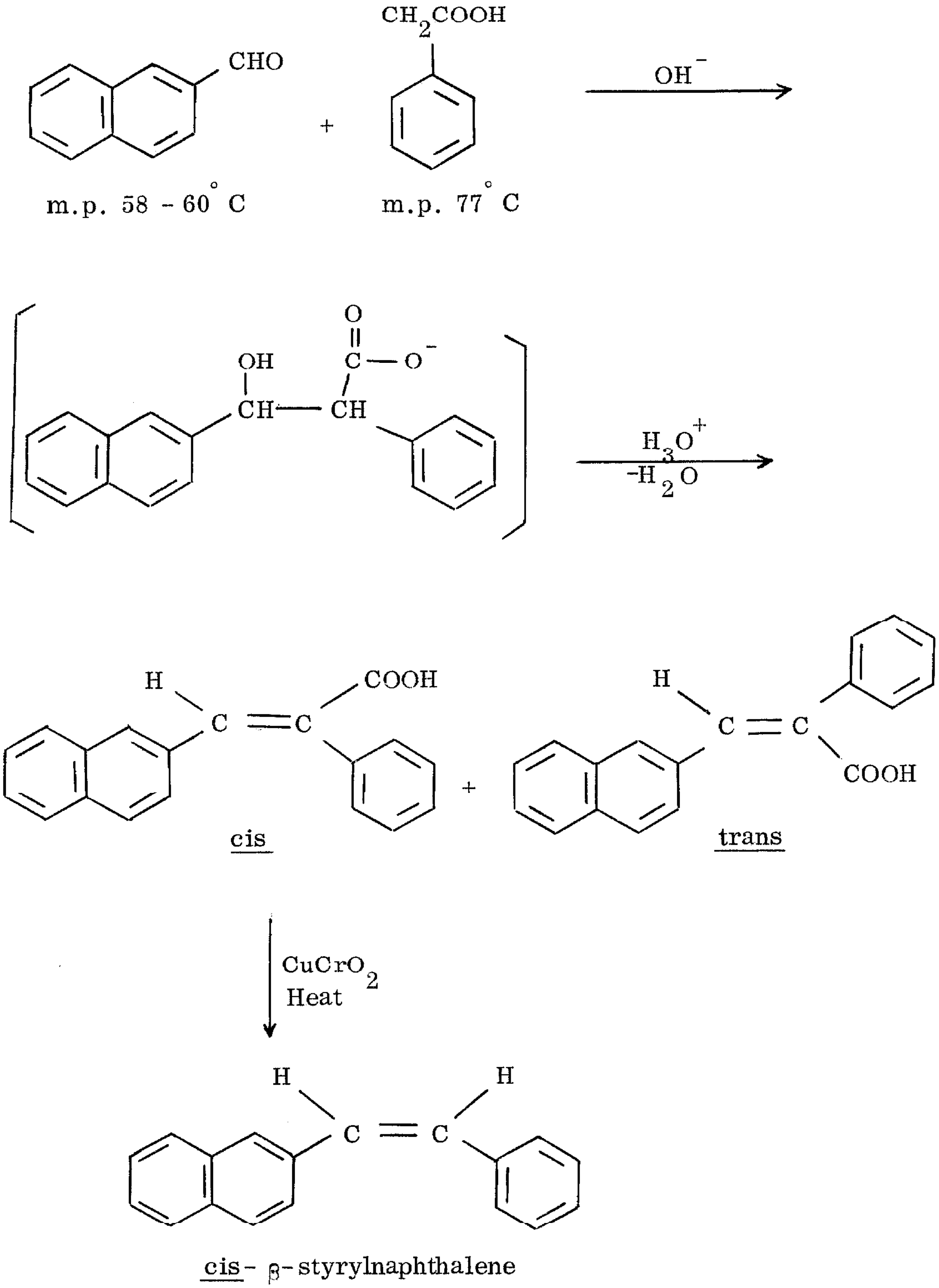


Figure 29 NMR Spectra of trans - β - Styrylnaphthalene



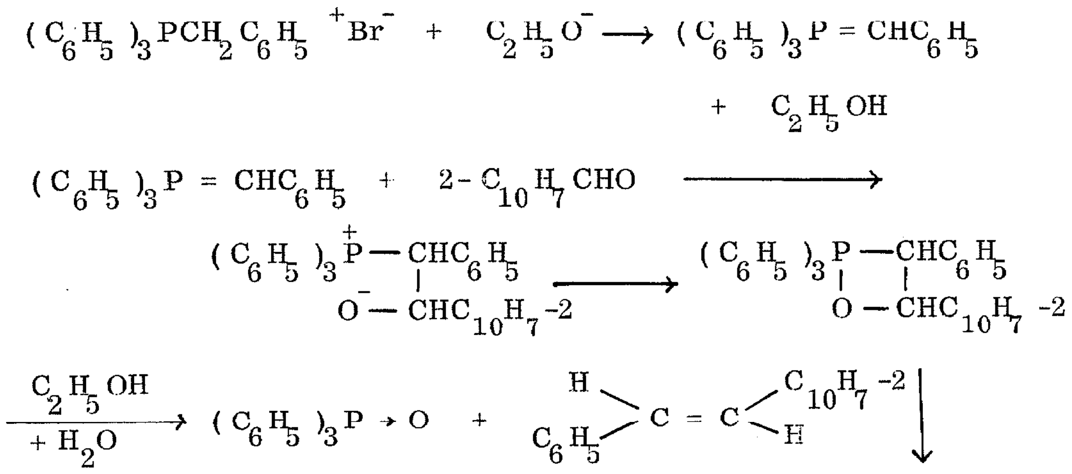
\+ Other products

(ii) Perkin Reaction and Decarboxylation (45) - Phenylacetic acid (2.5 g), 2-naphthaldehyde (4.6 g), triethylamine (2 ml), and acetic anhydride (2 ml) were measured into a 2.5 x 150 mm test tube and a few boiling stones were added. The test tube was attached to a cold finger condenser and refluxed for 35 minutes. The resulting yellow melt was cooled and 4 ml of conc. hydrochloric acid was added and swirled until the mixture set to a stiff paste. Ether was added and the mixture was warmed to dissolve the bulk of the solid and the solution was transferred to a separatory funnel with use of more ether. The etheral solution was washed twice with water and then extracted with a mixture of 25 ml of water and 5 ml of 10 % sodium hydroxide solution. The extraction was repeated twice and the dark colored etheral solution was discarded. The combined, colorless alkaline extract was acidified with 5 ml of acetic acid to pH 6 and the cis- β-(2-naphthyl)- α-phenylacrylic acid that precipitated (white precipitate) was collected. Crude acid was dried over phosphorous pentoxide under vacuum at 78.5 °C. The dry, crude acid (2.5 g) and copper chromite catalyst (0.2 g) were stuffed into a 20 x 180 mm test tube and 3.5 ml of quinoline (b. p. 237 °C) was added. The mixture was dried over a steam bath under vacuum (an aspirator) for 20 minutes to remove traces of moisture and was heated to 240 °C for 10 minutes with a microburner. The black solution containing suspended catalyst was cooled to 25 °C and 30 ml of ether was added. The solution was filtered by gravity using more ether. The quinoline was removed by extraction twice with water containing 3 - 4 ml of conc. hydrochloric


CHO
CH2COOH
+
OH−
m.p. 58 - 60° C
m.p. 77° C
O
OH
C — O−
CH— CH
H3O+
-H2O
H
COOH
C = C
cis
+
trans
CuCrO2
Heat
cis- β-styrylnaphthalene

acid in a separatory funnel. Then the etheral solution was shaken well with water containing a little sodium hydroxide solution, and the alkaline liquor was drawn off and acidified. Only a trace of precipitate indicated a near complete decarboxylation. The etheral solution was shaken with saturated sodium chloride solution for preliminary drying, filtered through sodium sulfate, and concentrated by evaporation to get a small amount of residual brownish oil which is impure <u>cis</u>- β -styrylnaphthalene. The yield was very poor.

(iii) <u>Wittig Reaction</u> - The same Wittig reaction was used as in the case of <u>trans</u>- β -styrylnaphthalene. The filtrate from the reaction of 2-naphthaldehyde and benzyltriphenylphosphonium bromide was extracted with benzene several times. The benzene solution was dried with magnesium sulfate and treated with 40 % of sodium bisulfite solution in water (3 ml of ethanol and 12 ml of sodium bisulfite solution) to remove any carbonyl compound. After drying over magnesium sulfate and evaporating benzene, the resulting brownish oil was chromatographed through an alumina column eluting with n-hexane. Repeated chromatography treatment yielded 99.5 % pure <u>cis</u>- β -styrylnaphthalene. Later it was observed that sodium bisulfite treatment is unnecessary. The product was characterized by IR, UV and NMR spectra.



$$(C_6H_5)_3PCH_2C_6H_5\;{}^{+}Br^{-} + C_2H_5O^{-} \longrightarrow (C_6H_5)_3P=CHC_6H_5 + C_2H_5OH$$

$$(C_6H_5)_3P=CHC_6H_5 + 2\text{-}C_{10}H_7CHO \longrightarrow$$

$$\begin{array}{l}(C_6H_5)_3\overset{+}{P}-CHC_6H_5\\ \qquad\quad\ \overset{-}{O}-CHC_{10}H_7\text{-}2\end{array} \longrightarrow \begin{array}{l}(C_6H_5)_3P-CHC_6H_5\\ \qquad\quad\ \ O-CHC_{10}H_7\text{-}2\end{array}$$

$$\xrightarrow[+H_2O]{C_2H_5OH} (C_6H_5)_3P \rightarrow O + \begin{array}{c}H\\C_6H_5\end{array}\!\!>C=C<\!\!\begin{array}{c}C_{10}H_7\text{-}2\\H\end{array} \downarrow$$

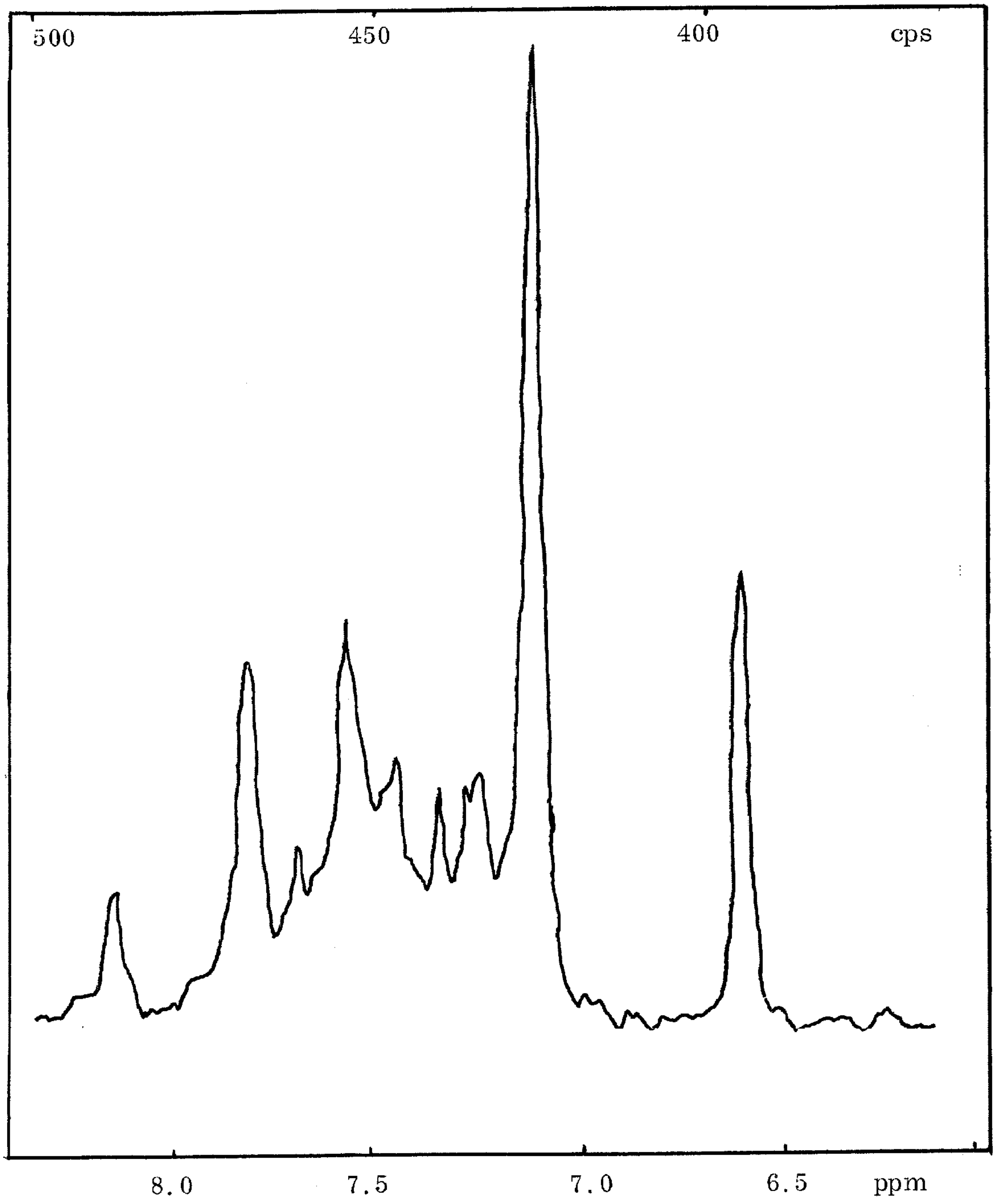
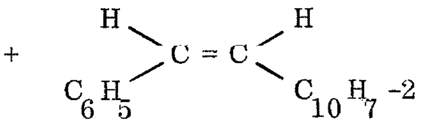


Figure 30 NMR Spectra of <u>cis</u> - β - Styrylnaphthalene



$\xrightarrow{\text{filter}}$ Filtrate $\xrightarrow[\text{benzene}]{\text{extract with}}$ $\xrightarrow[\text{and concentrate}]{\text{dry with } MgSO_4}$

$\xrightarrow[\text{alumina}]{\text{chromatograph through}}$ $\xrightarrow{\text{recrystalize}}$ pure cis-β-styrylnaphthalene

IR Spectra were taken in CCl_4 and shows $\bar{\nu}$ (cm^{-1}):
3022 (s), 1681 (vs), 1608 (s), 1575 (m) 1500 (s),
1445 (m), 1325 (s), 770 (vs), and 690 (s).
UV Spectra were taken in n-hexane. It shows $\lambda_{max.}$ in Å (log ε):
3020 (4.13), 2910 (4.18), 2770 (4.22), 2680 (4.25),
2433 (4.91), 2390 (4.93), and 2250 (4.96).
NMR Spectra are shown in Figure 30.

Solvents

Ethanol. - 5 g of magnesium turnings were added to 60 ml of absolute ethanol and refluxed after adding a few drops of carbon tetrachloride. After 2 hours, added 900 ml of absolute ethanol and refluxed for 8 hours and distilled on the column collecting middle portion (b. p. 77.5° C). Ethanol so prepared was transparent to UV above 2100 Å.

Ethyl Iodide. - The reagent grade ethyl iodide was chromatographed (Matheson, Coleman and Bell) through alumina (neutral, grade I, Woelm) and distilled in the dark from mercury collecting middle portion immediately before use (b. p. 71.0° C).

Benzene. - Analytical grade benzene (Mallinckrodt) was stirred with concentrated sulfuric acid for 4 hours. The colored sulfuric acid was separated with a separatory funnel and the process was repeated twice, once for 6 hours and the other for 12 hours. The third time, no colorization of sulfuric acid layer was observed. The benzene was washed with water and potassium carbonate solution in that order, the washing cycle was carried out twice, then dried with the mixture of magnesium sulfate and phosphorous pentoxide and distilled over phosphorous pentoxide on the column packed with glass helices. The middle portion (b. p. 80.0 °C) was collected. The benzene was redistilled if the phosphorous pentoxide layer was discolored during the distillation.

n-Hexane. - Technical grade n-hexane was stirred with conc. sulfuric acid three times (4, 4, 14 hours respectively in that order). No colorization of sulfuric acid occurred during the last operation. The liquid was washed with water and potassium carbonate twice respectively, dried over magnesium sulfate and distilled over phosphorous pentoxide on the column packed with glass helices. The middle portion (b. p. 69.0 °C) was collected.

Sensitizers

Acetophenone. - Acetophenone was obtained pure from Dr. DeBoer. It has been recrystallized from ethanol and water and twice from freshly distilled pentane which had been treated with conc. sulfuric acid until the acid layer was colorless, dried under high vacuum until it had melted at room temperature and distilled at 1 torr through a still which allowed no contact of either vapor or liquid with the stopcock grease.

Benzaldehyde. - Benzaldehyde (Matheson, Coleman and Bell, reagent grade) was distilled under reduced pressure right before use.

9-Fluorenone - 9-Fluorenone was obtained pure from Dr. Herkstroeter. It had been purified by recrystallization followed by zone melting. m. p. 83.8 - 84.0° C.

Anthracene. - Anthracene (Eastman Kodak, fluorescent grade) was used without further purification.

9,10-Dibromoanthracene. - 9,10-Dibromoanthracene was obtained pure from Dr. Saltiel. It had been recrystallized three times from carbon tetrachloride and sublimed under high vacuum. m. p. 228.6 - 229.0° C.

Mesitil. - Mesitil was obtained from Dr. Fry. It was recrystallized twice from purified petroleum ether immediately before use.

Azobenzene. - Azobenzene (reagent grade) was recrystallized from ethanol and sublimed under high vacuum right before use.

p-Benzoquinone. - p-Benzoquinone (Matheson, Coleman and Bell, practical grade) was sublimed several times in high vacuum immediately prior to use.

Benzophenone. - Benzophenone (Matheson, Coleman and Bell, reagent grade) was recrystallized three times from ethanol and zone refined. m. p. 45.9 - 46.0° C.

Miscellaneous

Naphthalene. - Naphthalene was obtained pure from Dr. W. G. Herkstroeter. It had been purified by zone melting.

Styrene. - Reagent grade styrene was chromatographed through alumina column and distilled right before use.

2-Vinylnaphthalene. - Reagent grade 2-vinylnaphthalene was chromatographed through alumina column and recrystallized twice from n-hexane.

Actinometry Materials

Phenanthroline. - Reagent grade 1,10-phenanthroline monohydrate (Matheson, Coleman and Bell) was recrystallized from redistilled water and stored in darkness. m. p. 99.0 - 100.0° C.

Ferric Ammonium Sulfate. - Ferric ammonium sulfate (Baker Chemical, reagent grade) was used without further purification.

Potassium Oxalate. - Potassium oxalate monohydrate (Allied Chemical, Analytical reagent grade) was used without further purification.

Potassium Ferrioxalate. - Potassium ferrioxalate was obtained pure from Mr. G. Vesley and used as obtained.

Preparation of Samples

Three ml of benzene or n-hexane solution of β-styrylnaphthalene, or β-styrylnaphthalene and sensitizers or quenchers in proper concentrations were placed in constricted 13 x 100 mm Pyrex or quartz test tubes.

Test tubes were simmered with aqueous solutions of orvus over steam bath for twelve hours, scrubbed carefully with a test tube brush, rinsed many times with distilled water and dried several hours in the oven at 110.0° C. Tubes prepared in this way were entirely wet by a single drop of water. The outside of sealed tubes were washed prior to irradiation.

All samples were evacuated by 3 - 4 freeze-pump-thaw cycles with cooling in liquid nitrogen to a pressure of less than 5×10^{-4} mm Hg using a vacuum line and sealed.

Samples for ^{60}Co γ-ray irradiation were prepared the same way but using only 2 ml of solution.

Irradiation of Samples

Irradiation of samples were carried out in the frequently described "merry-go-round" designed by Dr. G. Moses, or by taping the sample tubes to a immersion well in cases where duplication of conditions of light absorption was unnecessary. Various filter systems were used for different wavelengths. Samples were cooled in a water bath (30 - 31° C) during irradiation. A Hanovia 450 watt medium pressure mercury resonance lamp for 3130 and 3660 Å , and a Hanovia low pressure mercury lamp for 2537 Å were used.

Direct Irradiation

Quantum Yield Experiments. - Three duplicate tubes were made for each concentration in benzene or n-hexane. 3.0 ml of solutions were put into tubes which consisted of 13 x 125 mm Pyrex culture tubes attached with a constriction to a grease trap to prevent stopcock grease from flowing down into the tube during the degassing procedure and opening with a 14/20 standard taper ground glass female joint, or a similar tube with a bottom of 13 mm quartz tubing attached to the upper Pyrex by a graded seal. The tubes were made from new glass and washed after they came from the glass blower's annealing oven.

The tubes were degassed by freeze-thaw cycles on the vacuum line with cooling in liquid nitrogen. Two cycles were done at 10^{-4} torr with the forepump followed by three cycles with the oil diffusion pump at better than 10^{-6} torr. The tubes were sealed and stored in the dark until used.

The irradiation was carried out with the "merry-go-round" with various filters. The samples were irradiated until 3 - 7 % conversion was obtained.

Photostationary State Experiments. - Three to ten duplicate tubes were made for each concentration. These were irradiated for periods of time ranging from 5 hours to 2 weeks on the "merry-go-round" with the 3660, 3130, and 2537 Å filters. After irradiation, 0.5 - 1.0 microliter of solution was injected into the v. p. c. and both the total area and ratio of areas of the β -styrylnaphthalene isomers were measured. This process was repeated until the total area and the ratio of isomers remained unchanged which means the reaction had gone to completion. This experiment was carried out from both direction, cis to trans and trans to cis, and also with various concentrations of cis and trans isomers.

Sensitized Isomerization

Quantum Yield Measurements. - Specially purified cis- and trans-β -styrylnaphthalene were weighed out in a 10 ml volumetric flask with an appropriate amount of sensitizer and filled with the purified benzene to the mark to give proper concentrations. Same procedures were followed as in the case of quantum yield measurements with direct irradiation.

Photostationary State Experiments. - Stock solutions of various mixture of cis- and trans- β - styrylnaphthalene were weighed out to give proper concentration of β -styrylnaphthalene in benzene solution. An appropriate amount of sensitizer was weighed out in a 10 ml volumetric flask and the appropriate stock solution added. These solutions were then placed in 13 x 100 mm tubes, degassed by three freeze-pump-thaw cycle at 1 - 5.0 x 10^{-4} torr and sealed. The tubes were placed around a 450 watt Hanovia medium pressure mercury resonance lamp in a 31° C water bath and irradiated. Both stock solutions and the irradiated tubes were analyzed by v. p. c. .

Filter System

3660 F. - Corning C. S. 7 - 37 and 0 - 52 glass filters were combined and used in the "merry-go-round" for 3660 Å light. The transmission characteristics of this filter combination can be found elsewhere (46). The absorption spectra is shown in Figure 31.

3130 SF. - This filter consisted of an inner solution (nearest to the lamp) of 1.5 cm of 26 g of cobaltous sulfate in 100 ml of water and an outer solution of 0.8 cm of 132 mg of potassium chromate in 250 ml of aqueous 1 % of sodium carbonate solution. The solution holder was of quartz and was used with the "merry-go-round". Its transmission characteristics are shown in Figure 32.

2537 SF. - This consisted of an inner solution of 1 cm of 450 g of cobaltous sulfate and 300 g of nickelous sulfate in 1 l of water and an outer solution of 1 cm of 30 mg of p-nitrophenol in 1 l of water. The solution holder was of quartz and used with or without the "merry-go-round". Its transmission characteristics are shown in Figure 33.

Actinometry

Modestly improved version of the method of Hatchard and Parker (47) was used. Ferrioxalate solution was prepared by pipetting 3 ml of ferric alum (0.2 M) in 0.1 N sulfuric acid and 3 ml of potassium oxalate (0.6 M) in 0.1 N sulfuric acid into a 100 ml volumetric flask and diluting to 100 ml with 0.1 N sulfuric acid. Three ml of this solution was pipetted into clean test tubes to be used for reactions. One tube was saved for a blank. The tubes were irradiated for measured time intervals and 2 ml of irradiated solutions were pipetted into 10 ml volumetric flasks. One ml of 0.1 % phenanthroline solution in water and 1 ml of acetic-acetate buffer

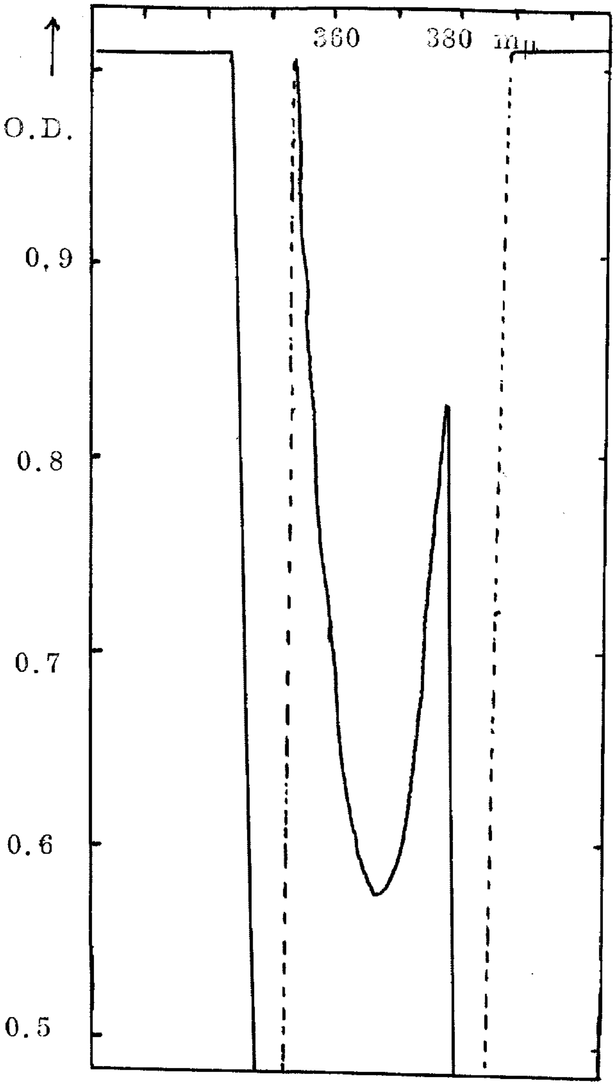


Figure 31 UV Absorption Spectra Of 3660 Å Corning Glass Filter

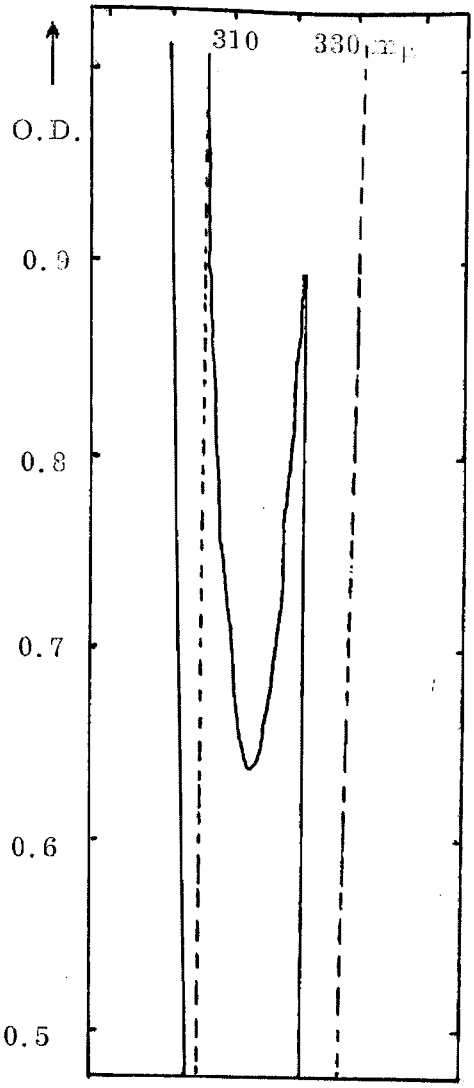


Figure 32 UV Absorption Spectra of 3130 Å Solution Filter

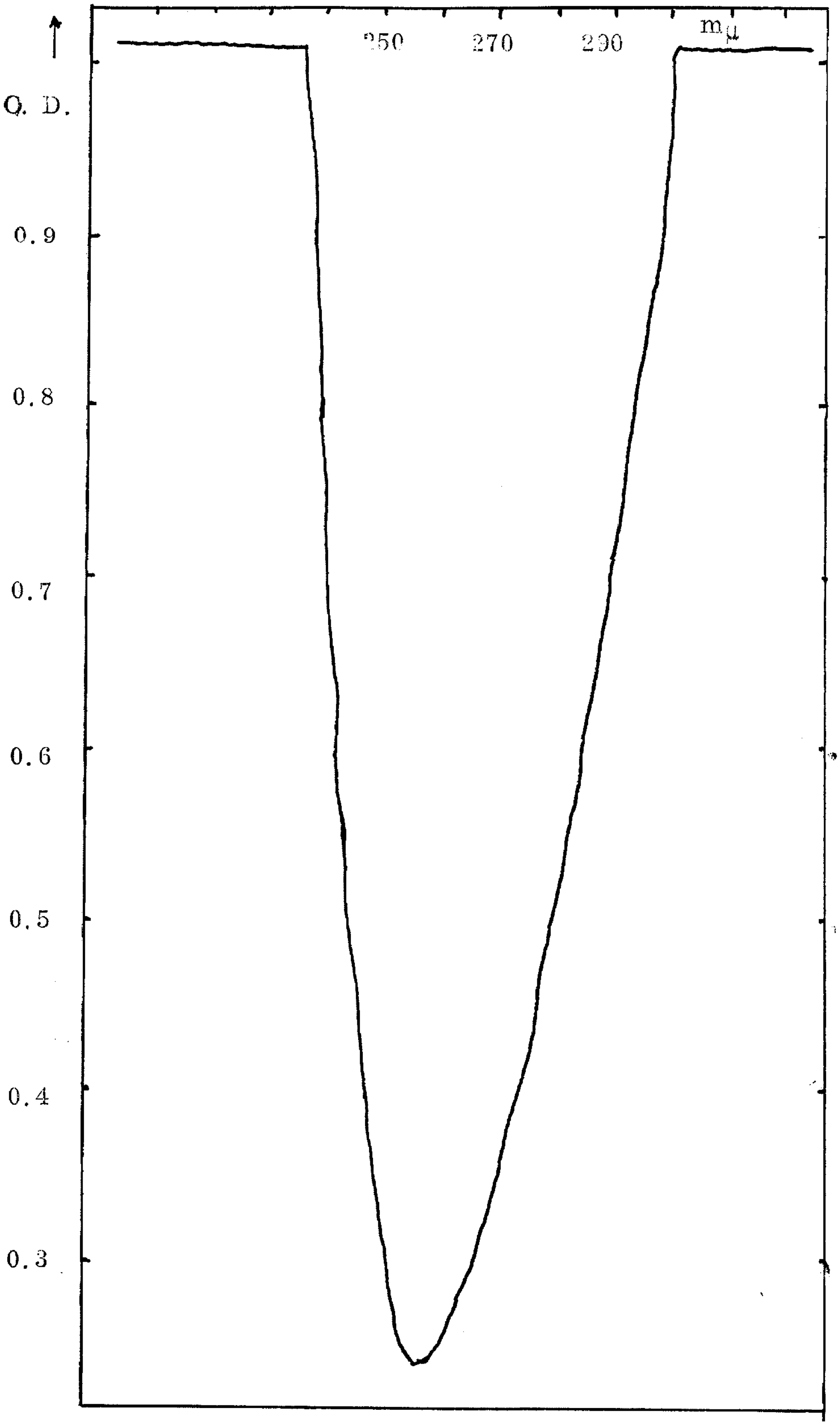


Figure 33 UV Absorption Spectra of 2537 Å Solution Filter

were added and diluted to 10 ml with water. After 25-30 minutes, the optical densities were measured at 5100 Å using unirradiated sample as a blank with Beckman D. U. Spectrophotometer and the light intensity was calculated by the following equation.

$$I = \frac{(\mathrm{O.D.})(F)(V)}{\Phi \times A \times t} \quad \text{Einstein/Min.}$$

where V: volume irradiated in ml, Φ: quantum yield at the wavelength of irradiation, $\Phi_{2537\,\mathrm{\AA}} = 1.25$, $\Phi_{3130\,\mathrm{\AA}} = 1.24$, $\Phi_{3660\,\mathrm{\AA}} = 1.21$,

A: % of light absorption at the wavelength of irradiation,

$$A_{2537\,\mathrm{\AA}} = 1, \qquad A_{3130\,\mathrm{\AA}} = 0.999, \qquad A_{3660\,\mathrm{\AA}} = 0.998,$$

$$F = \left((V)_{\mathrm{flask}} = 10 \,/\, (V)_{\mathrm{aliquot}} = 2 \right) \cdot \left(1 \,/\, \epsilon_{5100\,\mathrm{\AA}} \right) \cdot \left(1 \,/\, 10^{3} \right) = 4.53 \times 10^{-7},$$

$$\epsilon_{5100\,\mathrm{\AA}} = 11030,$$

t: time of irradiation.

^{60}Co γ-Irradiation

The samples were prepared the same way as in the case of UV irradiation in Pyrex tubes. Only 2 ml of various concentrations of cis and trans isomers in benzene were used. Irradiation were performed at Jet Propulsion Laboratory, Caltech, Pasadena by Dr. D. G. Whitten with ^{60}Co γ-ray sources. Both G values and radiostationary states were measured from v. p. c. analyses.

Vapor Phase Chromatography

All v. p. c. analyses were done with Loenco Model 70 dual flame gas chromatograph with independently heated column oven, detector oven and injector block. The helium flow rate was always 60 ml/min. . The column used for all analyses were hand packed in six foot lengths of 1/4 inch aluminum tubing. The packing material consisted of 5 % SE - 30 silicon grease on chromosorb W. or 5 % silicon gum rubber on chromosorb W. . The column temperature was 275 - 280 °C for all analyses and detector oven was at 290 - 300 °C for all analyses.

Emission Spectra

Fluorescence Spectra. - Fluorescence spectra were taken in purified benzene solution by Dr. D. G. Whitten at Jet Propulsion Laboratory, Caltech, Pasadena. They were also taken at Caltech by the author with an Aminco-Bowman Spectrophotofluorometer at various temperatures in benzene solution and in methyl cyclopentane-ethanol glass at 77 °K.

Phosphorescence Spectra. - Phosphorescence spectra were tried by Dr. D. G. Whitten at 77 °K in methyl cyclopentane-ethanol glass with an Aminco-Bowman Spectrophotofluoro- and phosphorometer.

Fluorescence Quenching Experiments. - Various amounts of purified piperylene were added to benzene solutions of cis- and trans β-styrylnaphthalene solution and fluorescence spectra were taken with various exciting wavelengths with an Aminco-Bowman Spectrophotofluorometer.

Flash Spectroscopy. - Flash spectroscopy was performed by Mr. G. Vesley.

Absorption Spectra. - All UV absorption spectra were taken with a Cary Model 14 Spectrophotometer. All optical densities were measured with a Beckman D. U. Spectrophotometer.

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PART TWO

PHOTOCHEMISTRY OF N - METHYL - 4 - PYRIDONE AND N - METHYLLUTIDONE

INTRODUCTION

It is well known that pyrimidine bases, uracil, cytosine, and thymine, undergo dimerization and hydration, along with other side reactions, when irradiated with ultraviolet light. Most of the recent investigations of the chemical and biological effects of UV irradiation on DNA and bacterial viruses were entirely concerned with this pyrimidine base reactions, specially the inter- or intramolecular dimerization of pyrimidine bases of nucleic acids (1). Even though thymine dimer is known to be mainly responsible for the biological damage by UV irradiation of DNA bacteria, and phages, photoproducts other than thymine dimers play an important role in the inactivation and various reactivation mechanism. Since the genetic information in the cell is borne and transmitted by the nucleic acids according to present concepts, it is very important to know how UV damages and reactivates DNA and consequently the photochemistry of pyrimidine bases is of great importance.

Since Sinsheimer and Hastings (2) opened up the field of photochemistry of pyrimidine bases, innumerable data have been accumulated. However, the mechanisms of the reactions are not yet solved.

When an aqueous solution of uracil is irradiated with 2537 Å light, 6-hydroxyuracil is formed with a quantum yield of 0.052 (2, 3, 4). The remainder of uracil is transformed to a number of other products. A similar behavior is observed by1-methyluracil and 1,3-dimethyluracil (5 - 9). However, the quantum yields and the extent of reversibility were different as shown in Table I (1). This is not unexpected since the reaction mechanism would be different as the substituted uracils will have different tautomers.

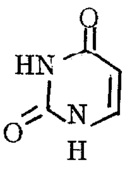
Uracil can exist in many forms of tautomers in aqueous medium. In nucleosides, nucleotides and DNA, the tautomers I, II, and IV are important since 1 - N is bound to sugar. The energy level scheme of these tautomers is not expected to be the same. Consequently the different reac-

TABLE I

Quantum Yields at 2537 Å for Some Pyrimidine Derivatives Irradiated in an Atmosphere of Air; in Neutral or Aqueous Medium at Room Temperature, at Concentrations of 10^{-3} to 10^{-4} M; and Nature of Reaction (Whether Reversible or Not by Heating at Neutral pH or by Acidification or, in Some Instances, by Alkalization). Calculated Quantum Yields Are for Initial Stage of Reaction and Based on Changes in Absorption Spectrum.

Compound	$\Phi \times 10^3$ (moles/einstein)	Reversibility
Uracil	5.2, 6.0, 2.5	50 %
1-Methyluracil	12.5	High
1,3-Dimethyluracil	10.4	100 %
Uridine	21.6, 16.0	90-100 %
2':3'-Isopropylidene-uridine	21	90-100 %
Uridine-2'-phosphate	21.6	90-100 %
Uridine-3'-phosphate	21.6, 19.0	90-100 %
Uridine-2':3'-phosphate	21.6	90-100 %
UDP, UTP, UDGP	-	High
2-Ethoxyuracil	8.0	Nil
4-Ethoxyuracil	very low	Nil
2,4-Diethoxypyrimidine	very low	Nil
Thymine	0.4, 0.03	Nil
Thymidine	0.65, 0.025	Nil
Thymidylic Acid	1.0, 0.3	Nil
5-Bromouracil	1.7	Nil
5-Nitrouracil	1.0	Nil
5-Bromo-1,3-dimethyluracil	10.4	Nil

tion mechanisms might be expected from different tautomers.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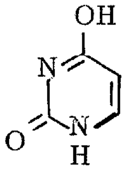
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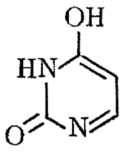
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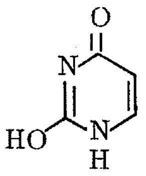
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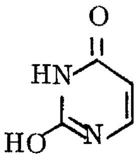
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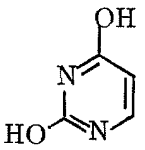
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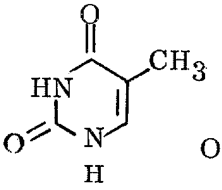
When a solution of thymine in water is frozen and then subjected to irradiation at 2537 Å in the frozen state, thymine dimer is formed with a cyclobutane ring (10, 11). This dimerization is not observed in aqueous solution. Wang et al. (15) recently reported that uracil, 5-hydroxyuracil, and 5-formyluracil were identified by paper chromatography as photo-oxidation products from an aqueous solution of thymine which was irradiated with gemicidal lamp. Thymine can also exist in several tautomeric forms.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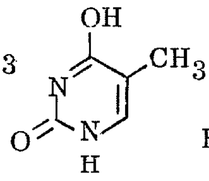
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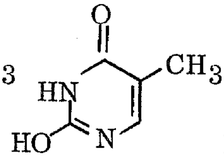
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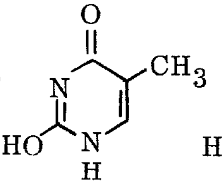
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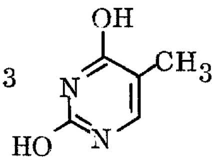
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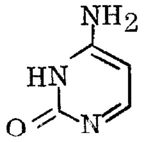
The forms I, II, and IV are important in nucleotides and are expected to play important role in dimerization.

The photochemistry of cytosine is the most complicated because of the amino group. It is reported that cytosine and 1-methylcytosine form photoproducts which, like the corresponding uracil analogues, revert to the parent substances in the dark under the influence of acid, base or heating at neutral pH (1). These products were interpreted as 6-hydroxycytosine and 1-methyl-6-hydroxycytosine. The hydrogen isotope effect, Φ_{H_2O}/Φ_{D_2O} , for both cytosine and 1-methylcytosine is around 2.2 which agrees with the hydration reaction (12, 13). However, it is also reported that deamination proceeds when cytosine is irradiated (14).

Cytosine can exist in several tautomeric forms.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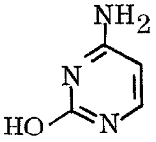
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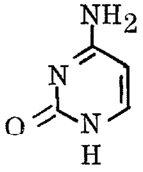
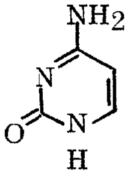
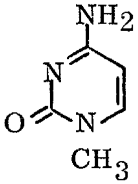
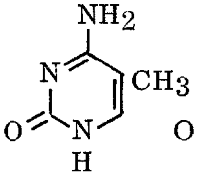
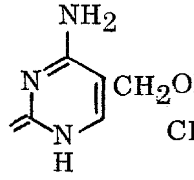
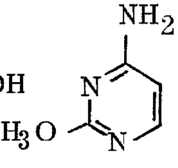
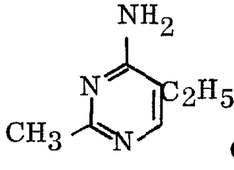
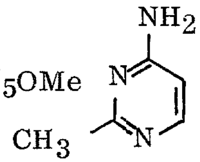

III

As shown in Table 2, the different tautomers are expected to undergo different reactions.

All these complicated reactions led us to investigate the photochemistry of model compounds, N-methyl-4-pyridone and N-methyllutidone, which would exist in only one form in aqueous solution. These compounds are fixed so that the tautomerism is impossible.

TABLE II

Photochemical Reactions of Some 4-Aminopyrimidines in Aqueous and Anhydrous Solvents(All λ's in Å)

Compound							
Principal long-wave absorption maximum in water at pH 7	2670	2740	2735	2700	2700	2720	2660
Principal absorption maximum of product in water	2400	2400	2850	2820	3020	3050	2950
Reversibility	50 %	50 %	nil	nil	partial	100 %	nil
Principal absorption maximum of photoproduct in ethanol	3000	3100	3100	---	Only slow drop in absorption	Only slow drop in absorption	2950
Reversibility	partial	partial	nil	---	---	---	nil
Remarks	----	----	Reaction optimal at pH 9 in water	Reaction optimal at pH 9 in water	---	In acid medium reaction is reversible	Photoproducts identical in water, ethanol or hexane

RESULTS AND DISCUSSIONS

Aqueous solutions of N-methyl-4-pyridone with various concentrations were irradiated with a low pressure mercury lamp, or a gemicidal lamp in a quartz tube.

No color developments were observed in dilute solutions ($10^{-5} \sim 10^{-4}$ M/l) but a drastic change in optical density at 2610 Å was observed as shown in Table III.

TABLE III

Optical Density Change at 2610 Å When Aqueous Solutions of N-Methyl-4-Pyridone Were Irradiated.

Irradiation Time (hours)	O. D.	
	1.91×10^{-5} M	8.24×10^{-5} M
0	0.314	1.355
5.5	0.141 (44.9 %)	0.930 (68.6 %)
19.3	0.023 (7.32%)	0.298 (22.0 %)

When concentrated solutions ($10^{-2} \sim 10^{-1}$ M) were irradiated, yellow color was developed at first, then turned into brownish yellow in 20 hours, and photoreaction of N-methyl-4-pyridone was stopped, possibly because of self-quenching or quenching by products. A polymerization reaction may be responsible for the color developments.

No regeneration of N-methyl-4-pyridone was observed when the irradiated solutions were left in darkness for 2 days or when the solutions were acidified with hydrochloric acid to pH 1 . When the solutions were heated to 150 ° C, a slight increase of optical density at 2610 Å was observed but not to a significant extent. In uracil, the recovery was very high since

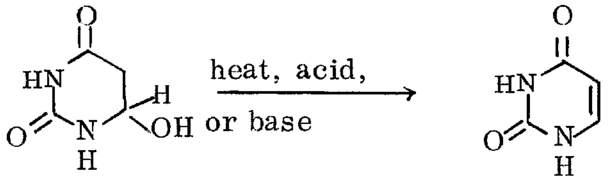
TABLE IV

Heating of Irradiated Solutions of N-Methyl-4-pyridone
(1.0×10^{-4} mol/l)

Temperature	Heating Time (hrs.)	O. D.*	Δ O. D.
120° C	0	0.572	
120° C	1.5	0.642	0.070
150° C	0	0.572	
150° C	1.5	0.652	0.080

* Optical density of original solution was 1.360.

the main reaction was hydration and dehydration can be achieved easily in these conditions. It seems that some other reaction, such as ring-opening,



proceeds after hydration. It is also probable that dimerization or reactions other than hydration occur during irradiation.

A few chemical characterizations were attempted.

(a) Benedict's Test. (16): Irradiated solution of N-methyl-4-pyridone (20 ml) was added to Benedict's reagent solution (10 ml) in a test tube and heated to boil in a water bath. A small amount of red precipitate was formed at the bottom of the test tube. No reaction occurred with starting material.

Benedict's reagent reacts with aliphatic aldehydes but not with aromatic aldehydes. This test suggests that some aliphatic aldehydes are formed by irradiation of N-methyl-4-pyridone.

$$\mathrm{RCHO} \quad + \quad 2\ \mathrm{Cu^{++}}\ (\text{Citrate Complex}) \quad + \quad 4\ \mathrm{OH^-}$$

$$\longrightarrow \quad \mathrm{RCO_2H} \quad + \quad \mathrm{Cu_2O}\downarrow \quad + \quad 2\ \mathrm{H_2O}$$

(b) Tollen's Test. (16): A few drops of irradiated solution was added to Tollen's reagent in a test tube. A black-grey silver deposit was observed on the upper layer. The original solution of N-methyl-4-pyridone did not react with the reagent.

Tollen's reagent is known to give a positive reaction with aldehydes, aromatic amines, α -naphthol and other phenols.

$$\mathrm{RCHO} \quad + \quad 2\ \mathrm{Ag(NH_3)_2OH} \longrightarrow 2\ \mathrm{Ag}\downarrow \quad + \quad \mathrm{RCO_2NH_4}$$

$$+ \quad \mathrm{H_2O} \quad + \quad 3\ \mathrm{NH_3}$$

(c) Fuchsin-Aldehyde Test. (16): A few drops of irradiated solution was added to 2 ml of reagent solution but no color change was observed in 24 hours. Aldehydes are expected to develop violet purple when treated with the reagent, but the test is not very sensitive and may fail with dilute solutions of aldehydes.

(d) Potassium Permanganate Test. (16): Potassium permanganate solution (2 %) in water was added to 2 ml of irradiated solution of N-methyl-4-pyridone drop by drop. The color of permanganate solution faded. No decolorization was observed with original sample solution.

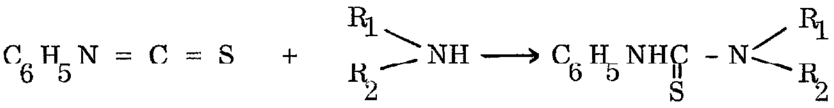
A positive test is expected with aldehydes, olefins, phenols, and aryl amines.

(e) 2, 4-Dinitrophenyl Hydrazine Derivatization (17): An irradiated solution of N-methyl-4-pyridone was lyophilized to get some black - brown oily residue. The residue was dissolved in 20 ml of 95 % ethanol. Freshly prepared 2,4-dinitrophenylhydrazine reagent solution was added to the oily residue. A tiny amount of unidentifiable black precipitate was obtained after standing at room temperature for several days.

(f) Sodium Bisulfite Test (16): The reagent solution was prepared by dissolving 20 g of sodium bisulfite in 30 ml of water and adding 5 ml of 95 % ethanol. One ml of this reagent was added to 1 ml of concentrated solution of irradiated N-methyl-4-pyridone sample. However, no precipitate was observed. The reagent gave a white precipitate with a drop of neat benzaldehyde. It seems that the concentration of photoproduct is too low to give positive test.

(g) Phenylisothiocyanate Test for Secondary Amine (16): A few drops of phenylisothiocyanate solution was added to 1 ml of concentrated, irradiated solution of N-methyl-4-pyridone and the mixture was shaken for 2 minutes. No change was observed. The solution was heated on a low flame for 3 minutes and cooled in ice beaker. It was stored in a refrigerator over night but no change was observed.

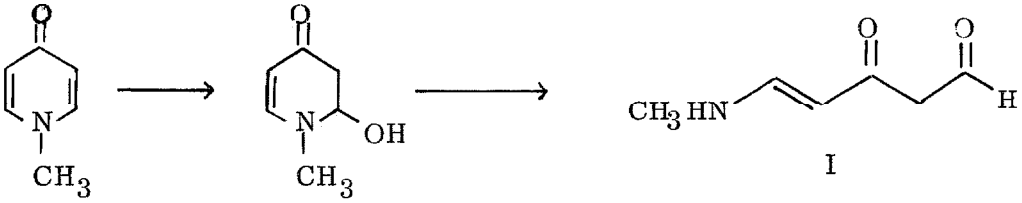
This test is expected to give positive results for secondary amines. However, it seems that the concentration of photoproducts is too low to give a positive reaction.



$$C_6H_5N = C = S \quad + \quad \begin{matrix} R_1 \\ R_2 \end{matrix}{>}NH \longrightarrow C_6H_5NH\overset{}{\underset{\overset{\|}{S}}{C}} - N{<}\begin{matrix} R_1 \\ R_2 \end{matrix}$$

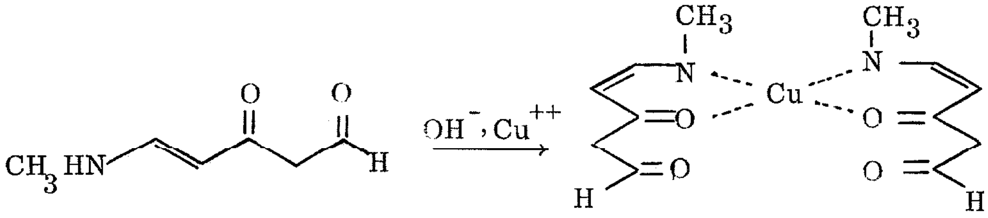
(h) Ferric Chloride Test (16): The production of color with ferric chloride solution is typical of phenols and enols. A drop of ferric chloride solution (1 %) was added to irradiated solution of N-methyl-4-pyridone. However, no color was produced. This negative result is not a proof that no enols are formed since this test is often negative to many of phenols and enols.

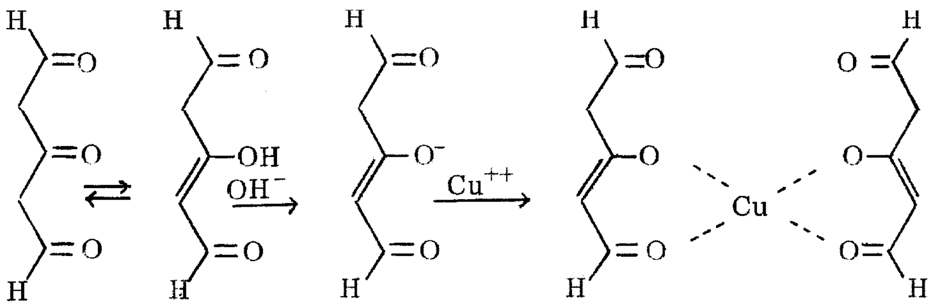
The tests show that one or more reducing compounds is formed from photolysis of N-methyl-4-pyridone. Dimers would be negative for those tests. If N-methyl-4-pyridone is hydrated, it would easily undergo ring opening since α-hydroxy amines decompose or polymerize very easily (17).


I

The compound I would give positive results in tests performed earlier. However, it will also undergo oxidation and polymerization very easily. Probably these polymerization products are responsible for the yellow and brownish-yellow colors of irradiated solutions of N-methyl-4-pyridone.

An attempt was made to make chelates of photoproducts of N-methyl-4-pyridone. If compound I is formed, it will form chelate with cupric acetate, or deaminated product would also form chelate with cupric acetate.





Irradiated solution (6 l of 6.8 x 10^{-5} M) was lyophilized and 10 g of cupric acetate was added with 50 g of sodium acetate. However, no chelate was formed. The negative result is not necessarily significant because the photoproduct is present as a very dilute aqueous solution.

A few chromatographic methods were tried to separate photoproducts without success. Thin layer chromatography with silica gel G plates was used and four spots were observed including N-methyl- 4-pyridone with R_f values of 0.27, 0.41 (N-methyl-4-pyridone), 0.8 and 0.9 when methanol was used as developing solvent. However, an attempt to isolate constituents with preparatory thin layer plates was unsuccessful. Separation of products with column chromatogram of silica gel G, alumina, and silicic acid was also unsuccessful.

The reaction was followed in CD_3OD and in D_2O by NMR, but no spectral change was observed even though the color of the solution was changed as irradiation time was prolonged. The residue obtained when the irradiated solution was lyophilized was mixed with potassium bromide to prepare pellets and IR spectra were taken. It suggested that N - H and COOH groups are present but in large the spectra were the same as those of N-methyl-4-pyridone.

When an aqueous solution of N-methyl-4-pyridone (9.0 x 10^{-4}) is irradiated, the optical density at 2610 Å decreases and a new maximum appears at 3266 Å . This new maximum may be attributed to an $n - \pi^*$ transition of a conjugated carbonyl compound, Compound I or a polymer from it could be responsible for the new maximum.

Mass spectra were taken but no useful information could be obtained from them since the products are expected to be very unstable at high temperatures.

The failure of identification of photoproducts from N-methyl-4-pyridone can be attributed to unstability of photoproducts and to the fact

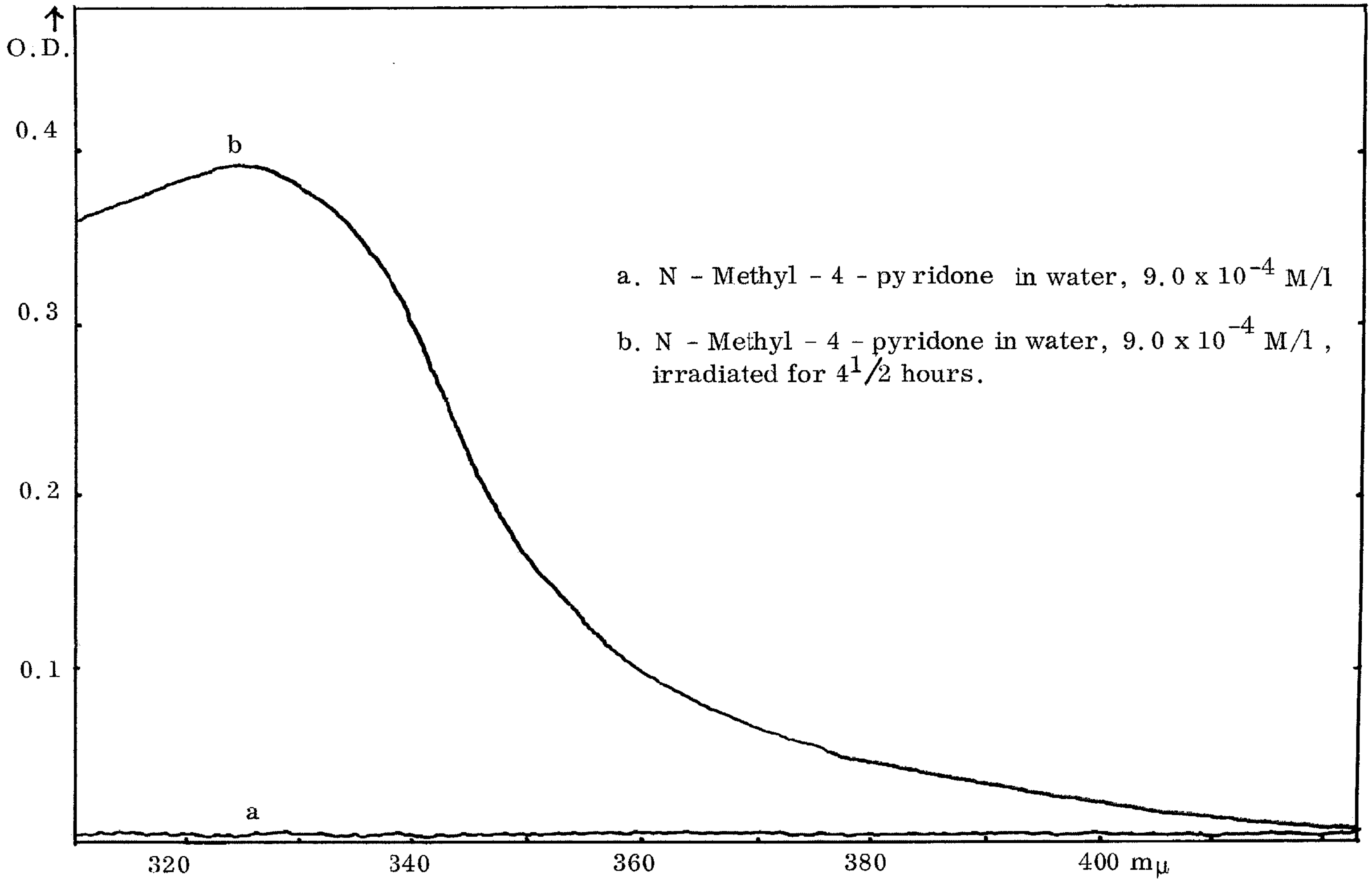
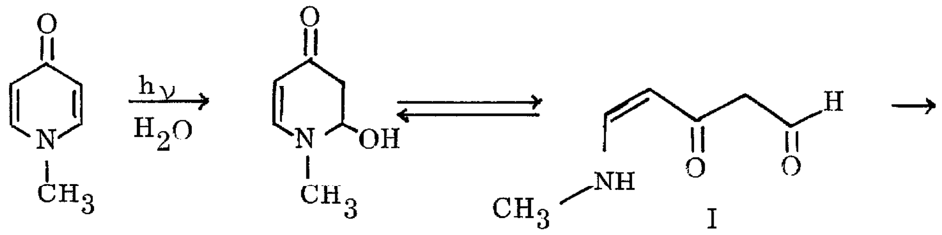
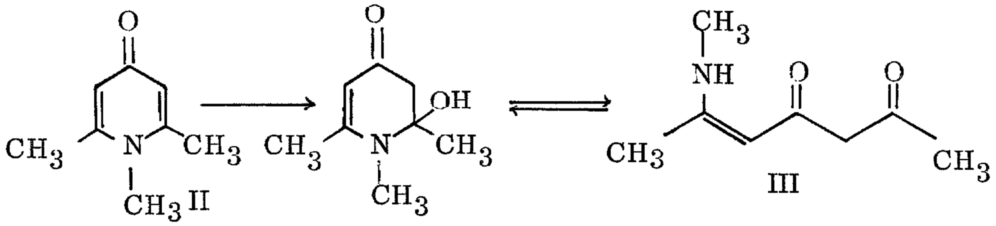


Figure 1 UV Irradiation of N - Methyl - 4 - pyridone in Water

that it can be produced only in very dilute solution. All the experiments suggest that the photoreactions of N-methyl-4-pyridone in aqueous solution follows the process:



If we methylate, the 1 and 6 positions of N-methyl-4-pyridone, the corresponding product to I, III, would be more stable than I.

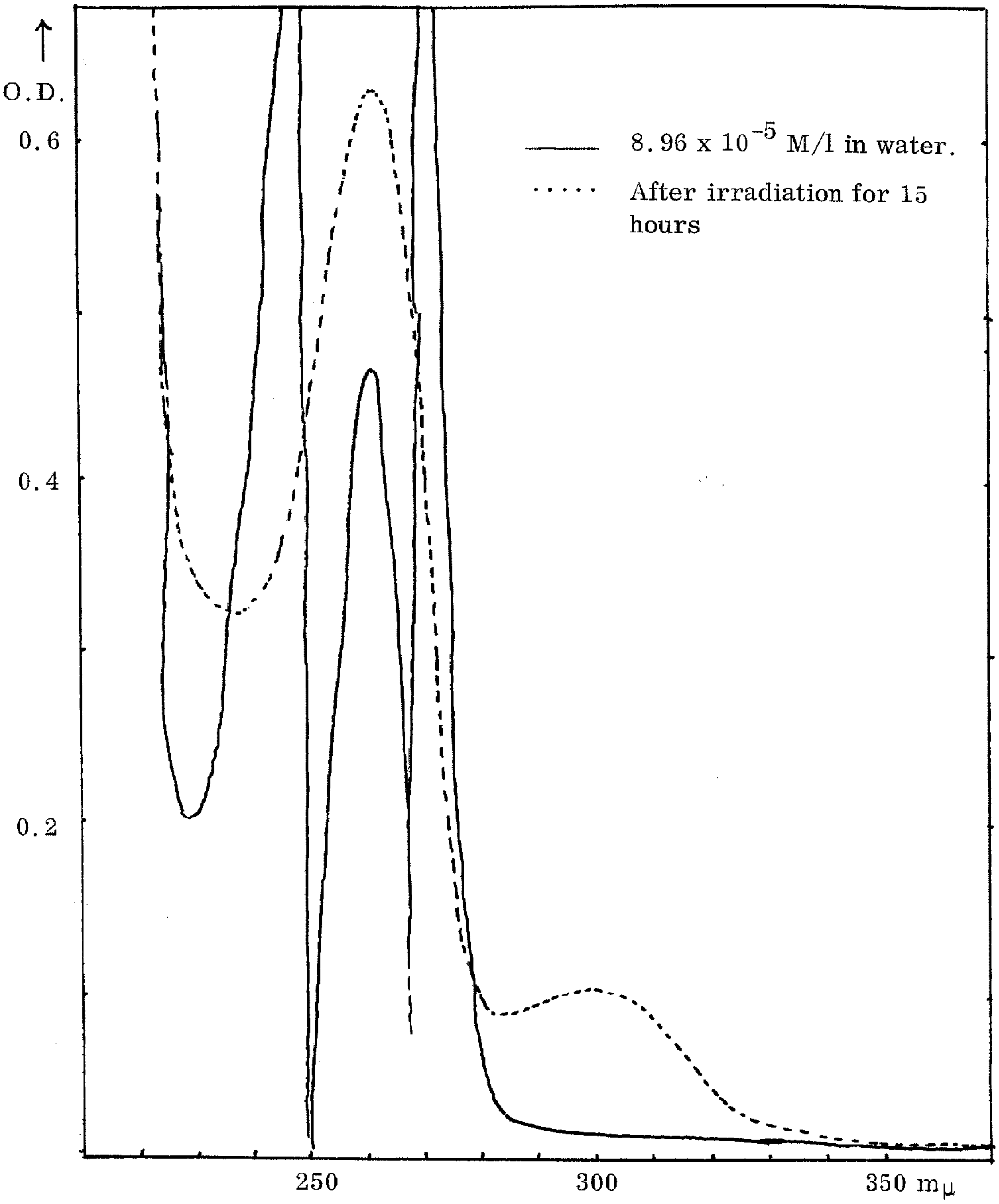


N-methyllutidone, II, was synthesized and irradiated with 2537 Å light in aqueous solutions. The same things which happened to N-methyl-4-pyridone was observed, i.e., the solution turned pale yellow and the optical density at 2578 Å decreases while that at 2920 Å increases as shown in Figure 2. This suggests that the product III is formed but some unknown reactions proceed further.

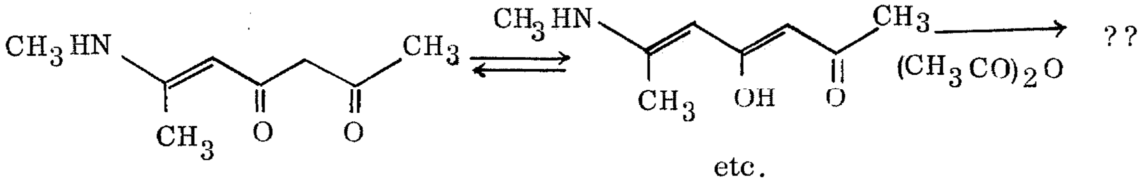
The iodoform test (16) was carried out with lyophilized photoproduct. A drop of 10 % sodium hydroxide and a aqueous solution of iodine-potassium iodide (10 ml) were added to the irradiated sample. When chloroform was added to the mixture, no color or odor of iodoform were detected in chloroform layer. This failure may be caused by β-keto groups (16).

If III is formed, it is very probable that some enolization would occur in aqueous solution. Acetylation of this enols were attempted. Aqueous solutions of N-methyllutidone photoproducts were prepared. To 5 ml of the

Figure 2 Irradiation of N - Methyllutidone



solution, a few drops of 5 % hydrochloric acid were added, followed by 5 ml of acetic anhydride in an ice bath with magnetic stirring. Previously prepared solution of sodium acetate (5 g in 25 ml of water) was added in one portion. However, no crystallization was observed.

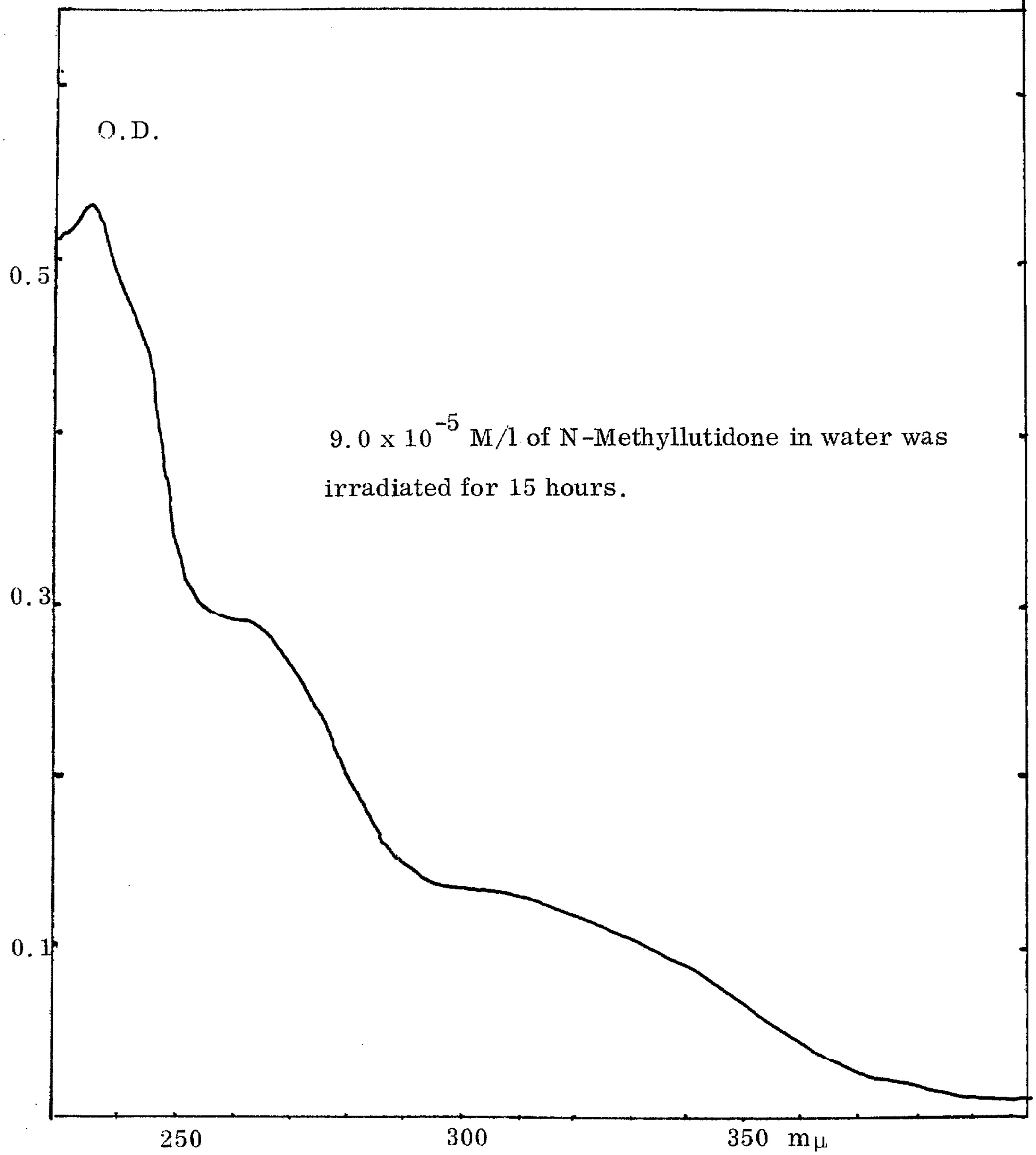


Even if III is present, the failure of the procedure is not surprising in view of the fact that water will probably compete very well in reaction with acetic anhydride, because of the low concentration of the photoproduct.

When N-methyllutidone was irradiated in acetonitrile, the optical density at 2578 Å decreased as in aqueous solution but the new peak was broad without giving a distinct maximum and starting at 3900 Å . This indicates clearly the addition of acetonitrile rather than dimerization of N-methyllutidone.

From all these data, we conclude that N-methyl-4-pyridone and N-methyllutidone undergo a hydration reaction when they are irradiated in aqueous solution. The hydration products undergo ring opening and the resulting products, I and III, proceed further through some unknown reactions.

Figure 3 Irradiation of N - Methyllutidone in Acetonitrile



9.0 x 10^{-5} M/l of N-Methyllutidone in water was irradiated for 15 hours.

EXPERIMENTAL

Syntheses

4-Chloropyridine. - 4-Chloropyridine hydrochloride (Aldrich Chem. Co.) (35.4 g) was dissolved in cold saturated potassium carbonate solution by adding it slowly in small portion. If the rate of addition is fast, orange slurry, supposedly N-(4-pyridyl)-4-chloropyridinium chloride (19), is largely obtained. The mixture was extracted with ether several times and the etheral solution was decolorized with one spatula of Norite. This was filtered and dried over solid anhydrous potassium carbonate. Ether was distilled off under the reduced pressure to yield colorless liquid, 4-chloropyridine. This was stored in the freezer until use.

4-Methoxypyridine.(20) - 4-Chloropyridine was refluxed with excess sodium methoxide in methanol at 100° C for 2 days. Sodium methoxide was prepared by dissolving sodium metal in methanol in nitrogen atmosphere at ice temperature immediately before use. The refluxed mixture was steam distilled until no basic liquid came over. The distillate was acidified with concentrated hydrochloric acid and water was distilled off under reduced pressure to get a white residue, 4-methoxypyridine hydrochloride. The residue was dissolved in cold, saturated potassium carbonate solution and the upper, colorless layer was separated This liquid was dried over anhydrous potassium carbonate and was distilled under reduced pressure to get pure 4-methoxypyridine. b. p. 57° C at 0.25 mm Hg. Yield = 77.5 %. UV absorption maxima: 2601, 2300 Å in water. IR Spectra show strong bands of $-OCH_3$ at 1293 and 1035 cm^{-1}. The NMR Spectra give a singlet at 3.88 ppm for $-CH_3$ protons and doublets at 7.08 and 8.77 p.p.m. for 3- and 2-protons respectively.

N-Methyl-4-pyridone.(21) - 4-Mehtoxypyridine was put into a thickwalled Pyrex combustion tube and methyl iodide (0.2 ml for each gram of 4-methoxypyridine) was added. The mixture was degassed to 0.005 mm Hg after freezing in liquid nitrogen. The tube was sealed and heated to 135 - 140° C in an oil bath for 3 days. Orange or brownish black liquid was obtained and when the thick liquid is cooled to room temperature, needle-shaped crystals were formed slowly. The solid mixture was extracted with chloroform and distilled under reduced pressure (0.08 - 0.1 mm Hg) in an oil bath at 200° C after chloroform was distilled off. With several repeated distillations using a microburner, pure colorless, or slightly cream colored N-methyl-4-pyridone was obtained. The product was very hygroscopic and a small amount of this compound turned into liquid in the air by absorbing moisture, m.p. 89.3 - 91.0°C (lit. 89 - 94).

The compound has a UV absorption maximum at 2600 Å in aqueous solution with extinction coefficient of 1.890×10^4.

NMR data are shown below.

		Chemical Shift	Lit.	Ratio
CH_3 proton	singlet	3.80 p.p.m.	3.74	3
2 - H	doublet	7.58 p.p.m.	7.78	2
3 - H	doublet	6.48 p.p.m.	6.50	2

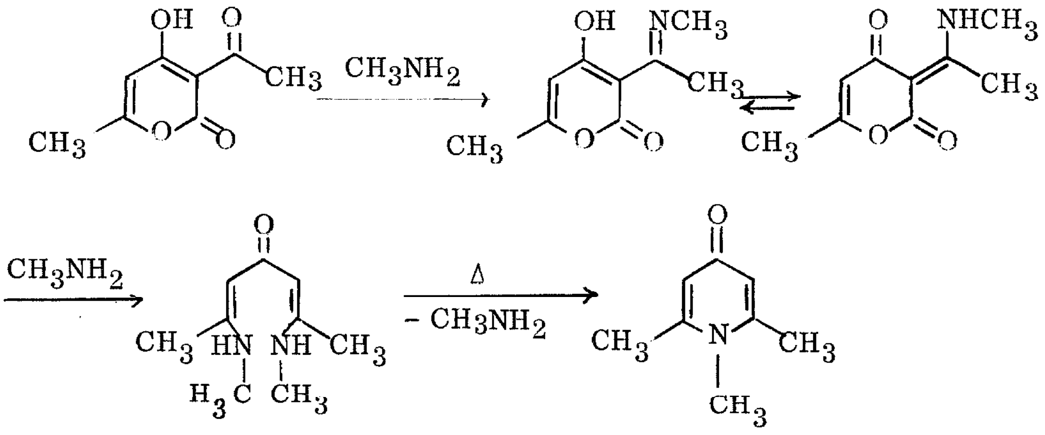
J_{cp} = 8 cps between 2 - H and 3 - H.

The IR Spectrum was taken with a Beckman IR 7 and bands are shown below:

$\bar{\nu}$ in cm^{-1}	Lit.
1017 (w)	
1150 (w)	
1280 (w)	

ν in cm^{-1}	Lit.
1362 (m)	
1401 (m)	1401
1513 (T)	1513
1580 (vs)	1581
1645 (vs)	1646
1665 (s)	1664
2500 (w)	
2990 (s)	2970

N-Methyllutidone. (22) - Dehydroacetic acid (10.0 g) was dissolved in 40 % aqueous methylamine (25 ml) and the mixture was warmed on a steam bath. After ten minutes, the mixture was cooled to get white solid aggregates. The product was recrystallized from absolute ethanol.



I

Bis-2,6-methylaminohepta-2,5-diene-4-one (I, 5 g) was dissolved in 150 ml of water and refluxed for an hour. Methylamine formed in the reaction was passed into picric acid solution (7.8 g in 150 ml of ethanol). The reaction mixture was cooled but no crystals were formed. The solution was concentrated with a flash rotary evaporator and cooled to get white needles. The crystals were recrystallized several times from water and dried over phosphorous pentoxide at 56° C. m.p. 248.0 - 249.0° C, lit. 247 - 248.

UV absorption maxima are shown below.

$\lambda_{max.}$ (in Å)	ϵ
2578	1.77×10^4
2155	1.58×10^4
2107	1.78×10^4

Solvents

Acetonitrile. - Spectrograde acetonitrile (Matheson Coleman & Bell) was distilled three times over phosphorous pentoxide and once over anhydrous potassium carbonate.

Chloroform. - Reagent grade chloroform (Allied Chemical) was stirred with conc. sulfuric acid for 5 hours twice and washed with water several times. The chloroform was distilled over calcium chloride and the middle portion was collected. b.p.60.0° C.

Cyclohexane. - Spectrograde cyclohexane (Matheson coleman & Bell) was used without further purification.

Ethanol. - The same method used in part one of this thesis was followed.

Ethyl Acetate. - Reagent grade ethyl acetate was washed with the same volume of 5 % sodium carbonate solution, then with saturated calcium chloride solution and distilled over anhydrous potassium carbonate collecting the middle portion. b.p. 76 °C.

Ethyl Ether. - Anhydrous analytical, reagent grade ether (Mallinckrodt Chemical Works) was used without further purification.

n-Hexane. - The same procedure described in part one of this thesis was followed.

Methanol. - Spectrograde methanol (Matheson Coleman & Bell) was used without further purification.

Methyl Iodide. - The same method described in part one of this thesis was used.

Water. - Distilled water was redistilled from alkaline-potassium permanganate. The water collected this way was redistilled using pure glassware immediately before use.

Reagents

Benedict's Reagent. - Benedict's solution was made by dissolving the following salts in distilled water:

Hydrated copper sulfate	(17.3 g)
Sodium citrate	(173.0 g)
Anhydrous sodium carbonate	(100 g)

The citrate and carbonate were dissolved by heating with 80 ml of water. Additional water was added to bring the volume of solution to 850 ml . The copper sulfate was dissolved in 100 ml of water, and the resulting solution was poured slowly, with stirring, into the solution of citrate and carbonate. The final solution was made up to 1 l by addition of water.

Tollen's Reagent. - In a thoroughly clean test tube, 2 ml of a 5 % solution of silver nitrate was placed and a drop of 10 % sodium hydroxide solution was added. A very dilute solution of ammonia (2 %) was added drop by drop, with constant shaking, until the precipitate of silver oxide just dissolved.

The Fuchsin-Aldehyde. - Pure fuchsin (0.5 g) was dissolved in 500 ml of distilled water and filtered. Distilled water (500 ml) was saturated with sulfur dioxide and mixed thoroughly with fuchsin solution and were stood overnight.

2,4-Dinitrophenylhydrazine Solution. - To 0.4 g of 2,4-dinitrophenylhydrazine in a 25 ml Erlenmeyer flask was added 2 ml of conc. sulfuric acid. Water (3 ml) was added dropwise, with swirling or stirring until solution was complete. To this warm solution is added 10 ml of 95 % ethanol.

Thin Layer Chromatography

Silica gel G plates were employed with several solvents as developing agents. An iodine chamber was used to develop color at the spots to which solutes had moved.

Preparatory Thin Layer Chromatography

Silica gel G plates of 1 mm thick were prepared and dried in the air for 3 hours followed by activation in the oven for several hours at 100 - 110° C. Methanol was used as a developing solvent.

Column Chromatography

Silica gel G Column; A column was packed with silica gel G which was used for the thin layer chromatography and methanol was used for elution. However, it was too fine to let the eluent through.

Alumina Column; Alumina grade IV (180 g) was deactivated by shaking vigorously with 20 ml of distilled water for 5 minutes and on the mechanical shaker for 2 hours. A column was packed with the alumina but it was too polar to use methanol as eluting solvent.

Silicic Acid Column; Three pounds of 100 mesh silicic acid was shaken in a big tray with 3 l of distilled water and allowed to stand for 10 minutes to settle the large grains. The supernatant liquid with fine silicic acid was discarded. The process was repeated several times shortening the settling time to 10, 10, 10, 5, 3, 3, 2, 1, 1, and 1 minutes in succession. Big silicic acid grains were collected and dried in the oven for 12 hours at 120 - 130° C. About 1.5 lb of silicic acid was recovered.

A column of 17 cm long with a diameter of 1.5 cm was packed with the silicic acid in methanol and used for separation of photoproducts of N-methyl-4-pyridone.

Irradiation of Samples

A Hanovia gemicidal lamp was used for earlier work with 1 cm of acetic acid (1 %) filter solution to eliminate 1849, 1942, and 2224 Å lights. A Hanovia low pressure mercury lamp was also used with 2537 Å solution filter which is described in part one of this thesis.

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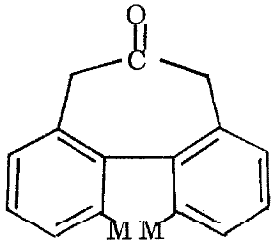
PROPOSITION I

An optically active ketone, 4',1''-dimethyl-1,2,3,4-dibenzcyclohepta-1,3-diene-6-one (I), is proposed to be used as a photosensitizer for optical induction and cis ⇄ trans isomerization of 1,2-diphenylcyclopropane (II).

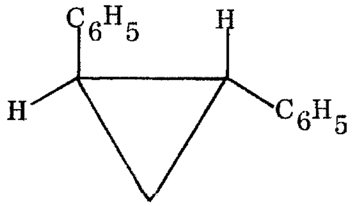
* * * * * * *

There is considerable evidence that transfer of triplet excitation requires molecular contact between donor and acceptor (1). Under such circumstances stereochemical factors may be of importance in determining the efficiency of transfer and one might anticipate that an optically active donor would show selection between the d and l isomers of a racemic substrate. Indeed, photochemical optical induction was achieved in the chemical isomerization of racemic trans-1,2-diphenylcyclopropane using optically active naphthalene derivatives (2). However, this reaction undergoes through singlet intermediate rather than triplet excitation (3). It is proposed to use the ketone I as a sensitizer for photoisomerization of 1,2-diphenylcyclopropane. The ketone I was prepared by Mislow et al. (4) and it has $n - \pi^*$ carbonyl excitation at 2895, 2975, 3070 and 3170 Å with log ϵ of 2.88, 2.88, 2.76, and 2.41 respectively. This ketone undergoes racemization thermally ($E_{act.} = 39$ kcal/mole) and photochemically via vibrationally excited ground state (5) which was formed thermally or from radiationless decay of excited singlet or triplet state. When this ketone is



$M = CH_3$.

(+), or (-) - I



d,l - II

excited with 3130 Å light, only n - π^* transitions would be obtained and the intersystem crossing yield will be high (6). The triplet energy of the ketone is expected to be high enough to transfer energy to 1, 2-diphenylcyclopropane and $k_1 \gg k_3$.

$$(\mathrm{I}) + h\nu \longrightarrow (\mathrm{I})^{\mathrm{S}^1} \longrightarrow (\mathrm{I})^{\mathrm{T}^1}$$

$$(\mathrm{I})^{\mathrm{T}^1} + (\mathrm{II}) \xrightarrow{k_1} (\mathrm{I}) + (\mathrm{II})^{\mathrm{T}^1}$$

$$(\mathrm{II})^{\mathrm{T}^1} \xrightarrow{k_2} \text{Isomerization}$$

$$(\mathrm{I})^{\mathrm{T}^1} \xrightarrow{k_3} (\mathrm{I})^{\overset{\circ}{\mathrm{S}}\mathrm{v}} \xrightarrow{k_4} \text{Racemization}$$

If the triplet energy transfer requires molecular contact, optically active 1, 2-diphenylcyclopropane will be obtained from racemates II after sensitized isomerization with ketone I as a sensitizer since I would preferentially transfer its triplet excitation to either *d*- or *l*- *trans*-1, 2-diphenylcyclopropane.

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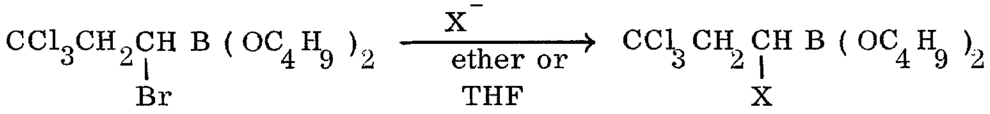
PROPOSITION II

It is proposed to investigate the mechanism of the displacement of halide ion from the α- haloalkaneboronic ester by a nucleophile by studying the stereochemistry.

* * * * * * *

Displacement reactions of α - haloalkaneboronic esters have been studied with dibutyl 1-bromo-3,3,3-trichloropropane-1-boronate, $CCl_3CH_2CHBrB(OBu)_2$ (I), the first compound of this class to become readily available (1 - 3). The displacement of bromide ion from (I) by nucleophiles such as iodide, n-butoxide, t-butoxide, and butyl mercaptide ion is greatly facilitated by the neighboring boron atom.



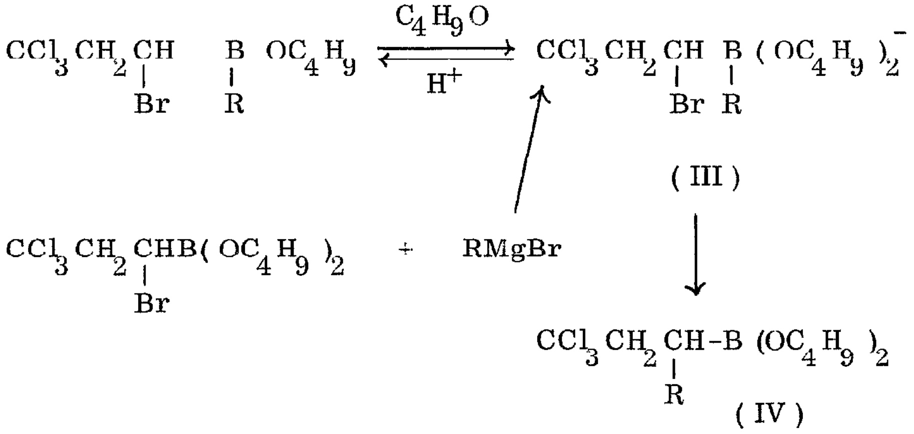
$$CCl_3CH_2\underset{\mathrm{Br}}{\underset{|}{CH}}\,B(OC_4H_9)_2 \xrightarrow[\text{ether or THF}]{X^-} CCl_3CH_2\underset{\mathrm{X}}{\underset{|}{CH}}\,B(OC_4H_9)_2$$

(I) (II)

a, $X = I^-$; b, $X = {}^-OC_4H_9$; c, $X = {}^-SC_4H_9$

I reacts rapidly with sodium iodide in acetone to yield IIa. This displacement is $1.5 \sim 2$ times faster than that of allylbromide, measured in competition experiments. Since allylbromide reacts 50 - 70 times as fast as n-butyl bromide with potassium iodide in acetone (4) and ethyl α- bromo - γ,γ,γ - trichlorobutyrate reacts only 0.2 - 0.3 times as fast as n-butyl bromide, I reacts 300 - 700 times as fast as the analogous carboxylic ester. In potassium ethoxide no dehydrobromination was observed during the displacement reaction of I, while 1,1,1-trichloro-3 bromopropane or α-bromo- β-methyl- γ,γ,γ -trichlorobutyrate was dehydrohalogenated under the same conditions.

Sodium butyl mercaptide with an excess of butyl mercaptan in butanol converted the bromide I to IIc (2). Although the concentration of butoxide ion in this solution must have been far below that of the butyl mercaptide ion and the mercaptide is normally several times more nucleophilic toward carbon than the alkoxide (5), about 5 % of the crude reaction product was the butoxy compound. From this, it appears that basicity toward boron is a more important factor than nucleophilicity toward carbon in determining which competing base will displace bromide ion from I. Also β-aryl-and β-alkyl- β-(1-bromo-3,3,3-trichloro-1-propyl)-borinates yield the displacement product with rearrangement in basic ether solution. So evidently the displacement reaction proceeds in no less than two steps. The first is the addition of a Lewis base (butoxide or other) to form anion III or an analogous species.



$$\mathrm{CCl_3CH_2\underset{Br}{CH}\;\underset{R}{B}\;OC_4H_9} \underset{\mathrm{H^+}}{\overset{\mathrm{C_4H_9O^-}}{\rightleftarrows}} \mathrm{CCl_3CH_2\underset{Br}{CH}\;\underset{R}{B}\,(OC_4H_9)_2^-}$$

(III)

$$\mathrm{CCl_3CH_2\underset{Br}{CH}B(OC_4H_9)_2} + \mathrm{RMgBr} \nearrow \text{III} \downarrow$$

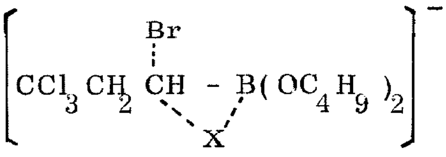
$$\mathrm{CCl_3CH_2\underset{R}{CH}{-}B\,(OC_4H_9)_2}$$

(IV)

$R = C_6H_5$; $2,5\text{-}(CH_3)_2C_6H_3$; $2,4,6\text{-}(CH_3)_3C_6H_2$; C_2H_5

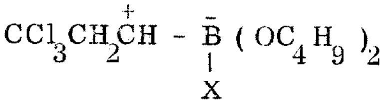
Second, expulsion of bromide and migration of the aryl or alkyl group from boron to carbon occurs to yield the boronic ester IV. For this step, two types of mechanism can be postulated.

One is concerted machanism (V) and the other is the formation of a "boron ylid" (VI) intermediate.



$$\left[CCl_3CH_2\overset{Br}{CH} - B(OC_4H_9)_2\right]^-$$

(V)



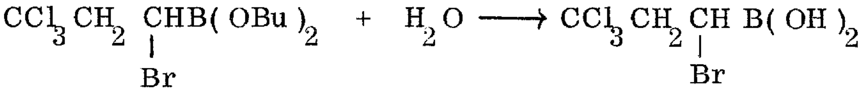
$$CCl_3CH_2\overset{+}{C}H - \underset{X}{\overset{-}{B}}(OC_4H_9)_2$$

(VI)

Matteson and Mah favor the transition state V over the intermediate VI from the energy diagram of the reaction. (Free energy vs. reaction co-ordinate). But no definite evidence has been found to explain which of the two mechanism occurs.

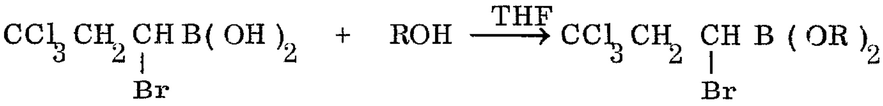
It is proposed to study the stereochemistry of the displacement reaction to determine which of the two mechanisms can be excluded.

It is necessary to make the optically active bromide of I, and the synthesis of the compound follows.



$$CCl_3CH_2\underset{Br}{CH}B(OBu)_2 + H_2O \longrightarrow CCl_3CH_2\underset{Br}{CH}B(OH)_2 \qquad (6)$$

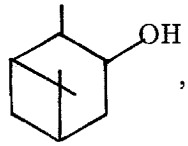
dl dl



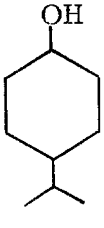
$$CCl_3CH_2\underset{Br}{CH}B(OH)_2 + ROH \xrightarrow{THF} CCl_3CH_2\underset{Br}{CH}B(OR)_2 \qquad (7)$$

dl diastereomer

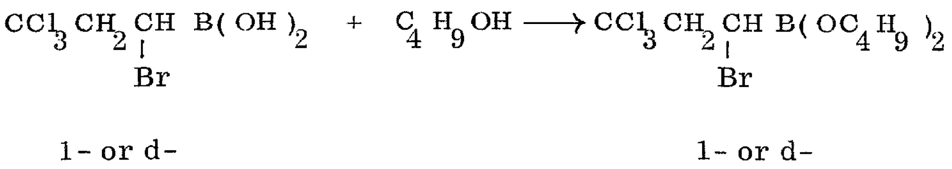
R = 1- or d-



, 1- or d-

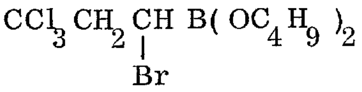


Separate the optical diastereomers by crystallization or by using chromatography (8) and hydrolyze the boronic ester in cold water.



$$\mathrm{CCl_3CH_2\underset{\substack{|\\ Br}}{CH}\,B(OH)_2 + C_4H_9OH \longrightarrow CCl_3CH_2\underset{\substack{|\\ Br}}{CH}\,B(OC_4H_9)_2}$$

1- or d- 1- or d-



$\mathrm{CCl_3CH_2\underset{\substack{|\\ Br}}{CH}\,B(OC_4H_9)_2}$ can be prepared by Matteson's method (3).

If the displacement reaction proceeds through the transition state V, the product should be optically active and complete inversion should result. If the reaction proceeds through the intermediate VI, the optically inactive racemate should result as the reaction product. If V and VI are both involved, then the product should be partially optically active. Also VI might be more important when X is an aryl group because the aryl group can stabilize the ylid by charge distribution (9).

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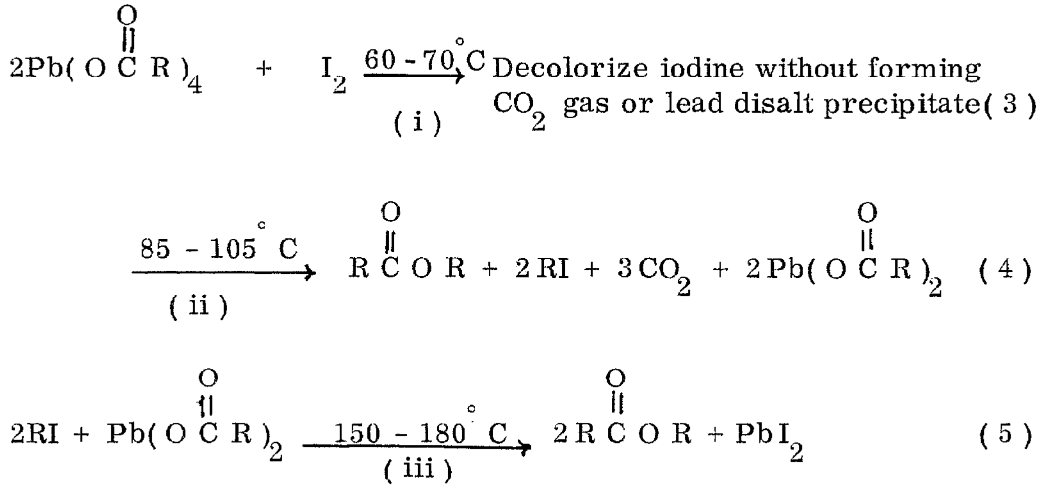
PROPOSITION III

It is proposed that the oxidation of carboxylic acids to esters by tetravalent lead proceeds via free radical intermediate.

* * * * * * *

Lead tetrasalts of aliphatic acids are oxidized by halogens to the corresponding esters and carbon dioxide in fair to good yields under anhydrous conditions (1). This method offers advantages in cost and simplicity of procedure over the Simonini and Hunsdiecker methods in which the starting materials are silver salts (2). Even though the reaction is very useful, the mechanism has not been so thoroughly studied as the Simonini and Hunsdiecker reactions which themselves are not well established.

In an experiment by Bachman and Wittmann (1), the following observations were made.



$$2\mathrm{Pb}(\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{R})_4 + \mathrm{I}_2 \xrightarrow[\text{(i)}]{60 - 70^\circ\mathrm{C}} \text{Decolorize iodine without forming } \mathrm{CO}_2 \text{ gas or lead disalt precipitate} \quad (3)$$

$$\xrightarrow[\text{(ii)}]{85 - 105^\circ\mathrm{C}} \mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OR} + 2\mathrm{RI} + 3\mathrm{CO}_2 + 2\mathrm{Pb}(\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{R})_2 \quad (4)$$

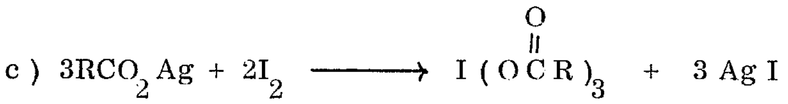
$$2\mathrm{RI} + \mathrm{Pb}(\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{R})_2 \xrightarrow[\text{(iii)}]{150 - 180^\circ\mathrm{C}} 2\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OR} + \mathrm{PbI}_2 \quad (5)$$

The highest yield of the ester formation was obtained with long-chain aliphatic acids with a salt to iodine ratio of 2:1 and when the reaction was carried out in a nonionizing solvent. Substantial amounts of free acid were formed with the following halogens: Cl_2 : 50 %. Br_2 : 20 % and I_2 : 10 - 20 %. Bachman rules out a free radical mechanism because no R - R could be found. He also rules out an ionic mechanism involving formation of a carbonium ion intermediate since no olefins or rearranged products were found. He suggests concerted and cage-type mechanism without a clear explanation of what he means. A free radical mechanism which is most probable to Simonini reaction is proposed for the process(ii). It is not justified to rule out a free radical mechanism just because no R - R dimer is observed. The yield of ester is the highest when high molecular weight and straight chain aliphatic acids are used. Pivalic acid in which the carboxyl group is attached to a tertiary carbon gave no ester. This may be attributed to the stability of tertiary alkyl radical and diffusion of alkyl radical into the solvent. This would form RH or RX rather than R - R or RCO_2R. From the low molecular weight acids, the expected radical RCOO· would decarboxylate rather easily compared to high molecular weight acids since thus formed alkyl radicals would diffuse readily before they combine with RCOO· to form esters. Unsaturated acids give polymers and benzoic acid give iodobenzene. These observations also support free radical mechanism. An equimolar mixture of benzoic and palmitic acids give pentadecyl ester but no phenyl ester. If concerted and cage-type mechanism is applied, this is not expected to occur.

Even though many people have studied the Simonini and Hunsdiecker reactions, the mechanism is still controversial. The most probable mechanism is a free radical reaction.

a) $RCO_2Ag + I_2 \longrightarrow RCO_2I + AgI$ (3)

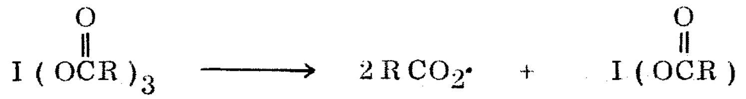
b) $2RCO_2Ag + I_2 \longrightarrow RCO_2Ag \cdot RCO_2I$ (4)



c) $3RCO_2Ag + 2I_2 \longrightarrow I(O\overset{\overset{O}{\|}}{C}R)_3 + 3AgI$ (5)

Initiation

d) $RCO_2I \longrightarrow RCO_2\cdot + I\cdot$

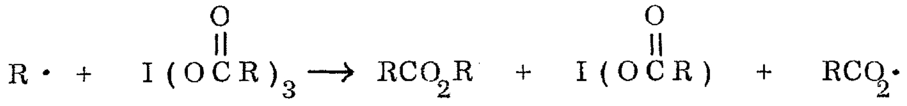
e)


$$\mathrm{I(O\overset{O}{\overset{\|}{C}}R)_3 \longrightarrow 2RCO_2\cdot + I(O\overset{O}{\overset{\|}{C}}R)}$$

Propagation

$$\text{f)}\quad \mathrm{RCO_2\cdot \longrightarrow R\cdot + CO_2}$$

$$\text{g)}\quad \mathrm{R\cdot + RCO_2I \longrightarrow RI + RCO_2\cdot}$$

h)


$$\mathrm{R\cdot + I(O\overset{O}{\overset{\|}{C}}R)_3 \longrightarrow RCO_2R + I(O\overset{O}{\overset{\|}{C}}R) + RCO_2\cdot}$$

Termination

$$\text{i)}\quad \mathrm{2R\cdot \longrightarrow R-R \text{ or } RH + Olefin}$$

$$\text{j)}\quad \mathrm{RCO_2\cdot + R\cdot \longrightarrow RCO_2R}$$

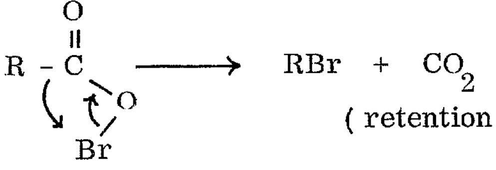
$$\text{k)}\quad \mathrm{RCO_2\cdot \xrightarrow{R'H} RCO_2H}$$

However, other mechanisms have been proposed, e. g.,

$$\text{1)}\quad \mathrm{CF_3COOAg + I_2 \longrightarrow CF_3COOI + AgI}$$

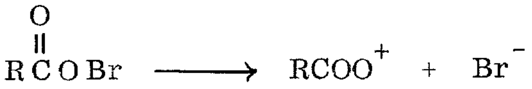
$$\mathrm{CF_3COOI \longrightarrow I^+ + CF_3COO^-}$$

$$\mathrm{\longrightarrow CO_2 + CF_3^- + I^+ \rightarrow CF_3I + CO_2} \qquad (6)$$

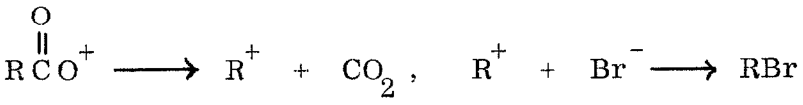
m)


$$\mathrm{R-\overset{O}{\overset{\|}{C}}-O-Br \longrightarrow RBr + CO_2}$$

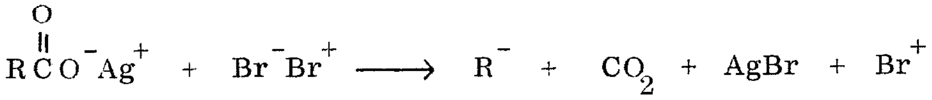
(retention of configuration) (7)

n)


$$\mathrm{R\overset{O}{\overset{\|}{C}}OBr \longrightarrow RCOO^+ + Br^-}$$



$$\mathrm{R\overset{O}{\overset{\|}{C}}O^+ \longrightarrow R^+ + CO_2,\quad R^+ + Br^- \longrightarrow RBr} \qquad (8)$$

o)


$$\mathrm{R\overset{O}{\overset{\|}{C}}O^-Ag^+ + Br^-Br^+ \longrightarrow R^- + CO_2 + AgBr + Br^+}$$

$$\mathrm{R^- + Br^+ \longrightarrow RBr} \qquad (9)$$

Since the reactants and products of the lead tetrasalt method are analogous to those in the Simonini and Hunsdiecker reactions, it is probable that the reaction mechanism of the lead tetrasalt method is the same as that of the silver salt reactions.

Since silver salts form iodine triacyls and $IO\overset{O}{\overset{\|}{C}}R \quad AgO\overset{O}{\overset{\|}{C}}R$ complexes as shown in (b) (c), it is very probable that iodine triacyls and $IO\overset{O}{\overset{\|}{C}}R \cdot 2\,Pb\,(O\overset{O}{\overset{\|}{C}}R)_2$ complexes are formed in step (ii) because the ratio of available carboxyl groups to iodine is 4:1 and tetravalent lead is a strong oxidizing agent.

It is proposed: 1) to attempt the isolation of the triacyls by the method of Oldham and Ubbelohde (5). If the triacyl is identified, then the reaction proceeds through free radical intermediate. 2) to use an optically active acid with the asymmetry center at α -carbon. Optically active alkyl halides would be formed if the reaction proceeds through the concerted and cage-type mechanism. Racemates are expected from free radical mechanism. 3) to use a high concentration of a strong scavenger such as galvinoxyl in step (ii). Under these conditions, one can expect that only free radical reactions should be affected. (10,11).

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PROPOSITION IV

It is proposed to investigate the photolysis of di - t-butyl ketone in condensed phase.

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The photochemistry of simple aliphatic ketones in the vapor phase has been studied extensively (1 - 3). In vapor phase, simple aliphatic ketones undergo two types of reactions, i.e., the reaction including the homolytic cleavage of a bond attached to the carbonyl group and the reaction of γ-hydrogen abstraction leading to α, β - C - C bond breaking (1).

$$CH_3COCH_3 \xrightarrow[\text{vapor}]{h\nu} CH_3CH_3 + CO \quad (\text{Type I})$$

$$CH_3COCH_2CH_2CH_3 \xrightarrow[\text{vapor}]{h\nu} CH_3COCH_3 + CH_2 = CH_2 \quad (\text{Type II})$$

It is well documented that the primary process in vapor phase reactions is radical formation. Quite a few works have been done on the photolysis of simple ketones in solution or in condensed phase (1 - 8). At room temperature, Type I reaction of simple aliphatic ketones are completely suppressed (1) even though Type II reactions occur as readily as in vapor phase. The poor quantum yield of Type I reaction in condensed phase is attributed to primary recombination of free radicals formed in solvent cage (6) or to the efficient vibrational deactivation of electronically excited molecules.

It is proposed to photolyze di-t-butyl ketone in condensed phase or in solution. If the primary process is radical formation and thus formed radicals recombinate in the solvent cage, di-t-butyl ketone would be more efficient in photolysis than other simple aliphatic ketones because of the relatively long lifetime of t-butyl radical. Type II reaction is not expected since there is no γ- hydrogen.

Surprisingly, the high quantum yield is obtained in the photolysis of pinacalone supporting the hypothesis of radical formation in the primary process of the photolysis of aliphatic ketones in condensed phase or in solution (9). However, the reaction products were not identified because of complicated cross combination and disproportionation between radicals formed from photolysis.

Di-t-butyl ketone has a great advantage because only two radicals will be formed from photolysis compared to three in the case of pinacalone. The number of products will be less and easier to identify. The following reactions are expected :

(1) $(CH_3)_3CCOC(CH_3)_3 \xrightarrow[\text{condensed phase}]{h\nu} (CH_3)_3C\cdot + \cdot COC(CH_3)_3$

(2) $(CH_3)_3CCO\cdot \longrightarrow (CH_3)_3C\cdot + CO$

(3) $(CH_3)_3C\cdot + (CH_3)_3C\cdot \longrightarrow (CH_3)_3CH + (CH_3)_2C = CH_2$

(4) $(CH_3)_3CCO\cdot + (CH_3)_3CCO\cdot \longrightarrow (CH_3)_3CCOCOC(CH_3)_3$

(5) $(CH_3)_3C\cdot + RH\ (\text{Solvent}) \longrightarrow (CH_3)_3CH + R\cdot$

(6) $(CH_3)_3C\cdot + (CH_3)_3C\cdot \longrightarrow (CH_3)_3CC(CH_3)_3$

(7) $(CH_3)_3CO\cdot + RH \longrightarrow (CH_3)_3CHO + R\cdot$

(8) $R\cdot + R\cdot \longrightarrow R-R$

(9) $(CH_3)_2C = CH_2 \longrightarrow \text{Polymerize}$

It is very probable that the reactions 4, 7, 8 and 9 are not important compared to other reactions and carbon monoxide, isobutane and isobutylene may be the main products obtained. The measurement of quantum yields of the reactions would not be so complicated as in the case of pinacalone.

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PROPOSITION V

It is proposed to study the α - chymotrypin-catalyzed hydrolysis of p- and m-nitrophenyl acetates with known reversible inhibitors.

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Hartley and Kilby (1) found p-nitrophenyl acetate hydrolysis by α-chymotrypsin . Since then many data have been accumulated on the α -chymotrypsin -catalyzed hydrolysis of this compound . They used this hydrolysis to check the hydrolytic activity of the enzyme or the active amino acid residue at the active site(2-3). However, it is surprising that only a few attempts have been made to clear the argument whether p-nitrophenyl acetate reacts at the active site or not and whether the mode of reaction is the same as normal substrates reaction if it reacts at the active site of the enzyme (4). For example, dinitrophenol itself inhibits hydrolysis of serum albumin by α- chymotrypsin with allosteric effect (5).

It is proposed to determine the bimolecular rate constants for the reaction of p- and m-nitrophenyl acetates and α- chymotrypsin in the presence of a known reversible inhibitor , such as benzamide ($K_I = 10 \pm 2$ mM), benzenesulfonamide ($K_I = 4.3 \pm 0.4$ mM) and cinnamoyl imidazole. The reaction can be followed with spectrophotometer.

The kinetics of enzyme reaction with reversible inhibitors can be written as:

$$E + S \xrightleftharpoons{K_m} ES \xrightarrow{k_2} ES' + P_1$$

$$E + I \xrightleftharpoons{K_I} EI$$

$$v = \frac{k_2 (E)}{1 + K_m/(S)\left[1 + (I)/K_I\right]}$$

where S is substrate , I inhibitor, v the velocity of hydrolysis. The effect of inhibitors on v should be determined and k_2 and K_m be measured.

The results of this experiment may give some significant information about enzyme-substrate combination and the acyl-enzyme mechanism such as with what amino acid residue in the enzyme the ester combines to form acyl enzyme and what kind of electronic or resonance effects the substrates would have on the acylation.

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ABSTRACTS OF PROPOSITIONS

I. An optically active ketone, 4′, 1″-dimethyl-1, 2, 3, 4-dibenzcyclohepta-diene-6-one (I), is proposed to be used as a photosensitizer for optical induction and <u>cis</u> ⇌ <u>trans</u> isomerization of 1, 2-diphenylcyclopropane.

II. The investigation of the mechanism of the displacement of halide ion from the α-haloalkane boronic ester by a nucleophile is proposed.

III. A radical mechanism is proposed for the oxidation of carboxylic acids to esters by tetravalent lead salts.

IV. The photolysis of di-t-butyl ketone in condensed phase or in solution is proposed.

V. The study of the α-chymotrypsin-catalyzed hydrolysis of p- and m-nitrophenyl acetates in the presence of known reversible inhibitors is proposed.