THE MECHANISM AND EFFECT OF THE QUENCHING OF AROMATIC HYDROCARBON SINGLET EXCITED STATES BY CONJUGATED DIENES

Thesis by

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ABSTRACT

Strong and rather specific quenching of fluorescence of aromatic hydrocarbons by conjugated dienes has been observed in solution at room temperature, despite the fact that the first excited singlet states of dienes lie considerably higher than those of the aromatic hydrocarbons involved. A study of various substituent effects on the quenching rates has been carried out and attempts have been made to ascertain those effects important in determining these rates and the stability of the (presumed) excited complex. A model based on delocalization of excitation energy through virtual states of the diene is proposed and is successful in rationalizing the correlation found between diene singlet state energies and quenching rates. The model will allow qualitative estimation of the effect of diene structure on quenching rates and will predict the susceptibility of various aromatic hydrocarbon singlets to diene quenching.

The quenching has been shown to be noneffective in producing diene excited states or in inducing any appreciable change in the diene or aromatic hydrocarbon. It is concluded, therefore, that dienes quench by acting as specific catalysts for the nonradiative decay of aromatic hydrocarbon singlets.

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INTRODUCTION

A detailed knowledge of the paths of deactivation available to molecules in electronically excited states is of increasing importance in photochemistry, photobiology, and other interdisciplinary fields. Aromatic hydrocarbons and carbonyl containing compounds have been the subjects of particularly searching studies due both to the fact that their spectroscopic states lie in regions accessible to most equipment and because, as classes, their properties are probably most easily related to theory.

A complete specification of the modes of deactivation which follow excitation in these molecules would include yields of luminescence, both fluorescence and phosphorescence, yields of nonradiative decay from both the excited singlet and triplet manifolds, and details of the photochemical transformations occurring in either of the two sets of states. In the past twenty years, as a first step toward an understanding of these processes, extensive compilations of fluorescence and phosphorescence yields were made (1a-g); however, for individual compounds these yields rarely summed to unity and no conclusions regarding the relative importance of *nonradiative* decay from the excited singlet and triplet states could be made.

A measure of the *absolute* yield of triplet states was of immense importance here and was also sought after for other reasons. Due to the forbidden nature of the ground state ← triplet transition, triplet lifetimes are commonly 10^4-10^8 times longer than their corresponding lowest excited singlet state lifetimes, and are accordingly much more often implicated in photoreactions of various sorts. This prominent position is further complicated by the fact that most photochemical reactions are conducted at or near room temperature where phosphorescence is rarely observed. Rigid solutions at low temperatures are generally required to observe the emission. Consequently little was known until recently regarding yields of this important state, either in frozen solution or at room temperature.

In 1965, Lamola and Hammond (2) reported the first practical method for the counting of triplet states of aromatic hydrocarbons and ketones at room temperature in solution. The determination is based on a chemical method in which the molecule whose intersystem crossing yield is desired is used as a sensitizer for the triplet state cis-trans isomerization of suitable olefins. The details of the olefin isomerization are well known and a measure of isomerization quantum yield leads directly to the intersystem crossing yield. A scheme suitable for the application of the method is shown in equations 1-9. Here S = sensitizer with singlet ($S^{*(1)}$) and triplet ($S^{*(3)}$) excited states, c = cis olefin and t = trans olefin. It is assumed that only c is originally present and that conversion to t is small.

$$S \xrightarrow{h\nu} S^{*(1)} \qquad \text{excitation} \qquad (1)$$

$$S^{*(1)} \xrightarrow{k_f} S + h\nu' \qquad \text{fluorescence} \qquad (2)$$

$$S^{*(1)} \xrightarrow{k_{ic}} S^{*(3)} \qquad \text{intersystem crossing} \qquad (3)$$

$$S^{*(1)} \xrightarrow{k_u} S \qquad \text{all other 1st order decay from } S^{*(1)} \qquad (4)$$

$$S^{*(3)} \xrightarrow{k_d} S \qquad \text{decay of } S^{*(3)} \qquad (5)$$

$$S^{*(3)} + c \xrightarrow{k_q} c^{*(3)} \qquad \text{energy transfer} \qquad (6)$$

$$c^{*(3)} \xrightarrow{k_t} t \qquad \text{decay to } \underline{\text{trans}} \qquad (7)$$

$$c^{*(3)} \xrightarrow{k_c} c \qquad \text{decay to } \underline{\text{cis}} \qquad (8)$$

since $k_d \ll k_q[c]$ in general

$$\phi_{c\to t} = \frac{k_{ic}}{k_f + k_{ic} + k_u} \quad \frac{k_t}{k_t + k_c} \qquad (9)$$

$$= (\phi_{ic})\ (\underline{\text{known}}\ \text{decay ratio})\ \ (\text{ref. } 3, 4)$$

Using this method and employing such olefins as *trans*-α-methylstilbene, *trans*-β-methylstyrene, and *cis*-1,3-pentadiene, the intersystem crossing ratios of many aromatic hydrocarbons, amines, and halo-compounds, and several carbonyl compounds, were determined (5).

At that time, all existing theories (6a, b) concerning rates of deactivation of excited states of aromatic hydrocarbons, and most chemical intuition (7) predicted that nonradiative decay from the excited singlet to the ground state would be much less important than decay of the analogous triplet state to ground state, if indeed, the former process occurred. This was attributed both to the larger energy gap involved and the availability of alternate rapid modes of singlet state decay such as fluorescence. This led to predictions, at least for aromatic hydrocarbons, that the sum of fluorescence and intersystem crossing yields would equal unity, that is $\phi_f + \phi_{ic} = 1$ (8).

An examination of a portion of Lamola's data indicates that this is not the case in several notable examples. See Table I.

The intersystem crossing yield measured for benzene is the subject of strong disagreement in the literature. The data of Lim (1c) had shown that the quantum yields for benzene fluorescence and phosphorescence were equal and amounted to 0. 20 at low temperatures; that is, $\phi_f = \phi_p = 0.20$. Now in EPA at 77° K benzene displays a phosphorescence lifetime of 7 sec., while that of benzene-d-6 is about 28 sec. If one assumes the latter to be the true radiative lifetime of benzene triplet then $\phi_{ic} = (28/7)(0.20) = 0.80$ and $\phi_f + \phi_{ic} = 1.00$. This result was further substantiated by Noyes and Ishikawa (9) with gas phase measurements. Here benzene was used to sensitize biacetyl phosphorescence, and while the experiments were not without difficulties, estimates of $\phi_{ic} = 0.78$ were obtained.

Other attempts to measure the intersystem crossing ratio of benzene in solution have been largely unsuccessful (10, 11). The rapid buildup of quenching impurities has been the source of many difficulties.

TABLE I

Selected Intersystem Crossing Efficiencies

Compound[a]	ϕ_{ic}	ϕ_f [b]	$\phi_f + \phi_{ic}$
Benzene	.24	.20 (.07)	<.44
Naphthalene	.40	.39 (.23)	.79 (.63)
Phenanthrene	.76	.10	.86
Fluorene	.31	.54 (.80)	.85 (1.11)
Triphenylene	.95	.06 (.08)	1.01 (1.03)

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[a] cis-1, 3-Pentadiene → trans-1, 3-pentadiene was used as the triplet counter.

[b] Values represent Lamola's judgement of best available data (5). Numbers in parenthesis are from Berlman (1g).

More recently, Wilkinson (12) has developed a method of triplet counting which is both elegant and apparently accurate. In this treatment various heavy atom containing solutes, such as bromobenzene, ethyl iodide, and xenon, are shown to quench fluorescence by enhancing intersystem crossing to the triplet.

$$ArH^{*(1)} + RX \xrightarrow{k_q} ArH^{*(3)} + RX \qquad (10)$$

Measurements of relative fluorescence yields both with and without added quencher, and of relative triplet populations both with and without added quencher*, are treated as follows with reference to equations 1-8 and 10, replacing c and t by RX (X = heavy atom) where appropriate.

$$\frac{(\phi_f)_o}{\phi_f} \quad \frac{\phi_{trip.}}{(\phi_{trip.})_o}$$

$$= \left(\frac{k_f}{k_f + k_u + k_{ic}}\right)\left(\frac{k_f + k_u + k_{ic} + k_q[RX]}{k_f}\right)\left(\frac{k_{ic} + k_q[Q]}{k_f + k_{ic} + k_u + k_q[Q]}\right)\left(\frac{k_f + k_{ic} + k_u}{k_{ic}}\right)$$

$$= 1 + \frac{k_q[RX]}{k_{ic}} = 1 + \frac{k_q \tau_s [RX]}{\phi_{ic}} \qquad (11)$$

As shown above a measure of k_q, a knowledge of τ_s, the singlet lifetime, and the slope of the quenching data plotted according

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*Relative triplet population described as a ratio of optical densities for the triplet-triplet absorption following flash excitation.

to equation 11 gives the intersystem crossing ratio. Results obtained by this method give ϕ_{ic} (naphthalene) = 0.75 and in general show that $\phi_f + \phi_{ic} = 1.00$ for a great variety of aromatic hydrocarbons (13).

In view of the several discrepancies noted, and because of the inherent simplicity and usefulness of the method, it seemed advantageous to initiate a reinvestigation of the triplet counting method developed by Lamola, particularly with respect to the widely employed triplet counter cis-1,3-pentadiene.

Of the several assumptions implicit in this method of triplet counting, the assumption of noninteraction between singlet sensitizer and diene ground state would seem to be most secure, as an examination of Figure I reveals. The singlet state of butadiene lies considerably higher than that of naphthalene (90 kcal/mole)*, a typical hydrocarbon sensitizer. It is this extremely large singlet-triplet splitting of most simple dienes and olefins which lies at the heart of the method, allowing optical excitation of the sensitizer without interference by counter, but permitting facile energy transfer in the triplet state.

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*Srinivasan (14) has presented evidence that the singlet state of dienes lies at considerably longer wavelengths than is indicated by inspection of band maxima. Light of wavelength 2537 Å is certainly capable of exciting the diene singlet state. For cis-1,3-pentadiene, however, the extinction coefficient has dropped from about 21,000 to 8 cm^2/mole at wavelengths of 2235 Å and 2537 Å, respectively.

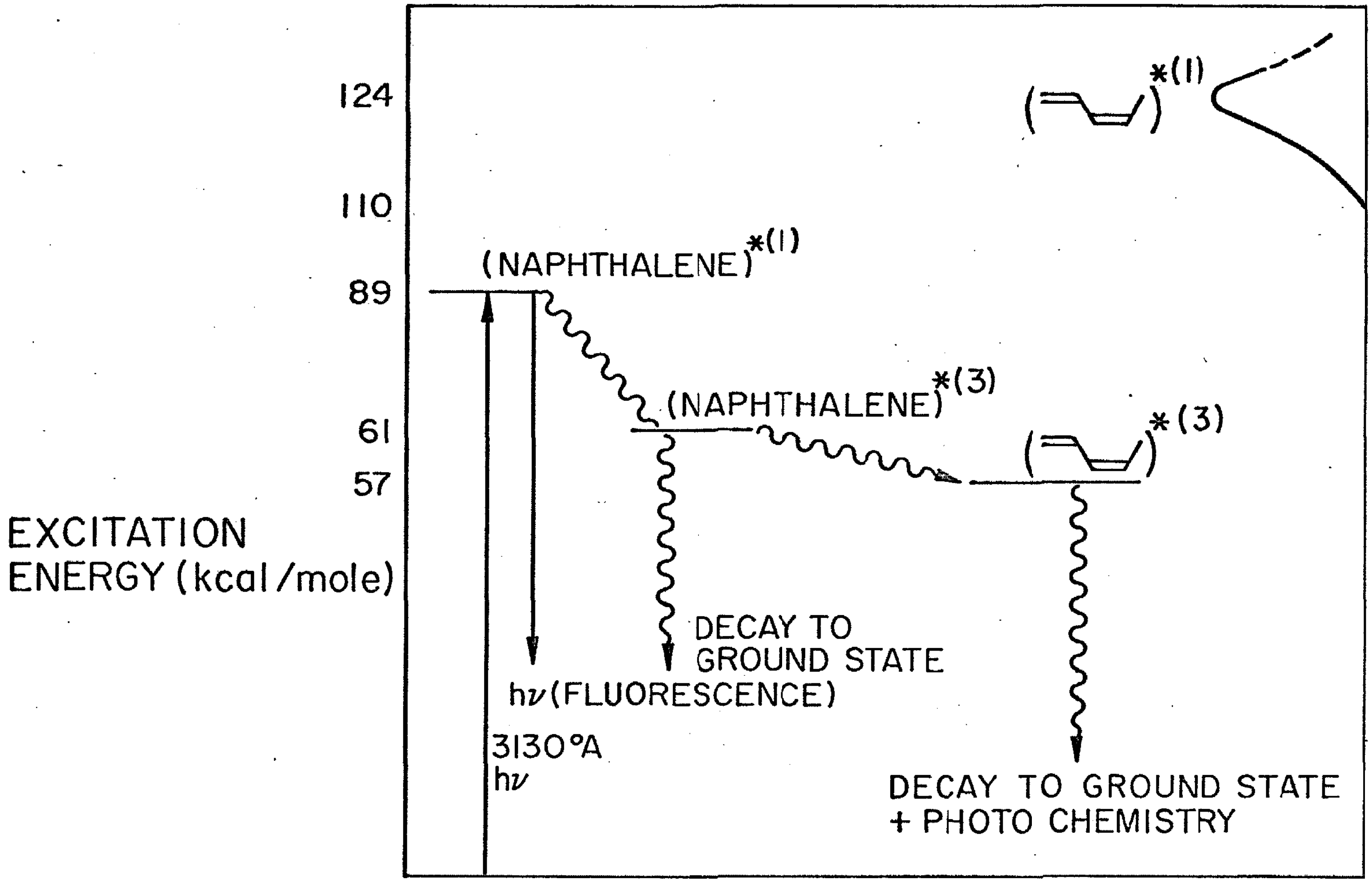

FIGURE I: Energy Levels of Naphthalene and Butadiene

Despite the existence of this large energy gap between excited singlet states, other modes of quenching could be operative (see Discussion). As will be described later, benzene was found to add photochemically to dienes in high quantum yield. It was felt that the interactions responsible for such photoreactions must surely arise from the benzene excited singlet state since energy transfer from benzene triplet to the diene is expected to be extremely rapid. This supposition was confirmed when the ability of added conjugated dienes in solution to quench the fluorescence of benzene, naphthalene and anthracene was demonstrated.

RESULTS

Rates and Efficiencies of Fluorescence Quenching by Conjugated Dienes

The most direct approach to a study of interactions between excited singlet states and added perturbing impurity employs the fluorescence from the singlet state and the ability of the impurity to quench, enhance, or shift this fluorescence. Conjugated dienes have been found to quench the fluorescence of various aromatic hydrocarbons without the appearance of new or shifted emission. In simplest form this finding demands the mechanism outlined in equations 12-18.

$$\mathrm{ArH} + h\nu \longrightarrow \mathrm{ArH}^{*(1)} \qquad \text{excitation} \tag{12}$$

$$\mathrm{ArH}^{*(1)} \xrightarrow{k_f} \mathrm{ArH} + h\nu' \qquad \text{fluorescence} \tag{13}$$

$$\xrightarrow{k_{ic}} \mathrm{ArH}^{*(3)} \qquad \text{intersystem crossing} \tag{14}$$

$$+\ \mathrm{D} \xrightarrow{k_q} \underline{\text{no fluorescence}} \qquad \text{quenching by diene} \tag{15}$$

$$(\phi_f)_o = k_f / k_f + k_{ic} = \text{fluorescence without added quencher} \tag{16}$$

$$\phi_f = k_f / k_f + k_{ic} + k_q[\mathrm{D}] = \text{fluorescence with D added} \tag{17}$$

$$(\phi_f)_o / \phi_f = 1 + k_q \tau_s [\mathrm{D}] \tag{18}$$

$$\tau_s = \text{singlet lifetime} = \frac{1}{k_f + k_{ic}}$$

In practice the measurements consist of a determination of $(\phi_f)_o / \phi_f$ * for four diene concentrations. A sample of the resulting spectra and plots is shown in Figures II and III.

Slopes obtained from data treated in this manner are equal to $k_q \tau_s$. Only comparisons of k_q data are valid especially when comparing diene quenching efficiencies toward different hydrocarbons. Therefore at this point a brief discussion of sources of fluorescence lifetimes will be given.

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*An explanation of these symbols is given in equations 16, 17, 18.

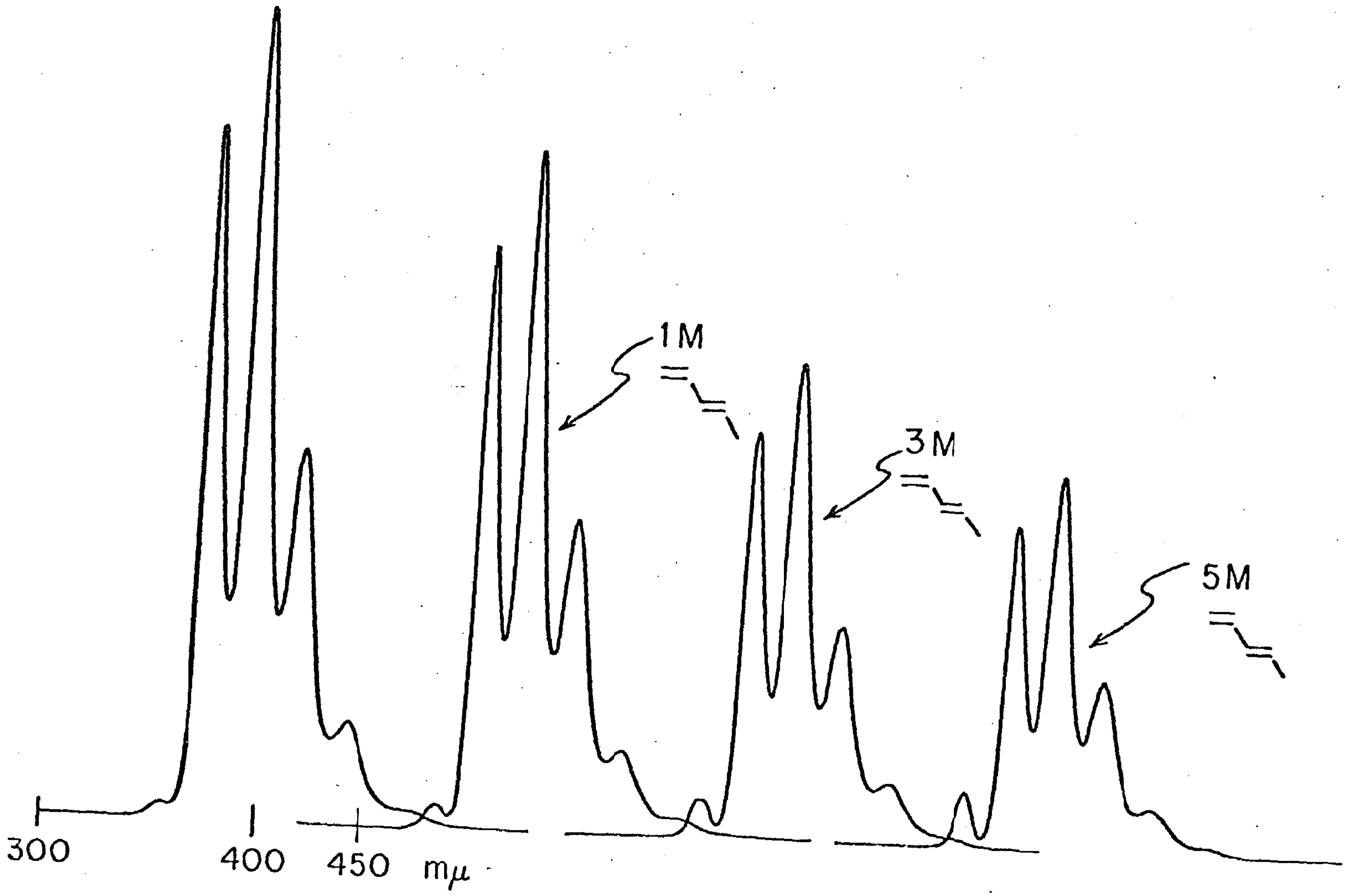


FIGURE II: Anthracene Fluorescence Spectra Showing Diene Quenching

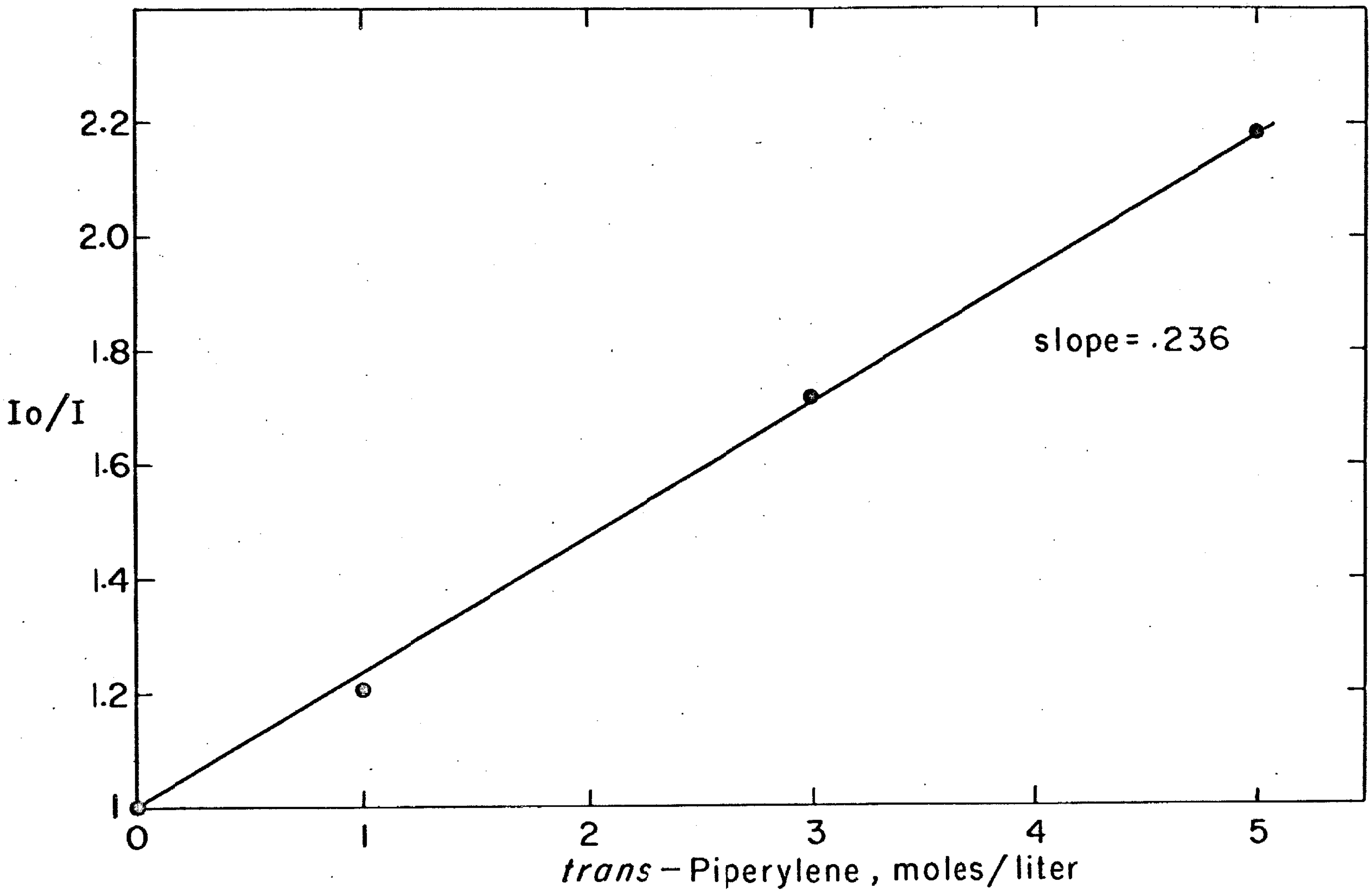


FIGURE III: Stern-Volmer Treatment of Data from Figure II

Determination of Fluorescence Lifetimes

Fluorescence lifetimes are difficult to measure. Rather sophisticated electronic equipment is required for the determination of decay times in the 1-100 nanosecond range. Perhaps the most popular device, first described by Rollefson (15), employs a sine-wave modulated light source, the focused beam of which passes partly to a detecting photomultiplier circuit, partly to a cell containing a molecule capable of fluorescence. Because of the inherent fluorescence lifetime of the molecule, the fluorescence detection circuit will display a certain phase lag with respect to the other detection unit. This phase lag is then directly converted into fluorescence lifetime.

Methods based on the direct observation of fluorescence decay curves following flash excitation are undoubtedly capable of providing more precise information, especially with regard to the exponential character of the decay. Flash excitation lamps of suitably short rise and fall times ($<$ 1 nanosecond) are not, however, available. In spite of this difficulty, Berlman (1g) has developed an analysis which takes the nonnegligible lamp pulse width into account, and a computer program to aid with the calculations has been devised.

It is principally the data of Berlman that are employed here. Berlman has also pointed out an interesting correlation which has been used to determine the lifetimes of those compounds where other data were not available.

The quenching of fluorescence by oxygen has been well known

(16) for some time. Berlman defines the quantity L_0/L as the ratio

$$ArH'^{*} + O_2 \xrightarrow{k'_q} \text{no fluorescence} \qquad (19)$$

$$\phi_{fo}/\phi_f = 1 + k'_q \tau_s [O_2] = L_o/L \qquad (20)$$

of fluorescence intensity with no oxygen/the fluorescence intensity with oxygen present in solution in equilibrium with the atmosphere. Bowen (16) had previously pointed out that k'_q was remarkably similar ($\sim 3.4 \times 10^{10}$ M^{-1} sec^{-1}) for a wide range of compounds. Berlman was able to confirm this by showing a linear relation between L_0/L and singlet lifetime, τ_s, both determined in cyclohexane solution at room temperature. Figure IV shows this relationship. Table II shows data which confirm the accuracy of the method within 20%.

TABLE II

Oxygen Quenching Efficiencies

Fluor	L_0/L	τ_s (from L_0/L)	τ_s (Berlman flash excitation)
naphthalene	5.43	77	96
1-methylnaphthalene	5.37	76	67
2-methylnaphthalene	3.64	46	59
2,3-dimethylnaphthalene	5.55	79	78
2,6-dimethylnaphthalene	2.59	27	38

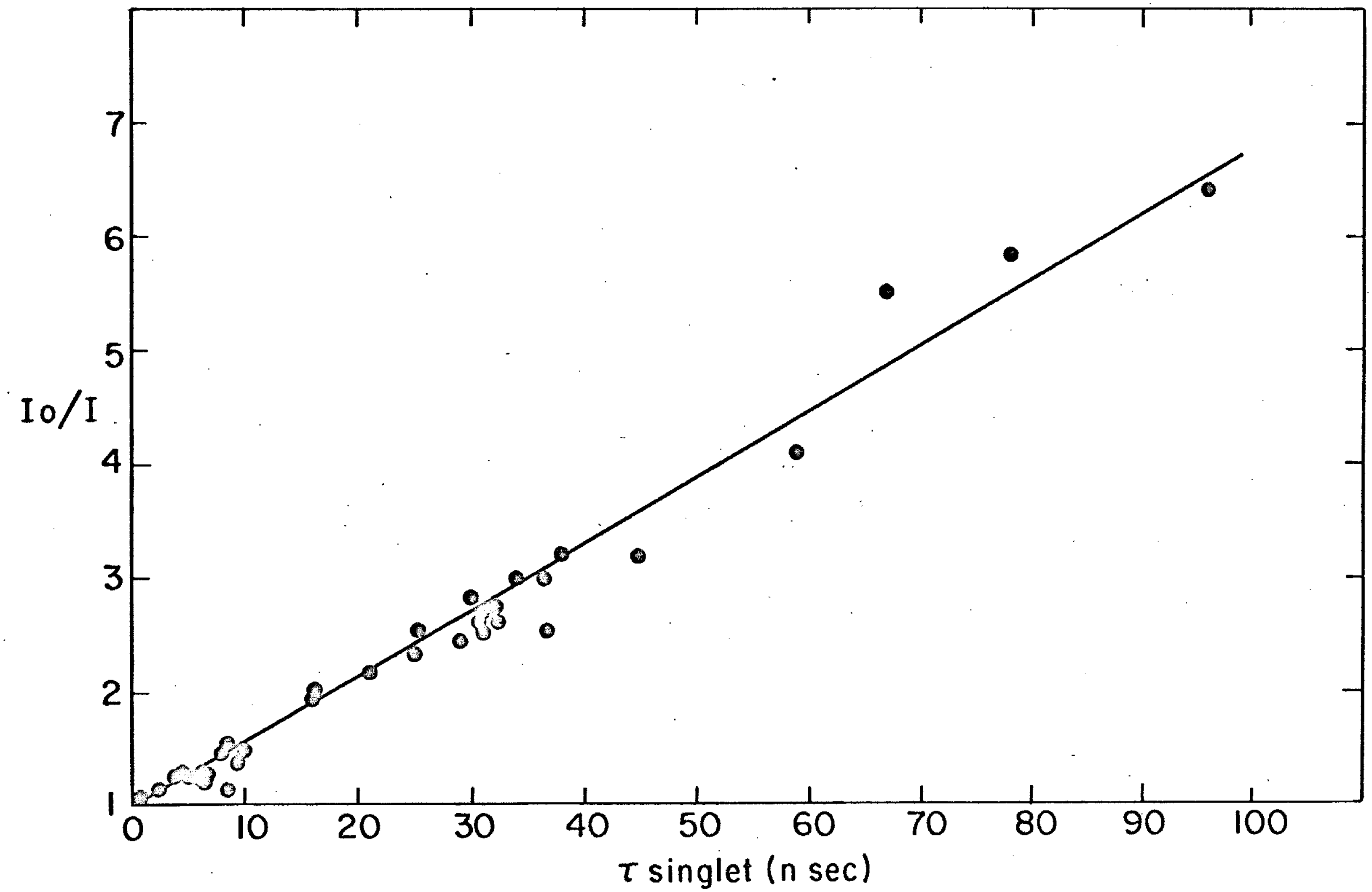


FIGURE IV: The Relationship between Oxygen Quenching and Singlet Lifetime (see Reference 1g)

In the absence of other accurate data, the oxygen quenching results were taken as a reasonable measure of τ_S.

Quenching Rate Data

Tables III and IV show data for flourescence quenching rates by conjugated dienes of the fluors naphthalene ($\tau_S = 96 \times 10^{-9}$ secs) and anthracene ($\tau_S = 4.9 \times 10^{-9}$ secs) (1 g).

A relatively large list of nonquenchers for naphthalene fluorescence is not shown; it includes a variety of substituted ethylenes including tetramethylethylene, and simple ketones (acetone). It is of interest to note that 1, 3-cycloöctadiene, in which the ethylenes show a tendency to assume orientations perpendicular to one another, will not quench naphthalene fluorescence.

A detailed error analysis of the data was not attempted. Where repeated, data are reproducible within 5%. Fits of data to Stern-Volmer equations were estimated visually, and no cases of obvious curvature were observed in the plotted data.

The mechanistic implications of the overall trends will be discussed later.

Table V gives quenching rate data for various substituted naphthalenes. The method employed in arriving at these constants has yielded numbers of unreliable accuracy. Quenching data were obtained in undegassed sample tubes. The slopes were corrected for oxygen quenching by multiplying by the oxygen quenching ratio, L_O/L, (see page 15), and the lifetime dependence removed by eliminating τ_S values arrived at from L_O/L. See equations 21 and 22 which follow.

TABLE III

Rate Constants for Naphthalene Fluorescence Quenching

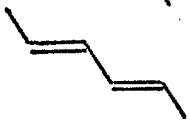
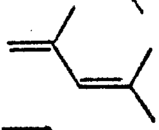
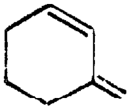
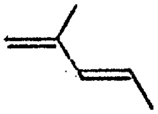
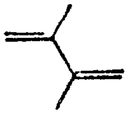
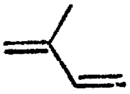
Diene		$k_q \times 10^{-7}$ (liters/mole sec)
2, 5-dimethyl-2, 4-hexadiene		400
1, 3-cyclohexadiene		250
4-methyl-1, 3-pentadiene		120
trans-2-trans-4-hexadiene		62
trans-2-cis-4-hexadiene		51
2, 4-dimethyl-1, 3-pentadiene		45
1, 3-cyclopentadiene		29
cis-2-cis-4-hexadiene		23
3-methylene-cyclohexene		17
trans-2-methyl-1, 3-pentadiene		11
trans-1, 3-pentadiene		11
cis-1, 3-pentadiene		9. 2
2, 3-dimethyl-1, 3-butadiene		1. 5
isoprene		1. 4

TABLE IV

Quenching of Anthracene Fluorescence by Substituted Dienes ($\tau_S C_{14}H_{10} = 4.9 \times 10^{-9}$ sec.)

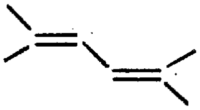
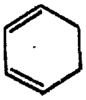
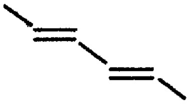
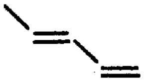
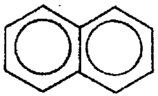
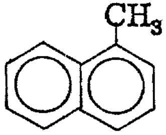
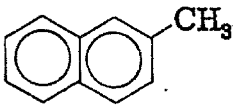
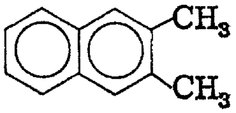
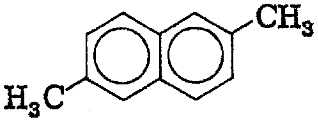
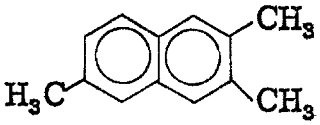
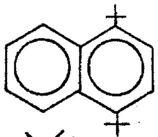
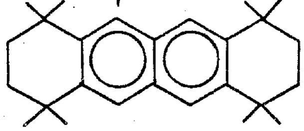
Diene		$k_q \times 10^{-6}$
2, 5-Dimethyl-2, 4-hexadiene		25
1, 3-Cyclohexadiene		30
trans-2-trans-4-Hexadiene		4. 1
trans-1, 3-Pentadiene		. 45

TABLE V

Quenching of Fluorescence of Naphthalene Derivatives

trans-1,3-Pentadiene

AH	$\tau_s \times 10^{+9}$	$k_q \times 10^{-7}$
	77	14.0
	76	7.9
	46	9.4
	79	5.6
	27	3.8
	46	2.4
	33	1.3
	31	.87

$$\frac{(\phi_f)_o}{\phi_f} = \left(\frac{k_f}{k_f + k_{ic} + k_q'[O_2]}\right)\left(\frac{k_f + k_{ic} + k_q'[O_2] + k_q[D]}{k_f}\right) \qquad (21)$$

$$= 1 + \frac{k_q[D]}{k_f + k_{ic} + k_q'[O_2]}$$

$$= 1 + \frac{k_q[D]}{k_f + k_{ic}} \times \frac{k_f + k_{ic}}{k_f + k_{ic} + k_q'[O_2]}$$

$$= 1 + k_q \tau_s [D] \frac{L}{L_o}$$

$$\text{slope} = \frac{L}{L_o} k_q \tau_s \qquad (22)$$

A short discussion of these trends can be found in the Discussion section.

Effect of Singlet Interaction on the Sensitized Photoreactions of Dienes

When promoted to triplet excited levels by means of sensitizers, conjugated dienes in solution are capable of phototransformations in high quantum yield (17). The cis → trans isomerization of 1,3-pentadiene described in the Introduction illustrates this point. The effect of strong interactions between diene ground state and sensitizer excited singlet state can only be one of complication. In the kinetically most simple case, the interaction would lead to complete wastage of excitation energy, in which event the quenching by diene would be viewed as a simple pseudo first order decay of the sensitizer singlet competing with fluorescence and intersystem crossing. Written for a generalized triplet-sensitized diene photoreaction producing product x the quantum yield for x production would be given as below, assuming complete energy wastage. Here α represents the efficiency of

$$\phi_{+\underline{x}} = \frac{k_{ic}}{k_f + k_{ic} + k_q[D]} \quad (\alpha\beta) \qquad (23)$$

energy transfer from the sensitizer triplet to the diene and β represents the efficiency with which the diene triplet forms product x. Note that the equation can be rearranged so that data available from Stern-Volmer treatments of diene quenching efficiency can be used to predict quantum yields at fixed diene concentrations.

$$\phi_{+\underline{x}} = (\phi_{ic})_o \frac{\phi_f}{(\phi_f)_o} \quad (\alpha\beta) \qquad (24)$$

If the singlet quenching is effective in producing diene triplet products (such as x) additional terms will be required for the above equations, and, in general, no prediction of quantum yield can be made.

To assay the effect of singlet quenching on the quantum yields of such triplet sensitized processes, three typical examples were chosen for study. They are the rearrangement of myrcene to 5,5-dimethyl-1-vinylbicyclo[2.1.1]hexane (17), the dimerization reactions of 1,3-pentadiene and 1,3-cyclohexadiene, and the *cis*→*trans* isomerization of 1,3-pentadiene and 2-methyl-1,3-pentadiene. These are shown in Figure V below, in the order listed.

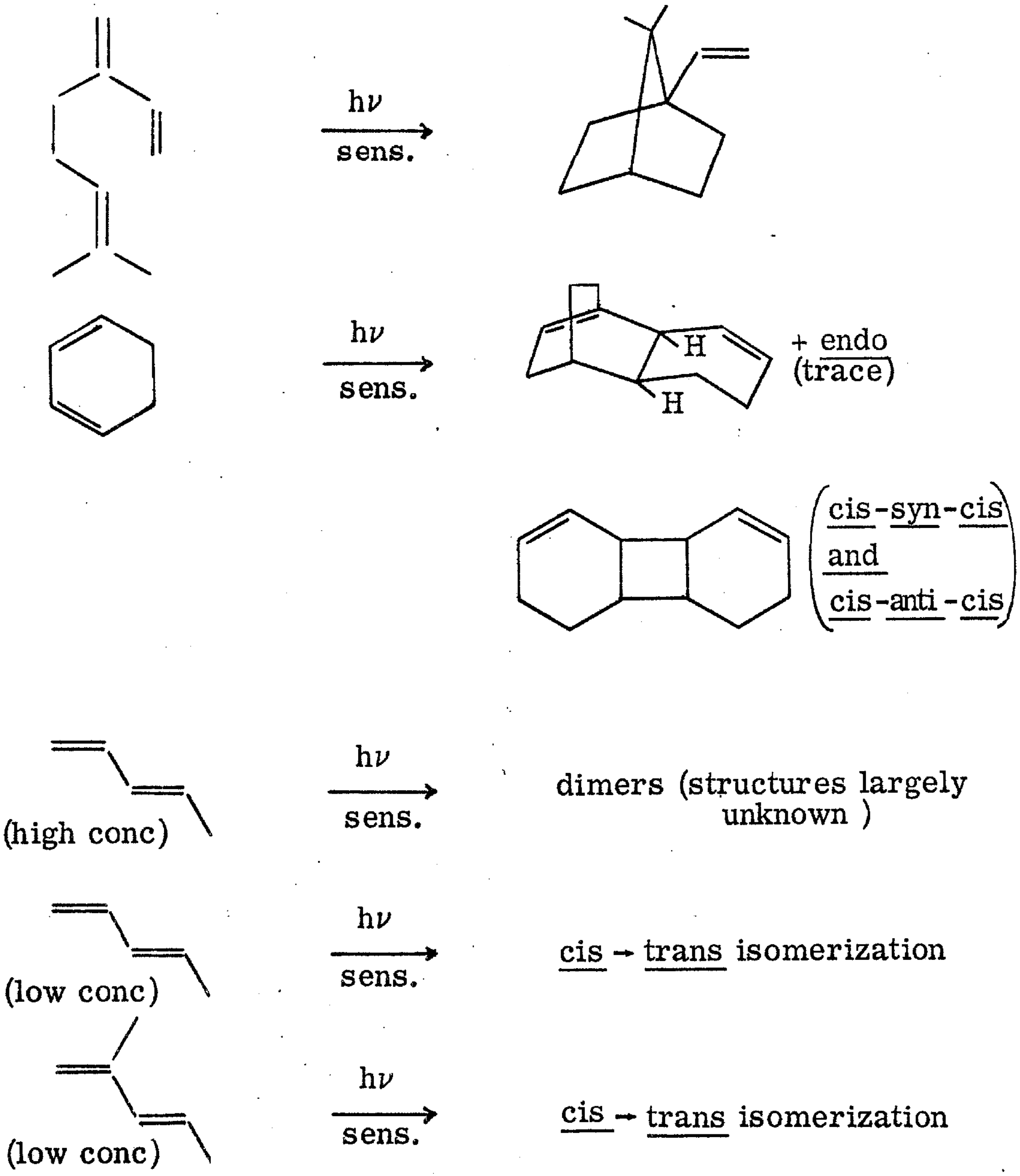


FIGURE V: Diene Triplet Reactions

Myrcene

With the use of sensitizers such as benzophenone, Liu was able to convert myrcene to 5, 5-dimethyl-1-vinylbicyclo[2. 1. 1] hexane smoothly, with a quantum yield of 0. 05 (18). No other products were observed.

Myrcene shows very low quenching activity toward naphthalene (see Table III). Half quenching occurs at 0. 29 M and at these high concentrations some polymerization (dimerization?) occurs which deposits intractable gums on the walls of the irradiation vessels. However a trend in quantum yield behavior can be noticed despite the fact that exact yields could not be obtained.

Hexane solutions containing myrcene (. 5 M, 1. 0 M, and 5. 0M) and naphthalene (. 05 M) were prepared, degassed, and irradiated for extended periods of time (due to the low absolute quantum yield), using carefully filtered 3130 Å light. At . 5 M the triplet product was easily observed; a reduced yield resulted at 1. 0 M, and none could be detected at 5. 0 M myrcene concentration.

Dimerization Reactions

Sensitized photodimerization of dienes proceeds with high quantum yield at high diene concentrations, if appropriate sensitizers are employed (19). With regard to high energy sensitizers, several systems have been well studied and the reaction can be understood in terms of the generalized mechanism on page 22. In this case, the factor β includes terms describing the efficiency with which diene triplet reacts with diene ground state, the competing process being diene triplet decay to the ground state. The product distributions can be rationalized in terms of the formation of the most stable diradical intermediates (20).

A study of the 1-methylnaphthalene sensitized* dimerization of 1, 3-cyclohexadiene and the naphthalene sensitized 1, 3-pentadiene dimerization showed marked quantum yield decreases at high diene concentration. Reference to Table VI will show the agreement between calculated (assuming energy wastage) and observed quantum yields. Values for benzophenone sensitized dimerization quantum yields are included for comparison.

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*In this case naphthalene interfered with dimer analysis by V. P. C. This study was performed by Dr. D. G. Whitten, whose permission to use the data is gratefully acknowledged.

TABLE VI

Diene Dimerization Quantum Yields

Sensitizer	Diene (conc)	ϕ_{ic} (sens)	$\frac{\phi_f}{\phi_{f\,o}}$	ϕ dimer
Benzophenone	1,3-pentadiene (1.0 M)	1.00	-	1.00[b]
Naphthalene	1,3-pentadiene (1.0 M)	0.70[a]	0.108	0.071[b] (calc) 0.077[b] (obs)
Benzophenone	1,3-cyclohexadiene (.21 M)	1.00	-	0.88[c]
1-Methyl naphthalene	1,3-cyclohexadiene (.21 M)	0.60[a]	0.054	0.028 (calc) 0.027 (obs)

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a. These data differ from that of Lamola. See Discussion for explanation.

b. Relative quantum yields since β is not known for 1,3-pentadiene

c. Unpublished data of G. F. Vesley.

cis → trans Isomerization

The effect of singlet quenching on rates of cis → trans isomerization reactions of suitable dienes is of paramount importance in this study. Once again the details of the high energy photosensitization are well worked out (3). The generalized scheme of page 22 applies here if β is replaced by the diene triplet decay ratio (see the Introduction for details).

In this case, the dissipation of between 75 to 90 kcal/mole excitation energy by the fluor during or shortly following singlet quenching, could conceivably lead to hot ground states of the diene capable of isomerization. However, Table VII demonstrates that at high diene concentrations isomerization quantum yields do fall off. Figures VI a and b illustrate the fit obtained between calculated (solid line) and observed values (data points) for the naphthalene sensitized cis → trans isomerization of 1, 3-pentadiene. The calculated line assumes complete energy wastage, and that $\phi_{\underline{cis}\rightarrow\underline{trans}}$ in the absence of singlet quenching is 0. 37.

TABLE VII

Quantum Yields of cis → trans Isomerization

Sensitizer	Diene	$\phi_f / \phi_{f\,o}$	ϕ
Naphthalene	cis-1, 3-pentadiene		
	0. 01 M	0. 92	0. 34
	0. 02	0. 85	0. 31
	0. 05	0. 69	0. 23
	0. 08	0. 59	0. 20
	0. 12	0. 48	0. 17
	0. 20	0. 36	0. 11
	1. 00	0. 10	0. 06
	trans-1, 3-pentadiene		
	0. 08	0. 54	0. 13
	0. 12	0. 46	0. 11
	0. 20	0. 32	0. 07
	trans-2-methyl-1, 3-pentadiene		
	0. 08	0. 54	0. 12
	0. 12	0. 46	0. 10
	0. 20	0. 32	0. 05

TABLE VII--2 (continued)

Sensitizer	Diene	ϕ_f / ϕ_{fo}	ϕ
2-Methylnaphthalene	*cis*-1, 3-pentadiene		
	0. 08	~0. 74	0. 26
	0. 12	~0. 66	0. 25
	0. 20	~0. 54	0. 18
	trans-1, 3-pentadiene		
	0. 08	0. 74	0. 19
	0. 12	0. 66	0. 17
	0. 20	0. 54	0. 12
2, 3-Dimethyl-naphthalene	*cis*-1, 3-pentadiene		
	0. 076	~0. 85	0. 26
	0. 114	~0. 79	0. 25
	0. 190	~0. 69	0. 18
	trans-1, 3-pentadiene		
	0. 086	0. 82	0. 19
	0. 128	0. 75	0. 18
	0. 214	0. 65	0. 13
1, 4-Di-t-butyl-naphthalene	*cis*-1, 3-pentadiene		
	0. 08		0. 34
	0. 12		0. 32
	0. 20		0. 30

TABLE VII--3 (continued)

Sensitizer	Diene	ϕ
	trans-1, 3-pentadiene	
	0. 08	0. 24
	0. 12	0. 23
	0. 20	0. 20
2, 3, 6-Trimethyl-naphthalene	cis-1, 3-pentadiene	
	0. 08	0. 29
	0. 12	0. 28
	0. 20	0. 25
	trans-1, 3-pentadiene	
	0. 08	0. 22
	0. 12	0. 20
	0. 20	0. 18

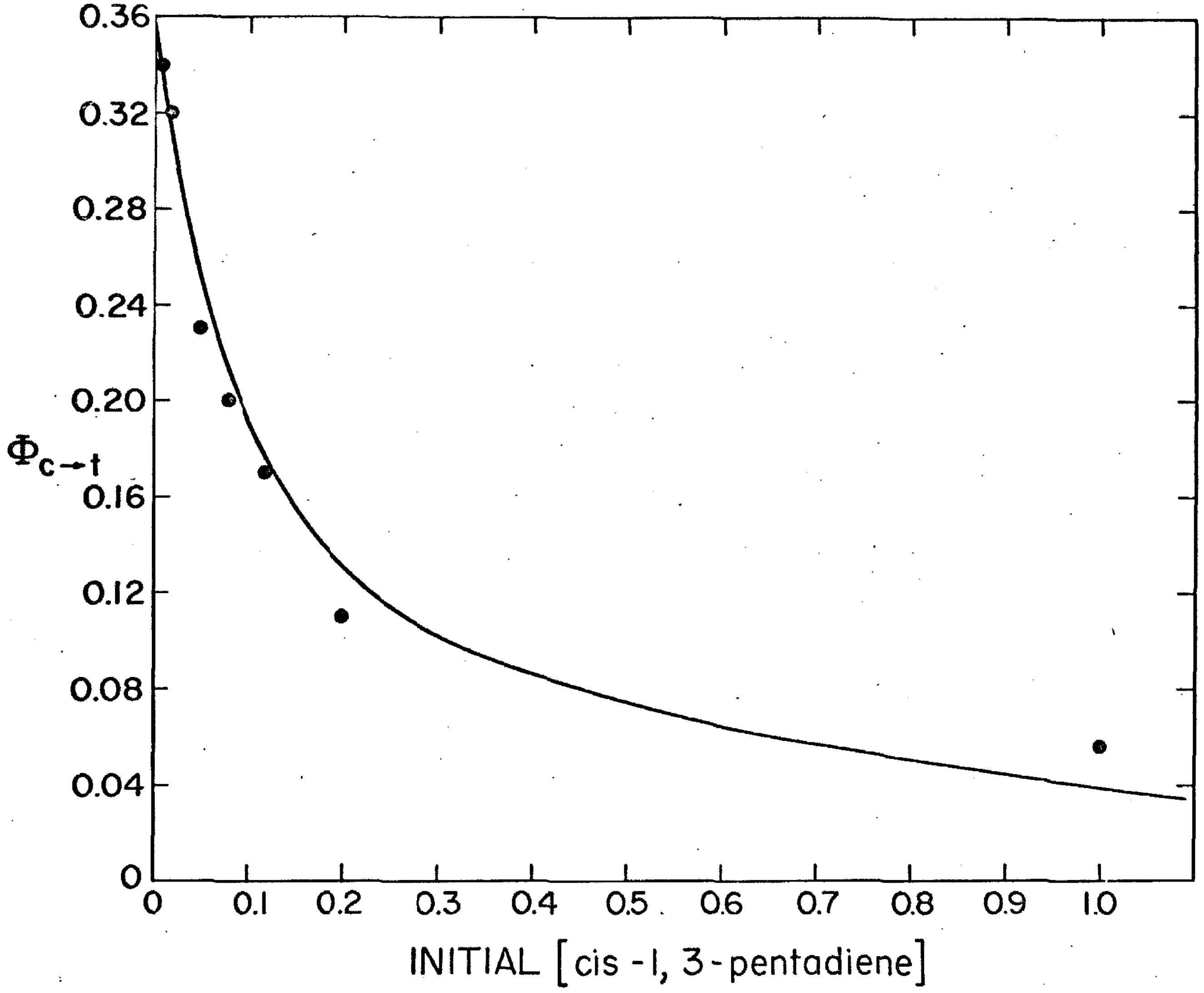


FIGURE VI a: cis→trans Quantum Yield as a Function of Initial 1, 3-Pentadiene Concentration

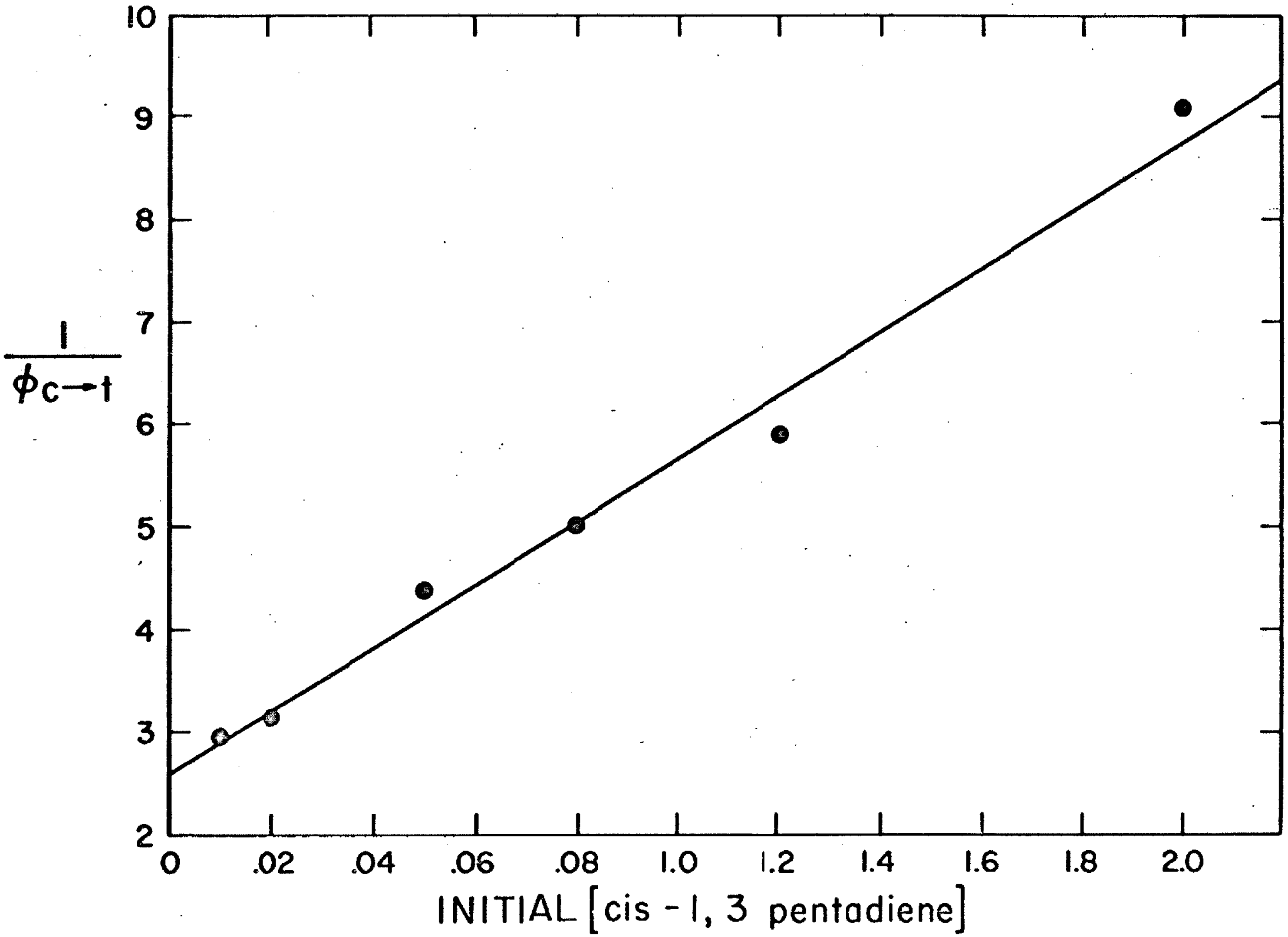


FIGURE VIb: cis→trans Quantum Yield as a Function of Initial 1, 3-Pentadiene Concentration

Photochemistry from Diene Excited Singlet States

As illustrated in Figure I, page 8, and implied in all discussion, the probability of quenching *via* energy transfer to the diene from the aromatic hydrocarbon singlet state is rather slight. In an attempt to confirm this hypothesis, and as an adjunct to other quantum yield studies, a careful search for products characteristically arising from diene singlet states was undertaken.

Dienes, as a class, are not known to undergo intersystem crossing from the excited singlet to the excited triplet manifold (17). This is evident when one examines the products derived from 1,3-pentadiene, myrcene and 1,3-cyclohexadiene (23) following direct excitation. See Figure VII.

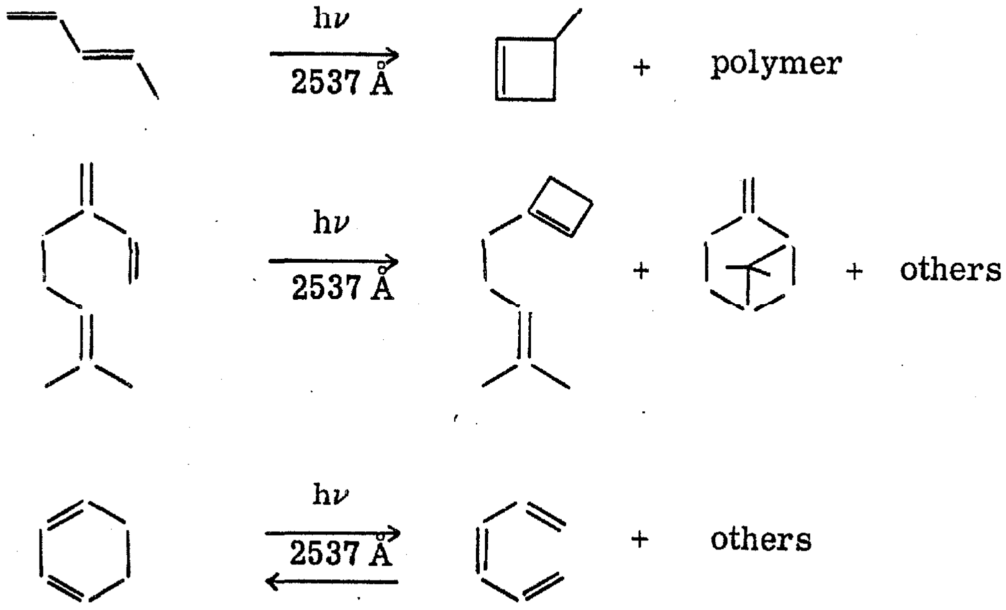


FIGURE VII: Diene Singlet Reactions

Despite the fact that irradiations were prolonged to the extent that quantum yields of triplet products as low as 0.02 could be measured easily (see Tables V and VI), no other products could be detected. In particular, no products characteristic of the diene singlet state could be observed in any of the three above mentioned examples.

In this manner energy transfer as a quenching mechanism can be rigorously excluded. A more thorough discussion of these results follows in the Discussion section.

EXPERIMENTAL

Olefins

Isoprene was obtained from the Phillips Petroleum Company. 2,3-Dimethyl-1,3-butadiene, and cis-2-cis-4-hexadiene were obtained from K & K Laboratories. cis- And trans-piperylene, cis-2-trans-4-hexadiene and trans-2-trans-4-hexadiene were purchased from the Columbia Organic Chemicals Company. Aldrich supplied 4-methyl-1,3-pentadiene, 2,4-dimethyl-1,3-pentadiene, and trans-2-methyl-1,3-pentadiene. All of the above mentioned dienes were further purified by distillation from lithium aluminum hydride immediately before use. All were examined by VPC and were found to be >99% pure. All cis-trans isomers were found to possess >99% isomeric purity.

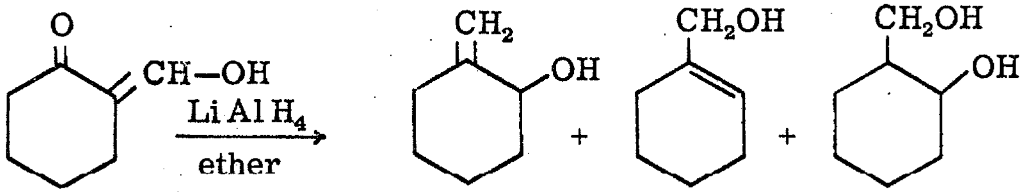
1,3-Cyclohexadiene and 2,5-dimethyl-2,4-hexadiene obtained from Aldrich Chemicals Company were both found to be extremely air sensitive, due to rapid polymerization and marked tendencies to form peroxides. Both were distilled over a slightly positive N_2 pressure from lithium aluminum hydride, then placed in constricted test tubes and degassed on the vacuum line (ultimate pressure 10^{-4} mm Hg) immediately.

Myrcene, obtained as a technical grade from Aldrich was purified by preparative scale vapor phase chromatography on Apiezon L columns (20% on Chromosorb G, $\frac{1}{2}$ inch × 12 ft) and maintained at 110° C. The use for this purpose of Professor J. D. Roberts' F & M

Prepmaster *Model 775* is gratefully acknowledged. Myrcene of >99% purity was obtained in this manner and was distilled from lithium aluminum hydride before use.

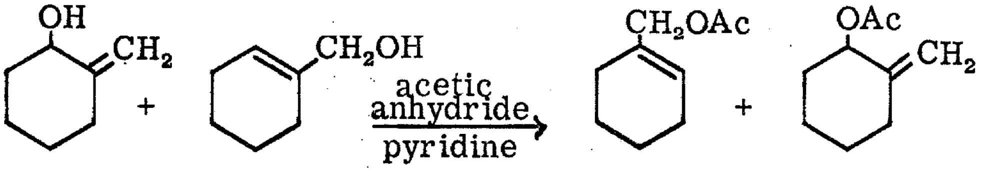
cis- And *trans*-4-methylpentene-2 were obtained from the Phillips Petroleum Company. VPC analysis showed no detectable amounts of the other isomer. They were used without further purification.

3-Methylenecyclohexene. Hydroxymethylenecyclohexanone, I, below, was prepared by duplication of the procedure described by Ainsworth (24). Eighty grams of I in an equal volume of dry ether was added over a three-hour period to a stirred suspension of 30 grams of lithium aluminum hydride in 500 cc of dry ether. The mixture was then refluxed $1\frac{1}{2}$ hours. The solution was cooled in an ice bath and 32 cc H_2O, 24 cc 20% aqueous NaOH, and 110 cc of H_2O were added slowly in succession with rapid stirring. Stirring was continued 1 hour and a grainy precipitate (sodium aluminate) was formed and filtered. The filter cake was washed liberally with ether; the combined ether extracts were removed under vacuum; and the pale yellow residue was distilled at 25 mm Hg pressure yielding 41 grams of a colorless material B. P. 81°-99° C (a mixture of II and III). This is essentially the procedure of Dreiding and Hartman (25) with base workup following the procedure of Amundsen and Nelson (26).



I II III not isolated

Forty-one grams of the alcohol mixture II and III were added to 350 ml of acetic anhydride and 200 ml of pyridine, and allowed to stand at room temperature for 24 hours. The mixture was then poured onto 1 kg of crushed ice, stirred 15 minutes, then extracted with 300 ml of ether twice. The ether layer was then extracted with water, aqueous bicarbonate, water, dilute sulfuric acid, and water in that order, then dried over magnesium sulfate. The ether was removed and the acetate distilled at 20 mm Hg pressure to yield 42 grams of a clear liquid BP 82°-98°, presumably IV and V (see reference 24).



IV V

Acetate pyrolysis followed exactly the procedure of Bailey (27). The product was purified by distillation for $LiAlH_4$ B. P. 110-111 (lit. 109° C). The nmr spectrum was consistent with the structure. The ultraviolet spectrum showed λ_{max} 231 mμ (ϵ_{max} = 22,000) literature λ_{max} 231 mμ (ϵ_{max} = 21,000).

Aromatic Hydrocarbons

Benzene was obtained from several sources. In fluorescence and in uses as a sensitizer, the benzene was obtained from either the Phillips Petroleum Company (Research Grade stated purity >99.9%) and distilled from potassium before use; or from James Hinton,Ph.D., Valparaiso, Florida, who supplies a zone refined grade of stated purity 99.97%. (See also solvent section below)

Naphthalene was obtained from Eastman Organic Chemicals stock. Samples for fluorescence studies were further purified by two recrystallizations from methanol, followed by a 31 pass zone refining treatment. The tube was then opened and the naphthalene sublimed out under vacuum. For quantum yield determinations the naphthalene was recrystallized and sublimed only once.

Methylnaphthalenes. All methylnaphthalenes were purified by Dr. L. J. Altman. A variety of purification techniques were employed. All samples were obtained from the Aldrich stock. In the case of liquid samples, two distillations were employed. Solid samples were recrystallized and sublimed at least once in all cases. No fluorescing impurity could be detected in the measurements.

Anthracene, blue-violet fluorescence grade, was obtained from Eastman Chemicals, and was twice sublimed before use.

Solvents

Hexane (Phillips Pure Grade) was further purified by stirring over hot (50°-60° C) concentrated sulfuric acid under a dry nitrogen atmosphere for several days. The acid layer was changed frequently and did not darken appreciably during the latter stages of treatment. The hexane was then decanted and washed with water, aqueous sodium carbonate and water in that order. After drying over anhydrous magnesium sulfate the material was distilled twice through an efficient glass bead packed column, taking only a middle cut ($\frac{3}{4}$ of total) on each occasion. By VPC only heptane is noted as an impurity.

Benzene for solvent purposes was stirred over concentrated sulfuric acid at room temperature. The acid layer was changed frequently until no further darkening occurred. It was then treated exactly as hexane (see above). VPC invariably revealed the presence of about 1% of (presumably) saturated hydrocarbons which occasionally interfered with 1, 3-pentadiene analysis. For this reason benzene was judged to be a much less suitable solvent than hexane.

Analyses

Vapor phase chromatographic instruments employed varied with the sensitivity needed. Loenco instruments used included those with thermal, dual thermal, single and dual flame detectors, Models 15B, 70, 15B with flame detection, and 160 respectively.

Columns employed were: for 1, 3-pentadiene, 2, 4-hexadiene, and 2-methyl-1, 3-pentadiene isomers; hexane, benzene and all other dienes under 7 carbons; $\beta\beta\beta$-tris-(cyanoethoxy)-propane (10% on Chromosorb G 80-100 mesh-50 ft × $\frac{1}{8}$ inch) maintained at room temperature or $AgNO_3$ saturated in Triethylene glycol (10% on Chromosorb G - 15 ft × $\frac{1}{4}$ inch) maintained at room temperature was satisfactory: for the dimers of 1, 3-pentadiene and 1, 3-cyclohexadiene a variety of columns were satisfactory, including 20% Carbowax 20 M, 10% Apiezon J, and 10% Fluorosilicone on Chromosorb G and P, however complete separation of the complex mixtures could only be obtained on a 250 ft capillary column coated with Apiezon J: myrcene and its various rearrangement products could be separated for analysis on 10% Apiezon J on Chromosorb G (10 ft) maintained at

110° C.

Sample Preparation and Apparatus

Fluorescence studies

In general, stock solutions of both the appropriate aromatic hydrocarbon and the quencher (diene) were prepared in hexane (and, occasionally, benzene) solution. Identical amounts of the stock hydrocarbon were then added to each of several 10 ml volumetric flasks. Varying amounts of the quencher stock were then added to all but one flask. Samples were then diluted to the mark. About 3 ml of each solution was added to a precision bore pyrex test tube (O.D.= $\frac{1}{2}$ inch) constricted about 3 inches from the bottom. These samples were then degassed on a conventional vacuum line (minimum pressure 10^{-4} mm Hg) using three freeze pump thaw cycles, and sealed at the constriction. Relative fluorescence intensities were measured on an Aminco-Bowman spectrophotofluorometer, maintained at room temperature.

Quantum Yield Determination

Samples for quantum yield determinations were also prepared from stock solutions of sensitizer and quencher, of appropriate concentration. These were loaded into 13 × 100 mm pyrex culture tubes constricted about three inches from the bottom and degassed as described above. In general, duplicate tubes were prepared with each being analyzed twice.

In most cases described the quantum yield of the appropriate reaction sensitized by benzophenone proved to be a well-known quantity from previous researches. Therefore identical tubes containing benzophenone instead as sensitizer were used as actinometry. This procedure proved more convenient and accurate than conventional ferrioxalate actinometry.

DISCUSSION

In this section other studies and theories of fluorescence quenching will be reviewed, followed by an application of these ideas to the diene quenching results. The consequences of singlet quenching will also be discussed.

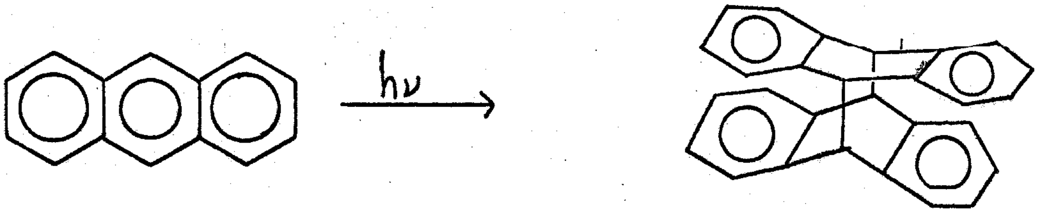
Collisional Fluorescence Quenching

In this section previous studies of fluorescence quenching brought about by interactions following collisions in solution will be reviewed. In keeping with the findings of the previous sections, those interactions involving energy transfer will not be discussed. This excludes such areas as sensitized fluorescence and Förster energy transfer, but by no means leaves a limited and uninvestigated area. The quenching of fluorescence has been a well documented, if not well understood, area for many years (16).

In general, fluorescence quenching can be divided into two major classes, which shall be designated as chemical and electronic. These will be discussed separately.

Chemical quenching will be defined as fluorescence diminuation due to bond-formation or -breakage in the excited state, brought about by interaction with another solute. Two examples are given.

In concentrated solutions ($> 10^{-3}$ M), anthracene will dimerize photochemically to dianthracene. Bowen and Tanner (28) have shown that the quantum efficiency for dianthracene formation parallels the



self-quenching of anthracene fluorescence and that greater than 90% of the self singlet quenching leads to dimer. This can be viewed as quenching of anthracene singlet by band formation with anthracene ground state. In this, as in many other cases, however, it is not always easy to demonstrate that the dimer formation is a cause rather than a result of the quenching.

A more interesting example consists of the excited state deprotonation of β-naphthol (29), whose first excited singlet state is much more acidic than its ground state (30) (see Figure VIII below).

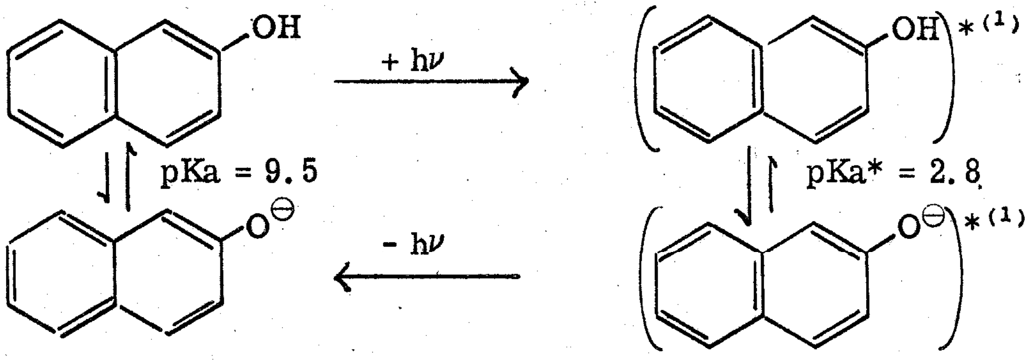


FIGURE VIII: Förster Cycle for β-Naphthol

In this case one has the additional advantage of fluorescence from the fragment excited state, the β-naphthol anion. This process may certainly be viewed as chemical quenching by the solvent, which acts as a base toward the proton.

The quenching mechanism is clear in these cases. If, following excitation, bonds are fragmented or new bonds are formed, the molecule has undergone such a large electronic reorganization that to expect unchanged fluorescence would be folly.

A wide range of other photochemical transformations may be viewed as fluorescence quenching in nature. A further discussion would be pointless, however, since a "mere" knowledge of the pertinent bond formations or ruptures is sufficient to completely describe the fluorescence quenching mechanism.

Electronic quenching,* broadly speaking, will be taken to include all interactions based on a mixing of electronic states of the excited fluor and quencher, and resulting in reduced fluorescence. No ground state-ground state interactions will be considered.† Included under this title then would be such diverse processes as eximer formation or "concentration quenching", quenching by various electron donors and acceptors, such as amines, oxygen, and halide anions, and quenching by various heavy atom containing solutes, such as bromobenzene or ethyliodide. These will be discussed separately.

Concentration quenching of fluorescence has been known for some time. Perhaps the first definitive discussion was given in 1944

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*Apologies are offered for the lack of a more elegant designation.

†Absorption spectra fail to reveal diene-aromatic hydrocarbon ground state complexes.

by Weil-Malherbe and Weiss (31). They noted the general nature of the self-quenching for aromatic hydrocarbons and proposed a charge transfer state to account for the stability of the excited complex.

$$\mathrm{ArH}^{*(1)} + \mathrm{ArH} \rightarrow (\mathrm{ArH}^{\oplus}\cdots\cdots\mathrm{ArH}^{\ominus}) \qquad (25)$$

Ferguson (32) has further developed this treatment and a charge transfer state has been supported by Hochstrasser (33). Other models based on excitation delocalization have also been proposed and supported. In actual fact a mixture of the two treatments may be more

$$\mathrm{ArH}^{*(1)} + \mathrm{ArH} \rightarrow (\mathrm{ArH}^{*(1)}\cdots\mathrm{ArH} \longleftrightarrow \mathrm{ArH}\cdots\mathrm{ArH}^{*(1)}) \qquad (26)$$

successful (34).

In 1955 the <u>fluorescence</u> of concentrated pyrene solutions was identified as arising from the excited dimer (35). The term <u>eximer</u>

$$\mathrm{Pyrene}^{*(1)} + \mathrm{Pyrene} \rightarrow \mathrm{Py}_2{}^{*} \rightarrow \mathrm{Pyrene} + \mathrm{Pyrene} + h\nu$$

was later proposed by Stevens and Hutton (36) and has gained widespread usage.

<u>Quenching by potential electron donors and acceptors</u> has been even more widely discussed in terms of charge transfer states, as one might expect. <u>Oxygen</u> is the oldest recorded quencher of fluorescence. As noted by Berlman (1g), nearly any substance that will fluoresce may be oxygen quenched, the extent depending only on the lifetime of the excited state and the oxygen solubility in the solution in question. Earliest attempts to rationalize this quenching were put forth by Weiss (37), who proposed a charge transfer mechanism and

$$ArH^{*(1)} + O_2 \rightarrow (ArH^{\oplus} \cdots\cdots O_2^{\ominus})^* \qquad (27)$$

later (38) considered the relationship between peroxide formation (39) and this quenching. More recently the enhanced intersystem crossing brought about by the oxygen interaction (40) has been emphasized, a proposal originally due to Reed (41). Mulliken and Tsubomura (42), in discussing charge transfer in general, were led to propose strong charge transfer interaction with both the singlet and triplet manifold resulting in a mixing of the states and increased probability of intersystem crossing. Other mechanisms such as that proposed by Kautsky (43), while overall spin allowed, have received little support.

$$ArH^{*(1)} + O_2 \rightarrow ArH^{*(3)} + O_2^{*(1)} \qquad (28)$$

More definitive evidence relating to the problem may be soon forthcoming. Gollnick (44) is now measuring quantum yields of sensitized oxidation (thought to proceed <u>via</u> $O_2^{*(1)}$) in an attempt to test this mechanism.

Other paramagnetic molecules such as NO also quench fluorescence (45). Recently O_2 and NO have enjoyed use as fluorescence quenchers in attempts to probe diffusion kinetics and their theoretical treatments (46, 47).

The quenching of fluorescence by amines has also been heavily investigated. Here a charge transfer treatment has once again been employed. Within a series the better quenchers are seen to be those

$$ArH^{*(1)} + R_3N: \rightarrow ArH^{\ominus} \cdots\cdots R_3N\cdot^{\oplus} \qquad (29)$$

amines with the lower ionization potentials (48) and, indeed, irradiation of amine-hydrocarbon mixtures has been used to generate aromatic radical anions for other studies (48). More recently, Ware found that the excited complex, presumably that shown above, displays emission spectra in nonpolar solvents. In polar solvents no emission is noted (49).

Other electron donors have also received considerable attention. Anions such as iodide strongly quench the fluorescence of dyes and other molecules. Rollefson (50, 51) in an elegant series of studies was able to show that iodide and thiocyanate quenching of acridone, quinine sulfate, and others was a simple bimolecular reaction depending only on the ionic strength of the quencher solute.

Once again a simple charge transfer mechanism was implicated. Quenching ability parallels redox potential of the quencher anion.

<u>Heavy atom quenchers</u> are perhaps the most interesting class. In the main their quenching action seems to proceed by enhancing the intersystem crossing ratio of the fluor (12). Polar effects (partial charge transfer) may also be important. Melhuish and Metcalf (52) have found that the quenching of R-Br is stronger if R is a better electron withdrawing substituent. An elegant method of determining intersystem crossing ratios based on this ϕ_{ic} enhancement is described in the Introduction.

The great importance of charge transfer in fluorescence quenching is not to be denied. It has been demonstrated to be the dominant interaction in amine quenching of aromatic hydrocarbon fluorescence, and is probably of lesser, but still significant, importance with O_2 and inorganic ion quenching. That both electron donors and acceptors function as effective singlet quenchers should not be viewed as surprising. *The hydrocarbon singlet state should be both a better electron donor and acceptor than its ground state.*

The relative importance of charge transfer states in eximer formation is a matter of much debate. Its principal advantage would seem to be the ease with which it can be visualized.

In all treatments of quenching efficiencies, the *stability* of the excited complex has been the property related to the rate of quenching. Thus those amines with low ionization potentials should give rise to the most stable amine-excited aromatic hydrocarbon complex. Linking this stability to the rate of quenching is a procedure fraught with peril, however, especially for reactions as fast as these ($k_q > 10^7$ liters/mole-sec). This may not, in this case, constitute a valid objection. Factors important in attaining a transition state leading to complex are expected to be related to the ease of the removal of the electron from the amine, the electron affinity of the acceptor, and factors related to steric requirements, and solvent reorganization. One might argue from Hammond's postulate that the various factors contributing to the stability of the complex need not be important in the transition state which probably occurs *very* early* in this very fast reaction. As it happens, the ionization

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*Very early is taken to mean early in the electron transfer coordinate system; that is, at a point involving slight electron reorganization compared to complete electron transfer.

potential is a measure of the ease of removal of an electron from the amine, and might reasonably be expected to be the dominant parameter in a description of the quenching mechanism.

A perhaps more fundamental correlation may be shown with the electronic polarizability of the quencher. This measure of electronic deformability of the quencher is probably a moderate gauge of its ability to attain transition states in which some electronic relocation is required. No accounting for steric requirements is made and one might expect a convenient separation of these variables. Polarizabilities of anions and amines mentioned above do correlate well with quenching rates. Unfortunately, polarizability correlates well with other fundamental properties, and no decision as to which is "more fundamental" can be made.

In the next paragraphs, a further development of these ideas will be related to fluorescence quenching by diene. Three models will be developed, one based on the polarizability, one based essentially on an excitation delocalization model, and one a form of "chemical quenching".

Conjugated Diene Quenching of Fluorescence

In part II strong evidence was presented for the specific and relatively efficient quenching of the fluorescence state of several aromatic hydrocarbons by conjugated dienes in solution. The quenching has also been shown to be completely energy wasting in nature, thus energy transfer to the diene, or catalyzed intersystem crossing by the diene (which would surely lead to diene triplets), cannot be considered seriously as mechanistic possibilities. Strong ground state interactions between the aromatic hydrocarbon and the diene might also lead to apparent quenching. A careful inspection of the absorption spectrum of naphthalene in 1 M cis-1, 3-pentadiene failed to reveal such a complex, however. We are left to conclude therefore that dienes catalyze the nonradiative decay of the aromatic hydrocarbon singlet state. The interaction models will be considered in rationalizing this effect.

Chemical quenching by dienes is a mechanistic possibility difficult to prove or disprove. The process may be visualized as the following:

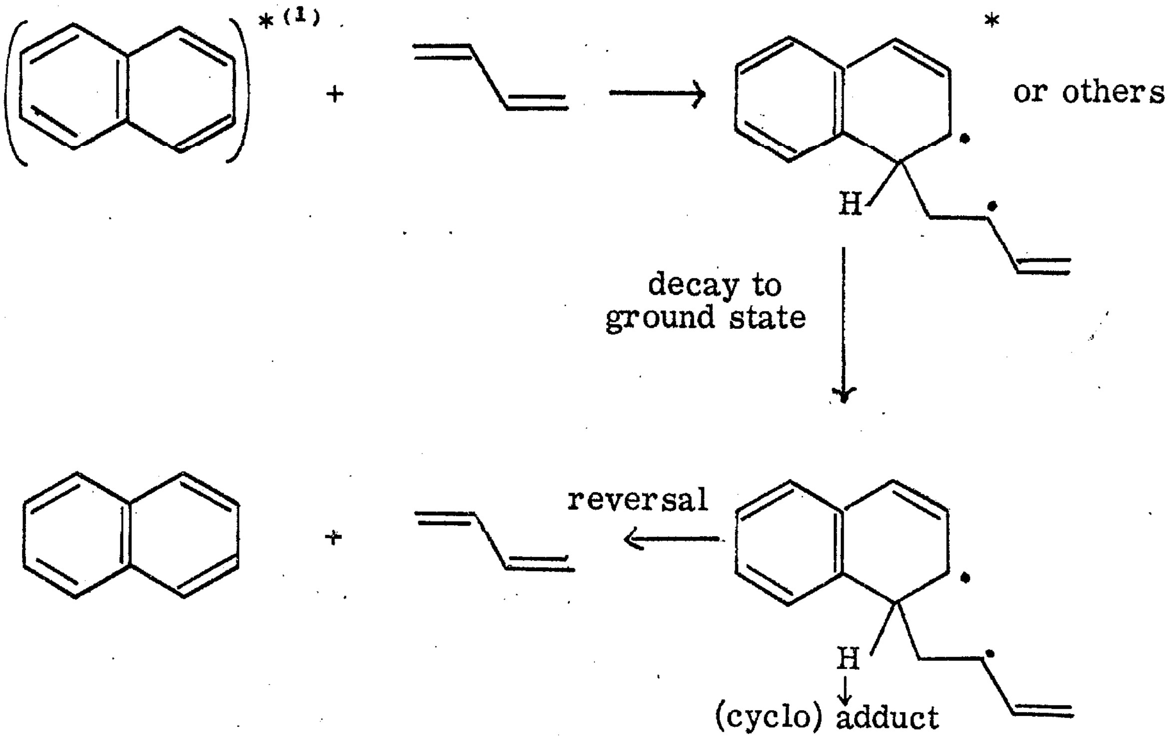
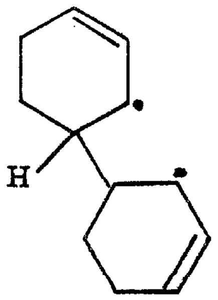


FIGURE IX: Possible Scheme for Chemical Quenching Mechanism

Yields of addition products between naphthalene and various dienes are quite low. The quantum yield for disappearance of naphthalene in 1 M cis- or trans-1, 3-pentadiene is less than 0. 01, even though ~90% of the singlets are quenched. However, the naphthalene will disappear after prolonged irradiation. Naphthalene will not add to 2, 5-dimethyl-2, 4-hexadiene.*

Although 1, 4-diradicals of the type shown above would seem to be likely candidates for facile reversals as shown, other extremely similar systems seem not to do so. For example, quantum yields for cyclohexadiene dimerization may reach unity if the diene triplets are effectively scavenged, and strong evidence has been presented for



the intermediate shown (20).

In view of these facts, chemical quenching will not be considered further as a mechanistic candidate in the naphthalene quenching. This process might be of greater importance in other systems where quantum yields for adduct formation are higher (for example, the quantum yield for adduct formation between benzene and 1, 3-pentadiene is about 0. 1).

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*Ronald Cole is acknowledged for communication of these results.

Rates of Quenching and Models for the Interaction

Cursory examination of Table VIII reveals several interesting trends, which might be useful in determining a quenching mechanism.

(1) Cyclic dienes are somewhat more effective than their "equally methylated" acyclic analogs; for example, k_q(cyclohexadiene) > k_q(2, 4-hexadiene).

(2) Addition of methyl groups to the terminal (1 and 4) positions of butadiene results in large rate increases, addition of methyl groups to internal positions (2 and 3) seems to effect little change.

In general, the increased methylation will bring about several changes, some of which may be related; these would be: lowering of the diene first excited singlet energy, lowering of the ionization potential, raising the electronic polarizability, and an increasing of the steric repulsions during interactions. The higher reactivity of cyclic dienes could be attributed to their low excitation energy, ionization potential or decreased steric requirements. Several correlations may now be attempted.

Polarizability correlates well with diene quenching efficiencies as reference to Figure X shows. Note that a clean division into steric classes can be accomplished. This is interesting because steric hindrance is a parameter which polarizability cannot take into account. If one assumes in the complex that aromatic hydrocarbon and diene lie nearly face to face, which is, generally, the geometry

TABLE VIII

Correlation Attempts for Naphthalene Singlet Quenching

Diene	log k_q	λmax	I. P.*	Rm†
2, 5-dimethyl-2, 4-hexadiene	9.60	241	-	53.63
1, 3-cyclohexadiene	9.40	256	8.40	35.20
4-methyl-1, 3-pentadiene	9.08	228	-	40.74
trans-2-_trans_-4-hexadiene	8.79	227	-	40.60
trans-2-_cis_-4-hexadiene	8.71	227	-	-
2, 4-dimethyl-1, 3-pentadiene	8.65	232	-	45.60
cyclopentadiene	8.46	238	8.58	28.89
cis-2-_cis_-4-pentadiene	8.36	227	-	-
3-methylene-cyclohexene	8.08	231	-	-
trans-2-methyl-1, 3-pentadiene	8.04	226	-	40.56
trans-1, 3-pentadiene	8.04	223.5	8.68	34.68
cis-1, 3-pentadiene	7.96	223.5	-	34.32
myrcene	7.56	221	-	-
2, 3-dimethylbutadiene	7.18	226	8.67	39.40
isoprene	7.15	220	8.86	33.79
butadiene	-	217	9.06	-

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*Ionization potentials taken from collection of J. L. Franklin (49).
†Rm = molar polarizability.

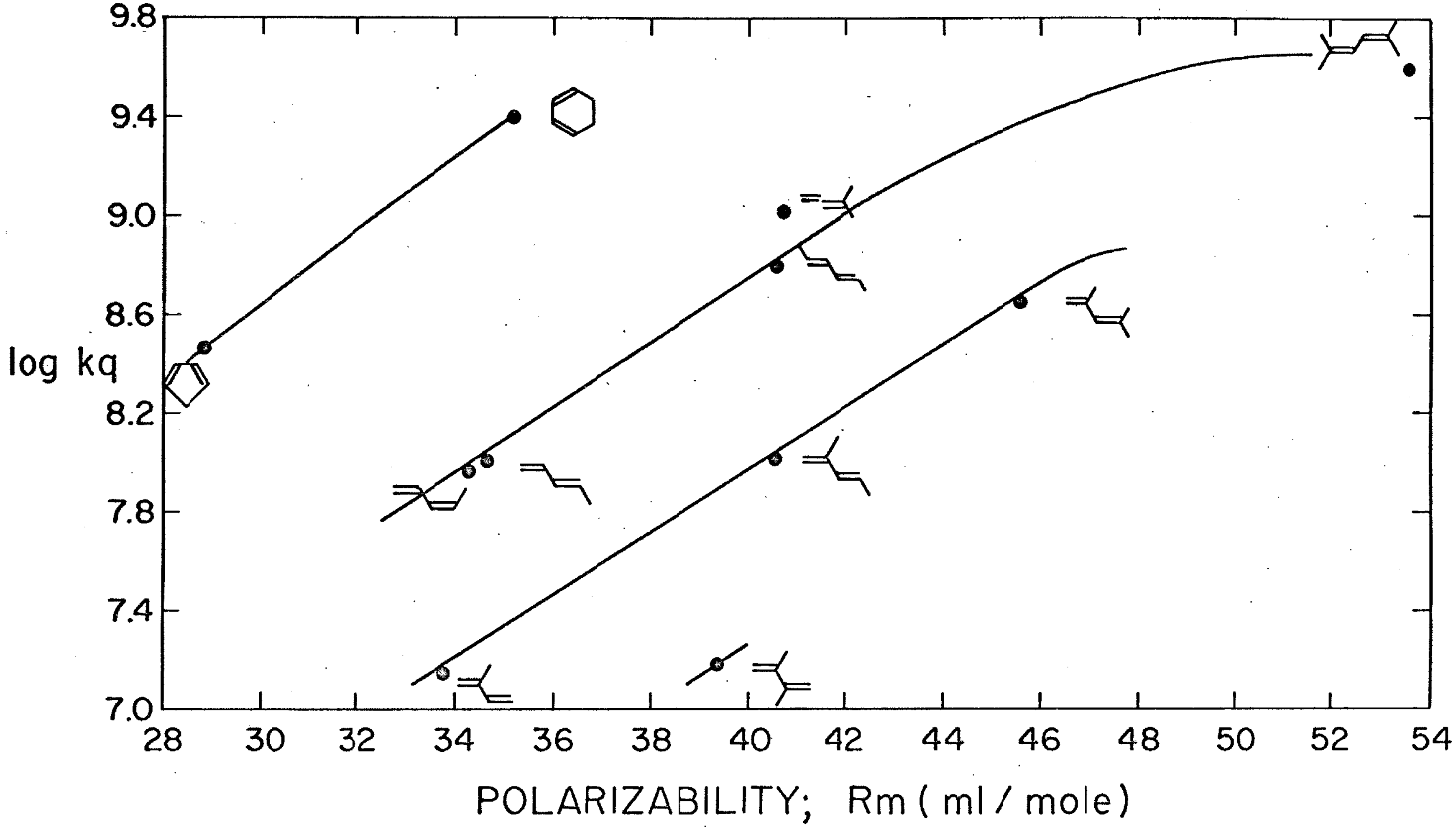

FIGURE X: The Correlation of Quenching Constants with Diene Polarizability allowing maximum interaction between two π-systems, the steric order seems physically reasonable. Cyclic dienes should present the least amount of steric repulsion in such a complex, and those dienes with methyls on internal (2 and 3) positions should present the greatest bulk to the aromatic nucleus. The slight curvature in the lines may be indicative of increasing steric factors with increasing methylation, however it can equally well be attributed to a "leveling effect" as the diffusion controlled rate is approached.

The correlation does not immediately suggest a mechanism. It would tend to indicate that the distortability of the π electronic cloud of the diene is of some importance and could be taken as evidence for a charge transfer type of interaction. No evidence accumulated to date would disprove such a formulation. Polarizability is

$$\mathrm{Np}^{*(1)} + \mathrm{D} \rightarrow (\mathrm{Np}^{\ominus} \cdots \mathrm{D}^{\oplus} \longleftrightarrow \mathrm{Np} \cdots \mathrm{D})^{*} \qquad (30)$$

successful in organizing a large range of quenching rate constants and successfully predicts that tetramethylethylene (and less highly methylated) olefins would not function effectively as quenchers.
(Rm tetramethylethylene = 29. 43)

In spite of these successes the treatment is unsatisfying for several reasons, not the least of which is strictly prejudice. The model takes no adequate account for the varying susceptibilities of aromatic hydrocarbons to diene quenching,* and intuitively must be

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*Dienes show little or no quenching activity toward *most* aromatic hydrocarbons. Naphthalene and anthracene seem to be among the few *strongly* affected. These results will be discussed fully in the following pages.

considered unlikely. Strong polar contributions in complexes formed between like nonpolar compounds are not to be expected. It is an unfortunate but perhaps obvious fact that in a series of closely related compounds polarizability will show good correlations with most other molecular properties. In order to maintain proper perspective the reader is referred to Figure XI.

Despite this reasoning, charge transfer contributions to the excited complex cannot be disregarded. This treatment can only be presented here as an alternate to the more satisfying but equally unprovable mechanism outlined on the following pages.

A more complete model for the quenching must attempt to answer the following questions:

(1) What is the basis for the interaction between excited singlet and diene?

(2) What is the relative configuration for the interaction; does it predict the observed steric ordering?

(3) Can the fast rates of nonradiative decay be accommodated within the model?

(4) Why are some aromatic hydrocarbons quenched strongly, others not at all?

A simple model for the interaction can be proposed which seems chemically reasonable. It will be developed below, with a discussion of its relative worth, for naphthalene quenching and then will be applied to other aromatics.

The quenching will be viewed as proceeding through a complex employing virtual states of the diene in an excitation

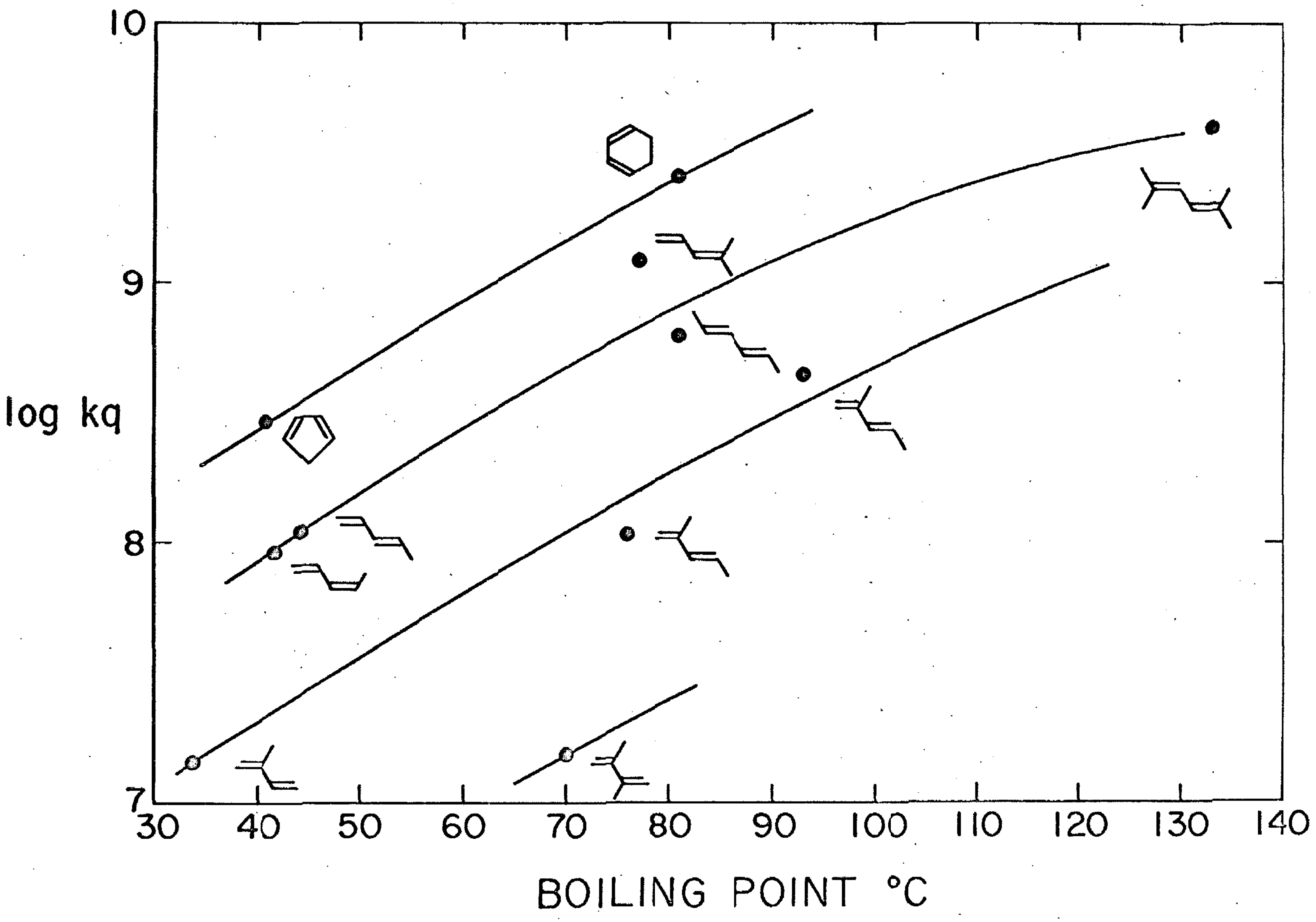


FIGURE XI: The Correlation of Quenching Constants with Diene Boiling Point delocalization scheme. This is crudely pictured as below. The overall effect is certainly a desired one. The complex is

$$\mathrm{ArH}^{*(1)} + \mathrm{D} \rightarrow (\underset{\mathrm{VI}}{\mathrm{ArH}^{*(1)} \cdots \mathrm{D}} \longleftrightarrow \underset{\mathrm{VII}}{\mathrm{ArH} \cdots \mathrm{D}^{*(1)}}) \qquad (31)$$

expected to have extremely fast rates of nonradiative decay for several reasons. Obviously a coupling of the aromatic hydrocarbon excited singlet and ground states has been accomplished. In addition, a component of the very large transition moment of the diene has been added to the complex. More crudely the reasoning may proceed as follows. Dienes have exceptionally rapid rates of nonradiative decay, since in spite of their large transition moments (which predict fast rates of fluorescence) dienes neither emit nor intersystem cross to the triplet manifold. Rates of nonradiative decay might be estimated to be as fast as $10^{10} - 10^{11}$ sec^{-1}. It is this property which the complex borrows from the diene. If you wish, decay proceeds as though originating from the ArH $\cdots$ $\mathrm{D}^{*(1)}$ resonance structure.

Now it must be expected that the energy of the first excited state of the diene will become a parameter of dominant importance. The relative contribution of resonance structure VII will increase as the energy of $\mathrm{D}^{*(1)}$ decreases, until it reaches the energy of $\mathrm{ArH}^{*(1)}$, at which point the contribution of forms VI and VII above should be equal. Roughly

$$\psi_{\text{complex}} = a\,\psi_{\mathrm{VI}} + b\,\psi_{\mathrm{VII}} \qquad (32)$$

and

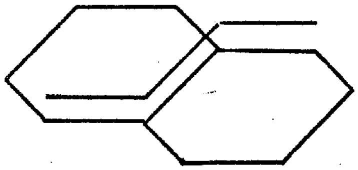
$$\frac{b}{a+b} \sim \frac{E(\mathrm{Np}^{*(1)})}{E(\mathrm{Np}^{*(1)}) + E(\mathrm{D}^{*(1)})} . \qquad (33)$$

The strength of the interaction increases as $E(D^{*(1)})$ decreases.

Unfortunately, first excited singlet energy values for dienes are difficult to obtain. The absorption spectra are usually broad structureless bands tailing out to the near u. v. (~ 300 mμ). O—O bands cannot be observed and band maxima are the only distinguishing feature. With full recognition of all the inherent inaccuracies λ_{band} maxima are plotted against log k_q in Figure XII.

The fit is not perfect. It can easily be argued at this point that the inadequacies of the fit are attributable to the use of band maxima for singlet energies. No defense is possible, and these arguments might indeed be especially applicable to the two cyclic dienes. However, valuable insight into the problem can be obtained by continuing with the assumption that $\lambda_{\max}$ is related strongly to $E(D^{*(1)})$.

A consideration of Figure XII leads to the postulation, for acyclic dienes, of an interaction geometry shown below for butadiene and naphthalene. The justification is several-fold, and is predominantly steric at this point. Methyl groups in certain positions on the diene are expected to inhibit the quenching more than in other positions. This is shown on the next page.



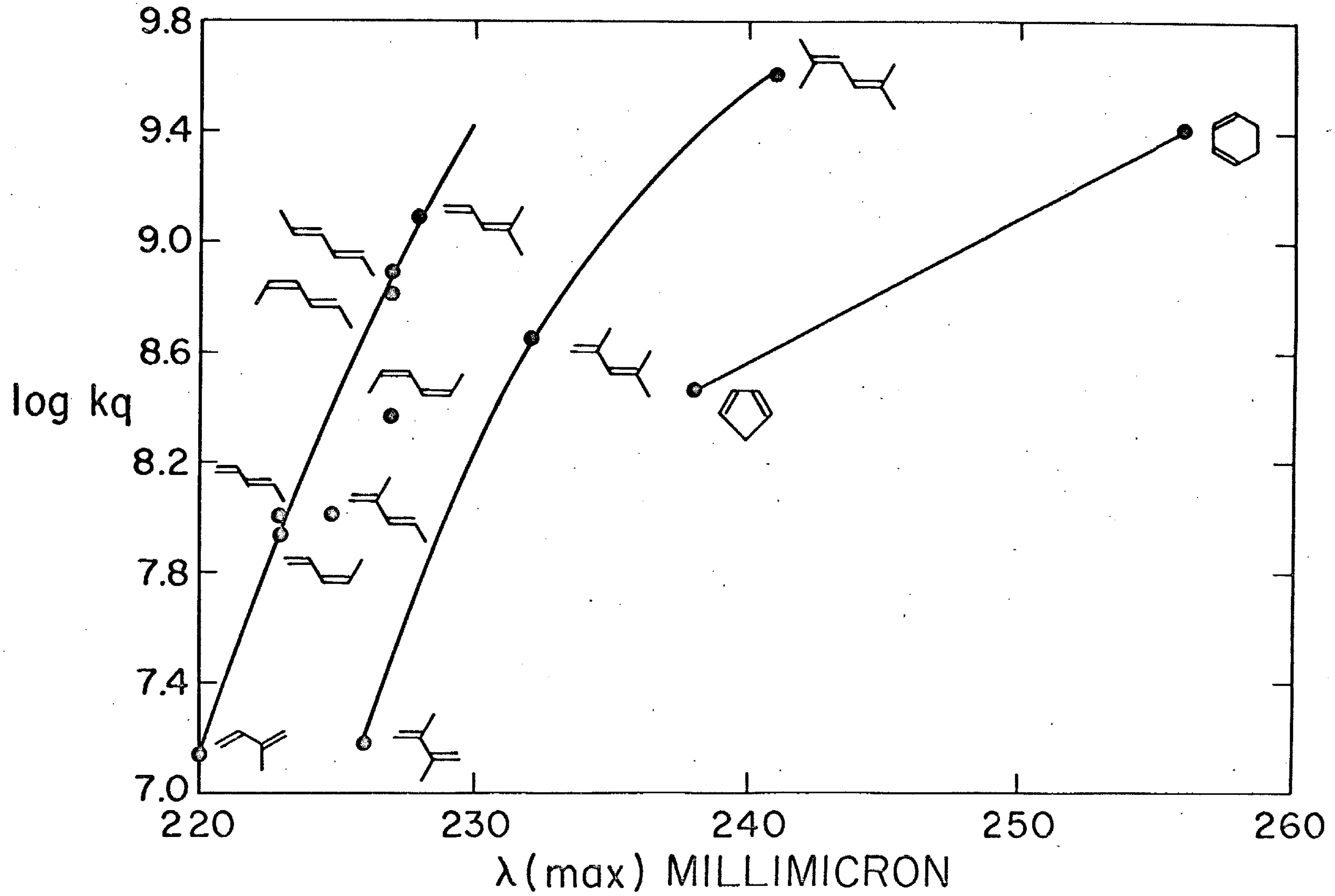
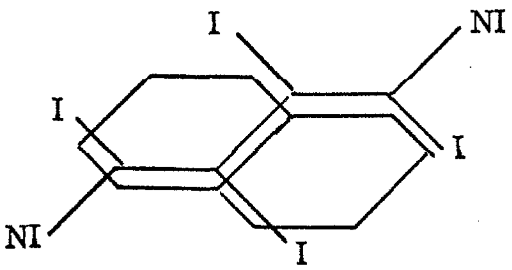


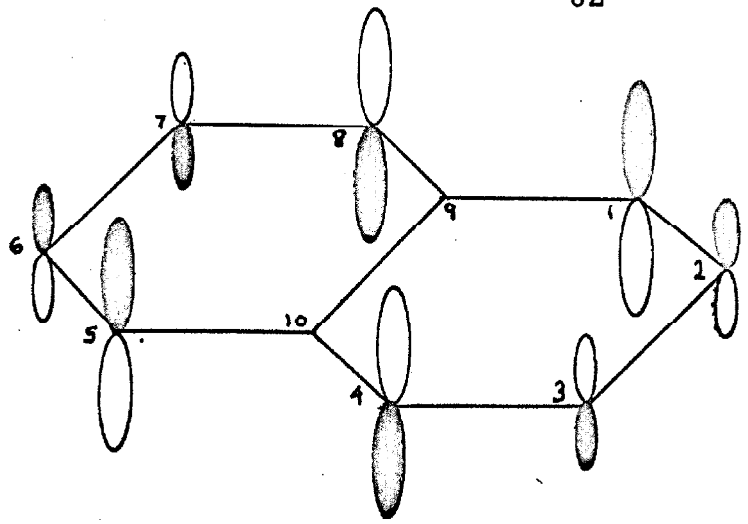
FIGURE XII: The Correlation of Quenching Constants with Diene Singlet Absorption Maxima



The positions which relatively should inhibit the quenching are shown as I groups. Noninhibiting positions are marked as NI . The factors can be seen clearly above. trans-Methyl groups (in the 1 or 4 positions) are the only NI groups. Their cis analogs should be slightly slower as is shown: k_q (trans-1,3-pentadiene) > k_q(cis-1,3-pentadiene) and k_q(trans-2-trans-4-hexadiene) > k_q(trans-2-cis-4-hexadiene). Methyl groups in 2 and 3 positions have a profound effect: k_q(trans-2-trans-4-hexadiene-λ_{max} 227 mμ) ≫ k_q(2,3-dimethyl-1,3-butadiene-λ_{max} 226 mμ). A noticeable division into steric classes is shown; those with zero or one, and two inhibiting groups are conveniently grouped.

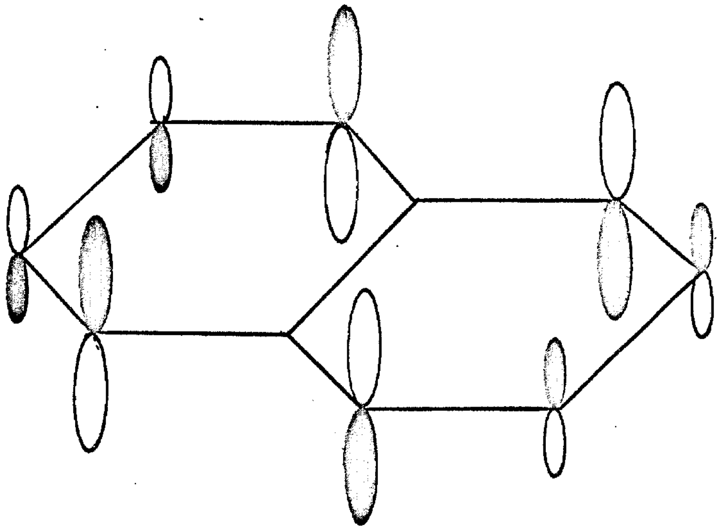
A physically more satisfying rationale for this particular geometric configuration can be seen by examining the symmetry of the highest occupied and lowest unoccupied orbitals on naphthalene and the dienes. The properties are shown as molecular orbital diagrams. The coefficients are those of the simple Hückel approximation. (See Figure XIII)

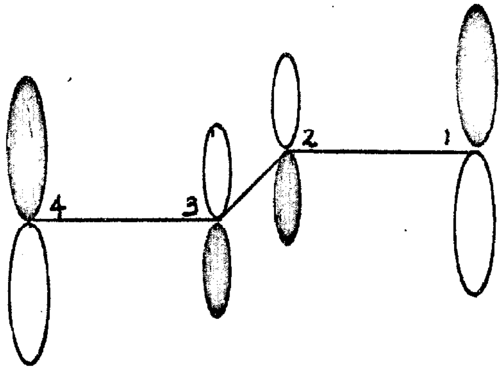
In the geometric configuration shown, bonding interactions between diene and naphthalene are obtained, with ψ_5 (naphthalene) and ψ_3 (butadiene) and ψ_6 (naphthalene) and ψ_2 (butadiene), exactly those

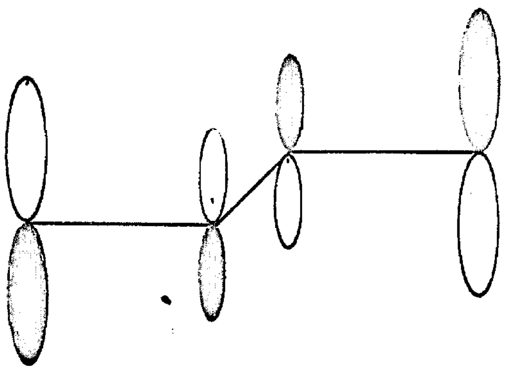


$$\psi_5 = .425(\phi_1-\phi_4+\phi_5-\phi_8)$$
$$+.263(\phi_2-\phi_3+\phi_6-\phi_7)$$

$$\psi_6 = .425(-\phi_1-\phi_4+\phi_5+\phi_8)$$
$$.263(\ \phi_2+\phi_3-\phi_6-\phi_7)$$







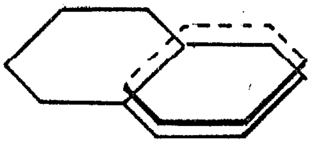
$$\psi_3 = .602(\phi_1+\phi_4)$$
$$+.372(-\phi_2-\phi_3)$$

$$\psi_2 = .602(\phi_1-\phi_4)$$
$$+.372(\phi_2-\phi_3)$$

FIGURE XIII: Symmetries of Orbitals on Naphthalene and Butadiene involved in the resonance pictured as

$$(Np^{*(1)} \cdots D \longleftrightarrow Np \cdots D^{*(1)}) \quad . \qquad (34)$$

Examination of Figure X reveals that cyclic dienes possess lower quenching rates than the λ_{max} would predict. The model seems capable of rationalizing this trend by demanding an alternate relative steric orientation. In order to obtain similar types of positive bonding interactions, the cyclic diene must position itself on the side of the ring as shown. Reference to Figure XII, page 60, will be helpful. The diene unit is shown in dark line. Low quenching activity can then

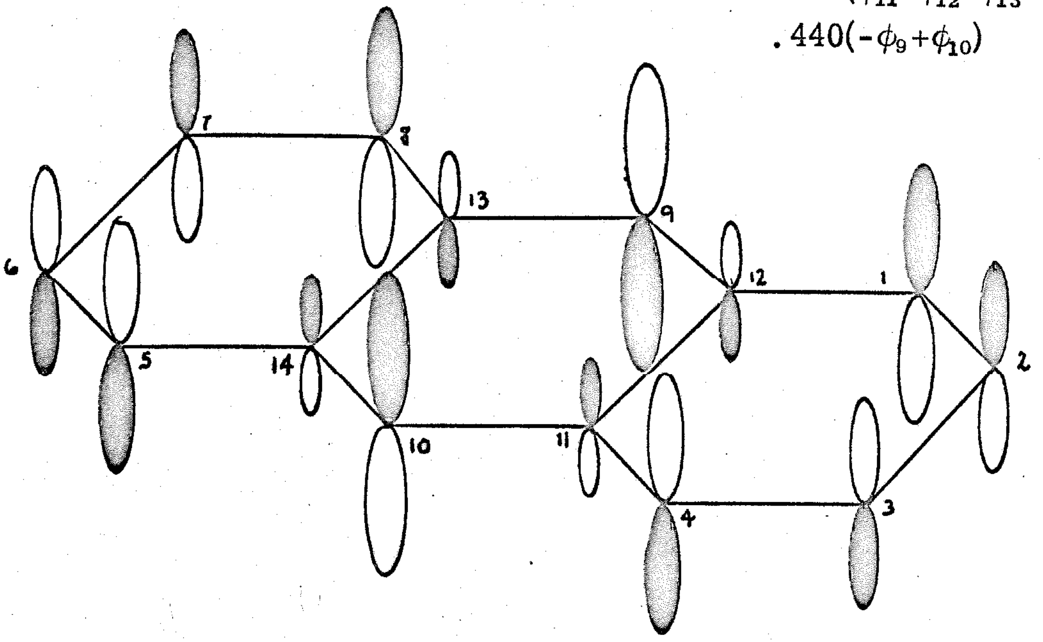


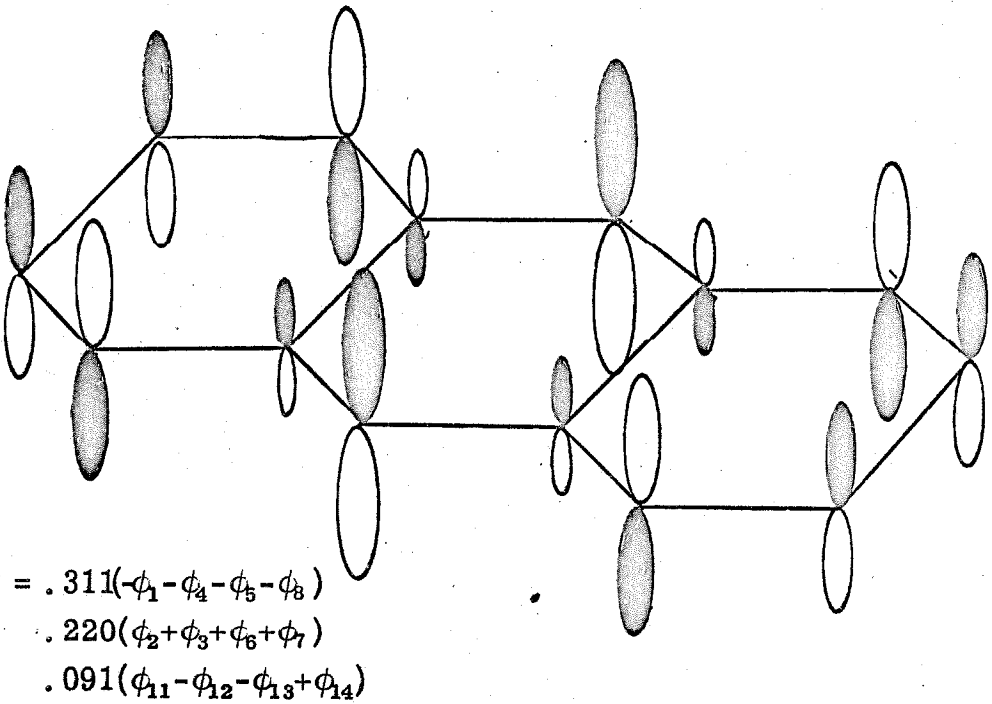
be attributed to less favorable bonding interactions or a less favorable steric environment for the methylenes (dotted lines) or both.

These developments now allow an explanation for the quenching activities of dienes toward other aromatic hydrocarbons.

Quenching by dienes of anthracene fluorescence proceeds at rates comparable to that of naphthalene despite its relatively low singlet energy (anthracene ~ 75 kcal/mole, naphthalene ~ 90 kcal/mole). In addition the relative rates maintain an order reasonably consistent with the pattern displayed for naphthalene quenching. Examination of the orbital scheme of anthracene reveals possible explanations. (See Figure XIV)

$$\begin{aligned}\psi_7 = \; & .311(\phi_1 - \phi_4 - \phi_5 + \phi_8) \\ & .220(\phi_2 - \phi_3 - \phi_6 + \phi_7) \\ & .091(\phi_{11} - \phi_{12} - \phi_{13} + \phi_{14}) \\ & .440(-\phi_9 + \phi_{10})\end{aligned}$$





$$\begin{aligned}\psi_8 = \; & .311(-\phi_1 - \phi_4 - \phi_5 - \phi_8) \\ & .220(\phi_2 + \phi_3 + \phi_6 + \phi_7) \\ & .091(\phi_{11} - \phi_{12} - \phi_{13} + \phi_{14}) \\ & .440(\phi_9 + \phi_{10})\end{aligned}$$

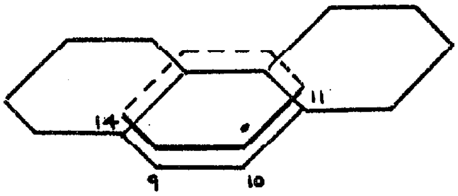
FIGURE XIV: Anthracene Orbital Symmetries

The coefficients of the orbitals involved in the bonding (e. g., ϕ_1, ϕ_{12}, ϕ_{11}, ϕ_{10}) present a picture similar to that of naphthalene, for acyclic diene quenching. The small orbital coefficients in the middle positions, ϕ_{11} and ϕ_{12}, yield overall nonbonding contributions. A slightly more favorable situation exists for the cyclic dienes, with bonding contribution at ϕ_3, ϕ_2, ϕ_1, and ϕ_{12} for example, than in the naphthalene case.

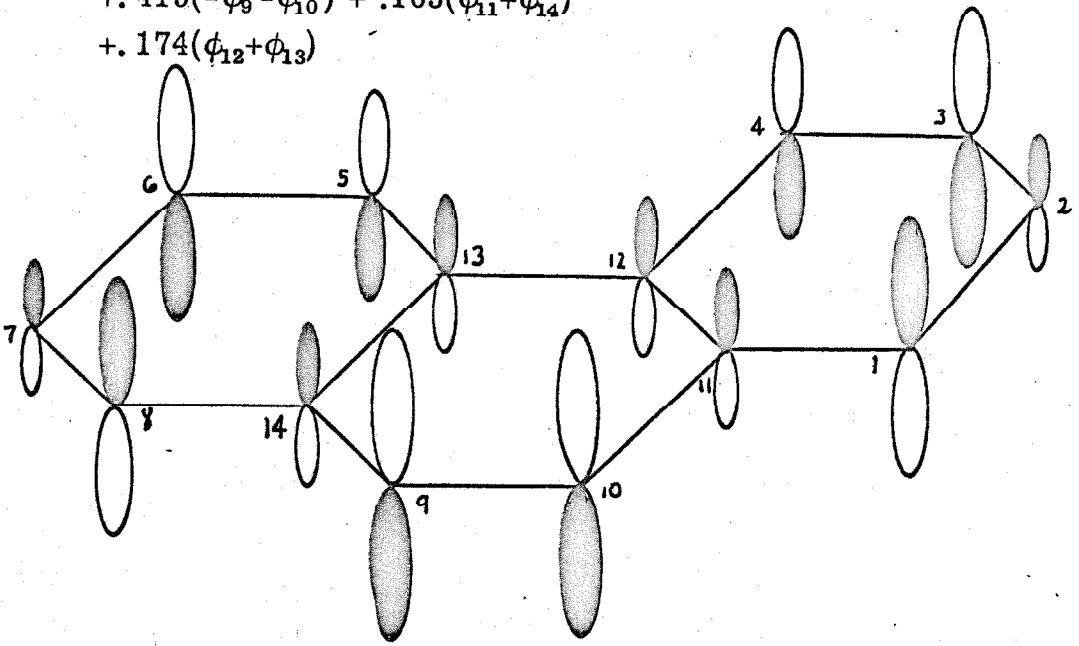
All orbital coefficients involved in diene bonding are larger in anthracene than in naphthalene. This fact may account for the similar rate constants despite the much lower energy, since better overlap would be expected to result, thereby giving stronger interactions than anticipated.

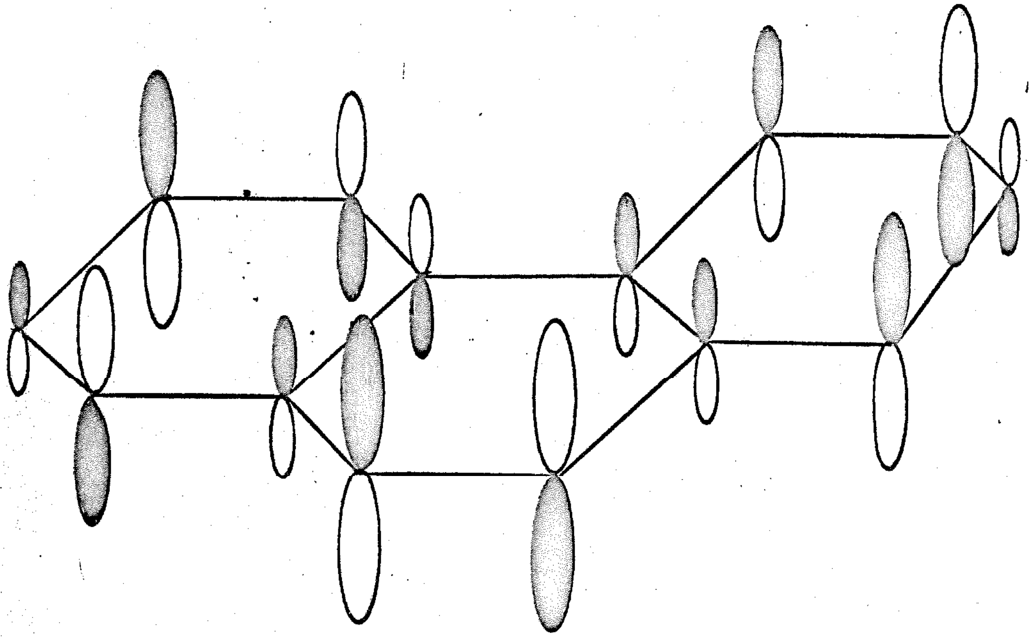
A much different situation is obtained in phenanthrene. Here no reasonable relative configuration of transoid diene and phenanthrene gives sizable overall bonding contributions. (See Figure XV)

In the case of the cyclic dienes a completely reversed situation exists. Placing the diene on the C atoms 14-9-10-11, excellent overlap is obtained (see below--diene unit in heavy line).



$$\begin{aligned}\psi_7 = \; & .340(\phi_1+\phi_8) + .042(\phi_2+\phi_7) \\ & .315(-\phi_3-\phi_6) + .233(-\phi_4-\phi_5) \\ & +.415(-\phi_9-\phi_{10}) + .163(\phi_{11}+\phi_{14}) \\ & +.174(\phi_{12}+\phi_{13})\end{aligned}$$





$$\begin{aligned}\psi_8 = \; & .340(\phi_1-\phi_8) + .042(-\phi_2+\phi_7) \\ & +.315(-\phi_3+\phi_6) + .233(\phi_4-\phi_5) \\ & +.415(\phi_9-\phi_{10}) + .163(-\phi_{11}+\phi_{14}) \\ & +.174(\phi_{12}-\phi_{13})\end{aligned}$$

FIGURE XV: Phenanthrene Orbital Symmetries

Using these predictions, one expects relatively high quenching activity by cyclic dienes and relatively low quenching activity by acyclic dienes. The agreement with experiment is shown below. Quenching rates are not known since a reliable estimate of the singlet lifetime, τ_S, was not available. The minimum detectable slope, $\tau_S k_q$ has been shown to be ~ 0.1 liters/mole.

TABLE IX

Quenching of Phenanthrene by Conjugated Dienes

Quencher	Slope (ℓ/mole)
cyclohexadiene	11.4
trans-2-trans-4-hexadiene	undetectably different from zero
trans-1, 3-pentadiene	undetectably different from zero

Aromatic hydrocarbons with even larger clusters of rings will not in general show fluorescence quenching by diene. Examination of Figure XII shows that quite a rapid falloff in quenching activity is noted over a rather small diene energy range. A similar falloff is to be expected with the aromatic hydrocarbon. Extremely weak quenching of tetracene fluorescence in 5M 2, 5-dimethyl-2, 4-hexadiene solution illustrates this point. Steric effects are expected to become more severe in higher nucleated aromatics also.

In summary, a quenching model has been proposed based on excitation delocalization which allows the prediction of steric factors, and permits a qualitative understanding of relative rate variations.

Consequences of Singlet Quenching

The triplet counting method of Hammond and Lamola using triplet sensitized photoreactions assumes an absence of deactivating interactions in the singlet states of the sensitizers. The most useful counter was found to be cis-1, 3-pentadiene, due principally to its very large singlet-triplet splitting (see Introduction).

The discovery of strong singlet interactions between dienes and several aromatic hydrocarbons has placed the validity of some of the earlier results in doubt. As was documented in the results section, at least in the cases of naphthalene and its derivatives, the singlet quenching leads to no diene excited states and no net diene photochemistry. As a result a simple knowledge of the extent of the singlet quenching allows a correction for its effect to be made. In other systems where singlet quenching may be found important, similar corrections could be made (see below).

$$\phi_{c \rightarrow t} = \frac{k_{ic}}{k_f + k_{ic} + k_q[D]} \qquad \frac{k_t}{k_t + k_c} \tag{35}$$

$$= \phi_{ic} \frac{(\phi_f)}{(\phi_f)_0} \qquad \text{(decay ratio)} \tag{36}$$

The 1, 3-pentadiene triplet decay ratio has been measured previously. This ratio is

$$k_t/k_c = \phi_{c\to t}/\phi_{t\to c} = 1.25 \pm 0.02^* \qquad (37)$$

As has been shown earlier the intersystem crossing ratio follows immediately.

$$\phi_{ic} = \phi_{c\to t} + \phi_{t\to c} = 1.80\ \phi_{c\to t} \qquad (38)$$

The data in Figure X are best fitted to an intercept of $\phi_{c\to t}$ of 0.37 for naphthalene sensitized 1,3-pentadiene isomerization. This yields $\phi_{ic} = .67$ in reasonable agreement with the data of Wilkinson. Other corrections to Lamola's data are shown below.

TABLE X

Corrections for Intersystem Crossing Efficiencies

Sensitizer	ϕ_{ic} (Lamola)	% Quenched	Corrected ϕ_{ic}
naphthalene	0.39	see text	0.67
1-methylnaphthalene	0.48	~20% at .05 M	~0.60
2-methylnaphthalene	0.51	~20% at .05 M	~0.64
1-fluoronaphthalene	0.63	~40% at .05 M	~1.00

---

[*] This ratio has been confirmed for naphthalene triplet sensitization, in experiments in which benzophenone (.05 M) is used to produce naphthalene triplets ([naphthalene] =.10 M) which in turn transfers energy to <u>cis</u>- or <u>trans</u>-1, 3-pentadiene (.01 M).

As can be seen the quenching is serious but by no means debilitating to the method. In the limited number of cases studied, simple corrections could be made and close agreement with the ϕ_{ic} values of Wilkinson (13) obtained. His conclusions that $\phi_f + \phi_{ic} = 1$ for aromatic hydrocarbons and related substances, therefore, must be fully supported by this study.

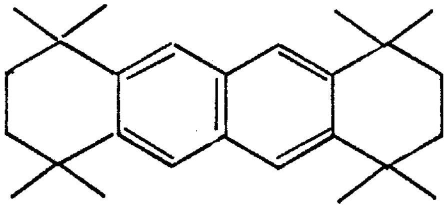
Concluding Remarks

The interaction between aromatic hydrocarbon singlet states and diene ground states has been shown to be quite strong, despite energetic considerations which preclude energy transfer reactions. A model based on excitation delocalization has been proposed and has proved to possess some predictive value.

The further documentation of this effect with additional aromatic hydrocarbon would probably prove unsuccessful. The higher anellated aromatic hydrocarbons would seem to possess singlet energies too low to result in strong interaction.

Further study of naphthalene derivatives might prove to be of immense value in confirming the steric effects discussed previously, however. A trend in these effects can be seen in Table V. The data are of only limited value since lifetimes were obtained by the oxygen quenching method of Berlman.

Of particular interest would be a study of the relative quenching efficiencies of dienes toward octamethyl-octahydrotetracene.



If the interaction model is valid, one would expect a much larger spread between cis and trans diene quenching ability than observed with naphthalene. In addition, the spread in reactivity between the cyclic and acyclic dienes observed in naphthalene quenching would be expected to diminish here. Other related effects with the methylated naphthanes might also be expected.

With respect to related interactions the triplet state should certainly be mentioned. It has been shown that naphthalene triplet behaves as a "normal" sensitizer toward 1,3-pentadiene. That this should be so is attributable to the low diene triplet energy which results in facile energy transfer from naphthalene to diene. The orbital symmetry scheme should apply equally well to triplet states, however, and those aromatic hydrocarbon-diene pairs for which strong interaction is predicted in the singlet state might show anomalous effects in triplet sensitization, provided energy transfer is sufficiently slow (rate $< 10^7$ liters/mole sec). This would be pictured as below. Once again strong coupling between the ground and excited

$$\mathrm{ArH}^{*(3)} + \mathrm{D} \xrightarrow{\text{slow}} \mathrm{ArH} + \mathrm{D}^{*(3)} \qquad (37)$$

$$\mathrm{ArH}^{*(3)} + \mathrm{D} \xrightarrow{?} (\mathrm{ArH}^{*(3)}\cdots\mathrm{D} \longleftarrow \mathrm{ArH}\cdot\cdot\mathrm{D}^{*(3)}) \qquad (38)$$

states of ArH is provided. Catalysis of nonradiative decay might once again be observed. As yet a complete study of diene photochemistry employing low energy sensitizers is unavailable.

A word concerning the potential value of studies of excited state quenching of the type described will conclude this section. Thinking concerning singlet quenching has undergone large changes during the course of this investigation. Indeed, the process has enjoyed a transition from an annoying complication to a sophisticated interaction with plausible physical models. If physical reality can be ascribed to the model, rare <u>experimental</u> insight into nonradiative decay processes may be obtained. Enlightened studies in the future, oriented in this direction could be of enormous value.

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8. This statement does not take photoreactions into account of course. In addition, when applied to other less rigid systems the statement is clearly inaccurate. With dienes, for example, $\phi_f + \phi_{ic} + \phi_{\text{chemical change}} = \phi_{\text{chemical change}} \leq 0.10$.

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PROPOSITION I

The use of the method of heterogeneous flash initiation to study the properties of catalyst surfaces is proposed.

- - - - - - - - - - - - - - -

A variety of techniques is available for perturbing a system sufficiently so that relaxation processes can be conveniently monitored. Among these are temperature jump methods, flash photolysis and shock wave generation. A method in principle analogous to that of shock wave methods, but inherently more complicated has been developed by Nelson and Lundberg (1). Irradiation of a medium containing suspended particles such as charcoal or various finely divided metals, by an intense and brief flash of light, produces very high local temperatures in the neighborhood of the particle, often as high as 2000° C.

Experiments were carried out by Nelson and Lundberg using flash energies on the order of 5000 joules (10^{-3} sec duration ~ intensity 10^{22}-10^{23} quanta/sec cm^2). They were able to evaporate metals (silver, tungsten, nickel, zinc) in vacuum and initiate explosions in the gas phase ($CH_4 + O_2 \xrightarrow[\text{glass wool}]{h\nu}$ explosion). Few experiments have been conducted dealing with liquid phase reactions. In a single experiment, Nelson and Lundberg were able to partially decompose mineral oil by flashing suspensions of carbon (radius $< 36\mu$), molybdenum (r. $< 74\ \mu$), and tungsten wool (r. $< 7.5\ \mu$). Blue fluorescing compounds were produced.

To date no experiments have been conducted designed to assay the effect of this heterogeneous flash initiation on molecules adsorbed on finely divided particle surfaces. A study of the chemical changes brought about in systems described below is proposed.

Olefins and dienes are known to adsorb strongly to surfaces of finely divided substances such as carbon, or platinum and other metals. It is anticipated that *cis*-*trans* isomerization and perhaps various bond fragmentations might result following flash excitation.

Of initial importance in this study would be a determination of the effect of this hot catalyst on substrate molecules which diffuse to its surface. The variation in the extent of the induced chemistry with substrate concentration might be expected to provide this information. Ideally it would be hoped that chemical response per flash (call it quantum yield if you wish) would level off as the catalyst surface becomes saturated.

Studies of this type might also be expected to yield information regarding selectivity of catalyst adsorption (for example the ability of the catalyst surface to differentiate between *cis* and *trans* olefins or to detect other structural changes); the mechanism of catalyst poisoning; and solvent effects on these surface properties.

The proposal could provide a useful adjunct to studies of catalyst properties using other methods. Since much of the same information to be gained above is available in principle from hydrogenation rate data, an interesting comparison would be possible.

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PROPOSITION II

Experiments designed to elucidate the mechanism of photochemical oxetane formation are proposed.

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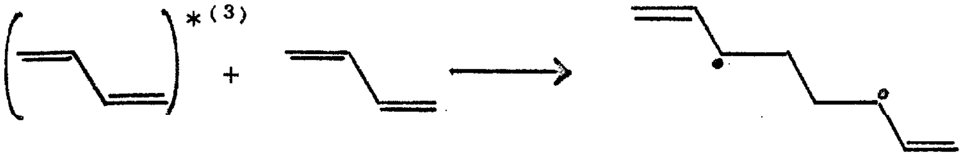
Diradical intermediates are often invoked in photochemical cycloaddition reactions. For example, Hammond and co-workers (1) have successfully employed the diradical hypothesis in rationalizing the products encountered in sensitized diene dimerizations. The isolation of not only 4- but 6- and 8-membered ring systems was valuable



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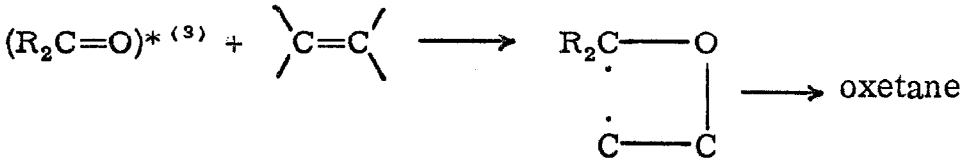
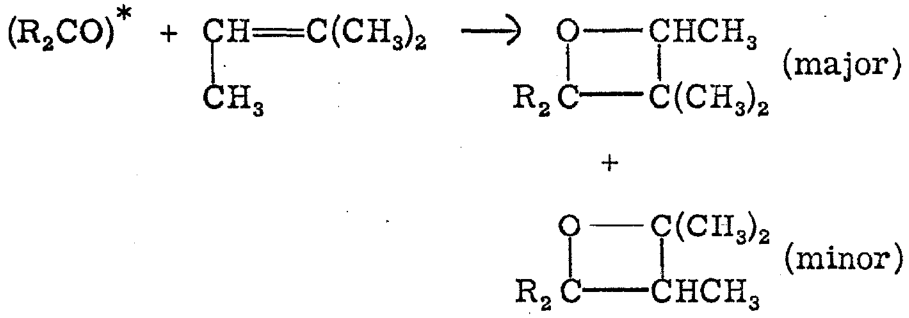
in demonstrating the intermediacy of I.

Diradical species have also been invoked in the reaction between excited state carbonyl compounds and olefins (The Paterno-Büchi Reaction). Experiments are proposed which are designed to

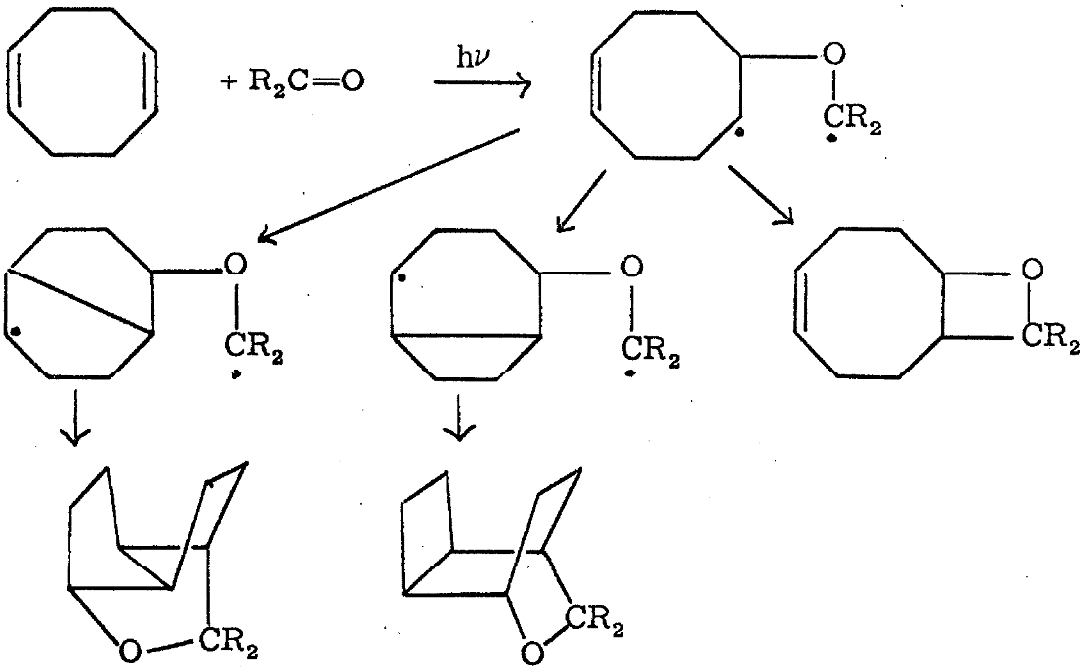


confirm the existence of this diradical. An additional experiment is proposed which would reveal the selectivity of such a radical combination.

Several studies have been made relating to this problem although none are of a quantitative nature. In his original paper Büchi (2) noted the tendency of products to form which were thought to proceed through the most stable radical species, see below. A slightly more definitive result was reported by Arnold, Hinman, and Glick (3). They were able to show that cis- and trans-butene-2 leads to identical mixtures of stereoisomeric oxetanes which could certainly be adduced as evidence for free rotation about the C—C bond in a diradical complex. Quantum yields were not obtained however and the authors claimed that photosensitized isomerization of the olefin preceded oxetane formation. In this case it is felt that a careful study of quantum yields would allow the two possibilities to be distinguished. To date however no convincing evidence compels the existence of the diradical.



A study of several reactions in which the intermediate diradical might rearrange before cyclization is proposed. Candidate systems are shown below.


+ R₂C═O
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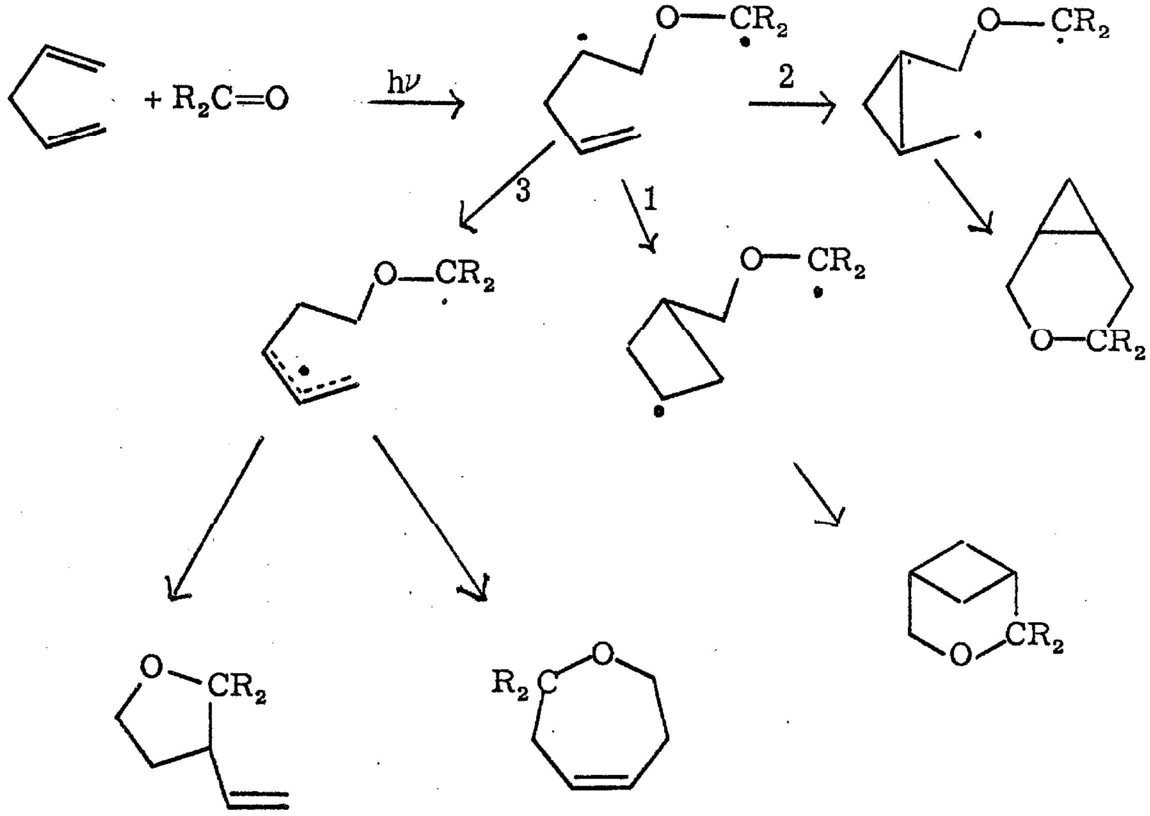
+ R₂C═O
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O—CR₂
2
O—CR₂
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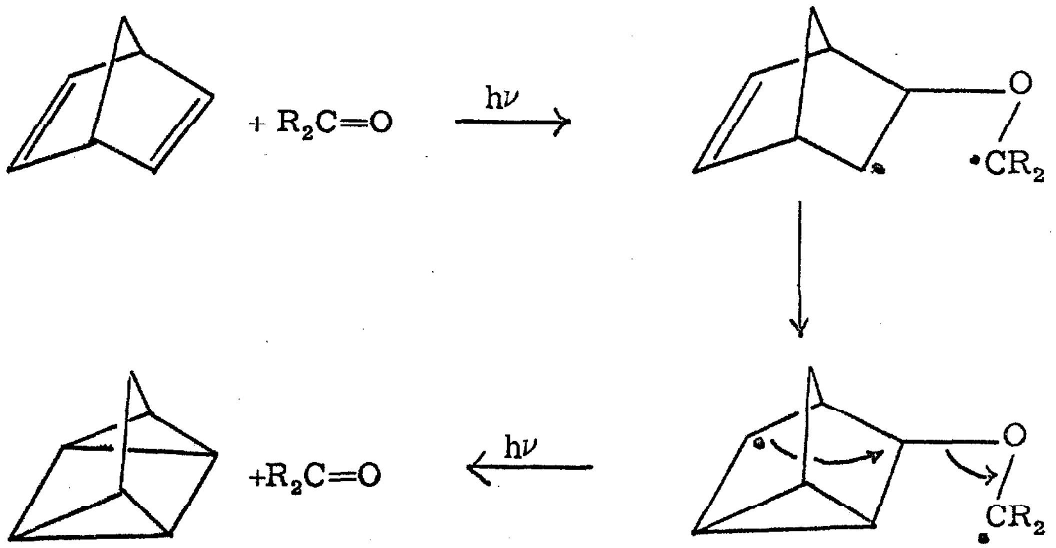
1
O—CR₂
O—CR₂
O—CR₂
CR₂
O
O—CR₂
O
CR₂
R₂C

Cycloöctadiene is an attractive candidate because of the proximity of the double bonds. Photochemical cross additions of the double bonds are known to occur.

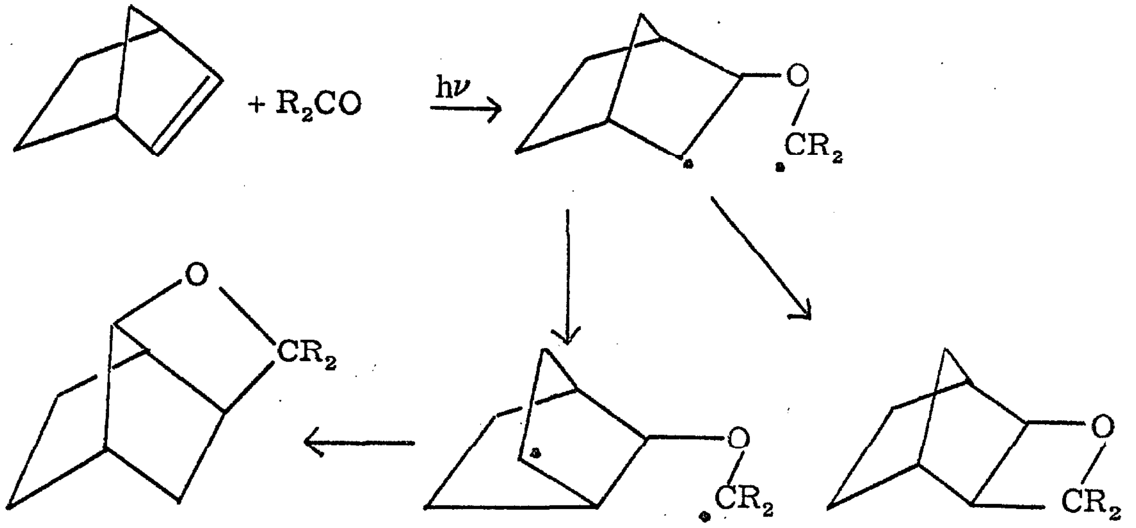
1,4-Dienes, such as 1,4-pentadiene, possess several potential rearrangement paths. Path 1 involves a competition between two four-membered ring formations. The process appears to be quite reasonable. Path 2 leads from a secondary to a primary radical plus a cyclopropane ring. Energetically it seems least favorable. Path 3 is the most appealing, involving H shift to produce the allyl radical; ring closure is expected to lead predominantly to five-membered rings.

Norbornadiene would also be of interest; however, its photochemistry has been thoroughly investigated. The products seem to be variable mixtures of starting material and quadricyclene when carbonyl sensitizers are employed (4).

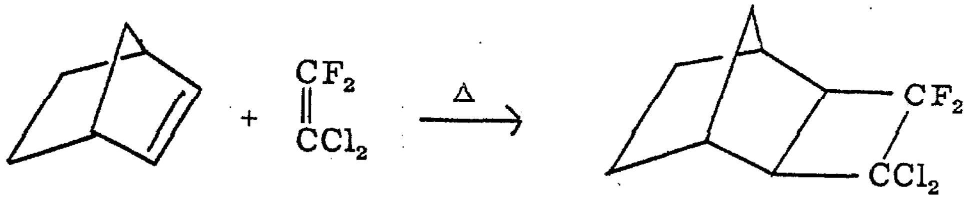
A formulation such as given below is possible, and is



consistent with other features of this proposal. However, an explanation based on energy transfer is generally favored. It was originally hoped that norbornene would also prove a suitable candidate. Radical rearrangements in this system would lead to interesting products.

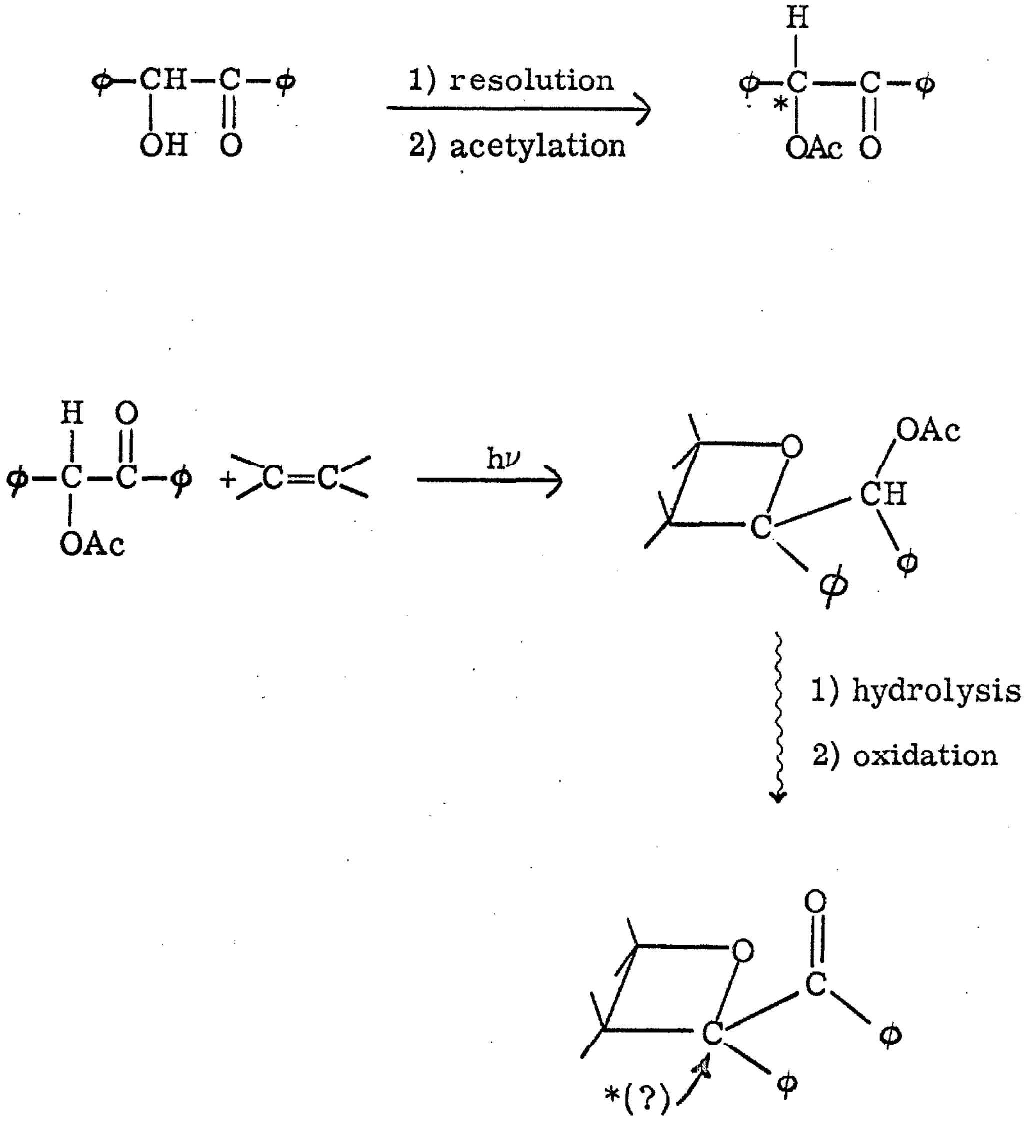


Analogous systems known to proceed through diradical species fail to show rearranged products, however (5).



Related to this problem is the difficulty associated with defining existence as it relates to these diradicals. Ring closure of these species could be so rapid that the detection via chemical means would be unlikely. An additional experiment is proposed here to test the reaction selectivity as a possible gauge toward the determination of the lifetime of the assumed diradical.

The ability of an optically active ketone to induce asymmetry into the oxetane would constitute a convincing proof of high reaction selectivity. A scheme for this proposal is shown below (6) in outline form. This incorporation of optical activity in the site marked would



give valuable information concerning the selectivity of the cyclization. However, the interpretation of the result would not be without complication. The incorporation of activity by no means demands a diradical mechanism. One is tempted to speculate, though, that if a diradical intermediate is involved, and substantial optical activity can be induced, the lifetime of the species is sufficiently long so that radical rearrangement should be observable. The incorporation of optical activity coupled with the nonoccurrence of rearrangement products, might then be adduced as evidence for the concerted addition.

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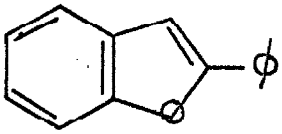
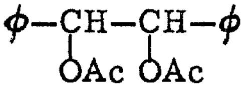
5. See P. D. Bartlett, G. E. H. Wallbillich, and L. K. Montgomery, *J. Org. Chem.*, **32**, 1290 (1967) and earlier papers. The adduct shown represented about 90% of the reaction product. The remainder was unidentified.

6. Benzoin acetate seemed a simple choice for this system; it undergoes photochemical transformations on its own, however, yielding



and  $\phi\text{—}\underset{\text{OAc}}{\text{CH}}\text{—}\underset{\text{OAc}}{\text{CH}}\text{—}\phi$ (7). Quantum yields are thought to be low, and it is anticipated that these phototransformations could be quenched by high olefin concentrations.

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PROPOSITION III

A mechanistic rationalization of the mass spectral fragmentation patterns of conjugated dienes is offered, and is shown to be useful in understanding the origin of the ions derived from several simple compounds.

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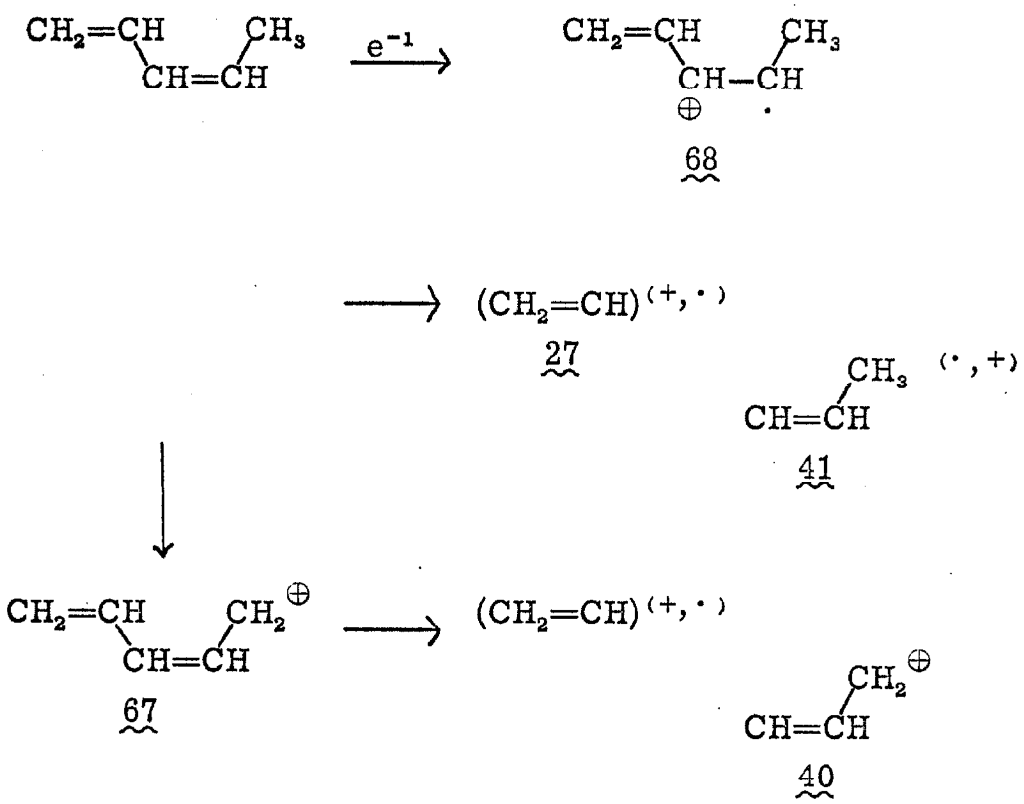
The mass spectral fragmentation products of simple hydrocarbons have been the subject of few mechanistic investigations. Saturated hydrocarbons (1, 2) and monoolefins (1, 3) have received limited treatment; dienes and other polyolefins have received no attention at all. The spectra of the pentadienes first aroused our attention in connection with studies mentioned in this thesis. The major features of the spectra, obtained with an ionizing potential of 70 e.v. are shown in Table I.

TABLE I

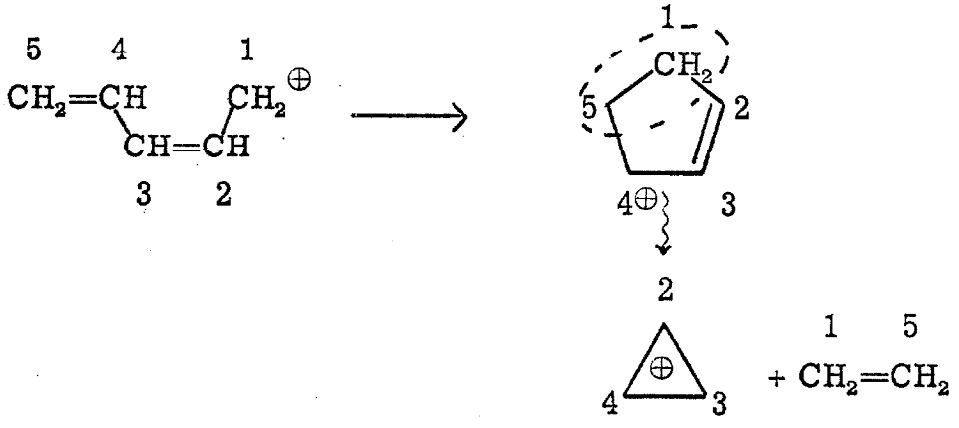
Relative Intensity

Mass	cis-1, 3-pentadiene	trans-1, 3-pentadiene	Origin
68	79	83	M
67	100	100	M-H
53	71	73	$M-CH_3$
41	42	50	$M-C_2H_3$
40	44	45	$M-C_2H_4$
39	87	88	$M-C_2H_5$
27	43	42	$M-C_3H_5$

The spectra may be interpreted as follows:



The m/e fragment difficult to rationalize lies at m/e = 39 representing loss of C_2H_5. The following mechanism is proposed to account for this species.



Mechanisms based on the appearance of unusually stable fragments such as the cyclopropenyl cation can be viewed as highly suspect; indeed, the fragment can be observed in the mass spectral patterns of many hydrocarbons, saturated or unsaturated. Implied in this case is that the m/e = 39 fragment arises from a well-defined set of processes and includes only certain carbon atoms.* The proposal should now be useful in the rationalization of other diene fragmentation patterns, or perhaps in the elucidation of unknown diene structures.

2, 4-Hexadiene would not be expected to show large M-29 (C_2H_5) fragments as in the case of 1, 3-pentadiene. See below.

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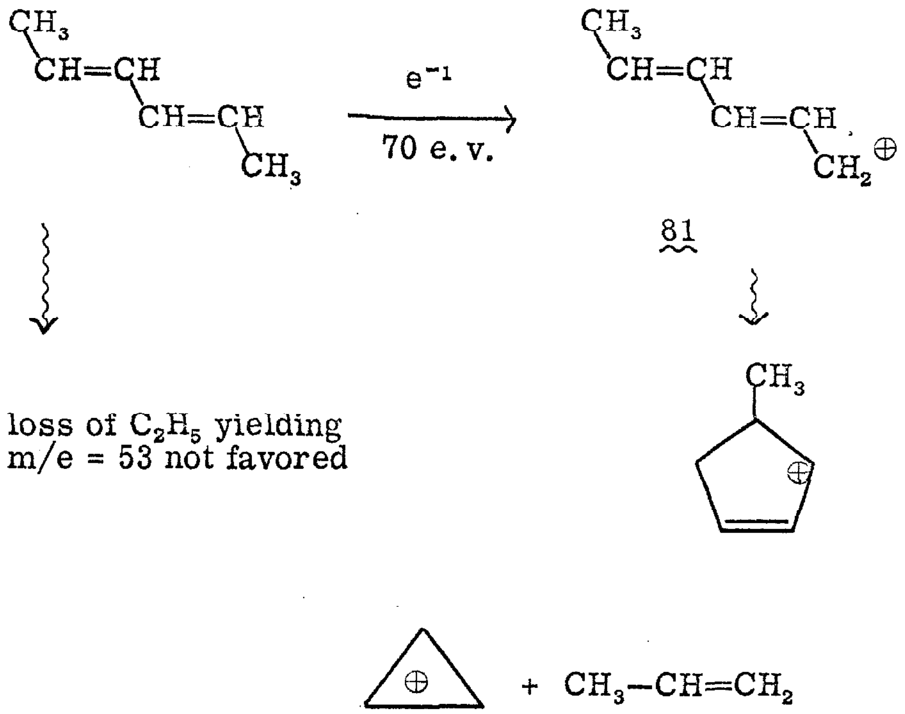
*"Molecular explosion" mechanisms in which carbon and hydrogen atoms leap into the "air" and return to land in the most stable molecular aggregates are rejected. Fragmentation patterns of certain saturated hydrocarbons might well be described in this manner, however.

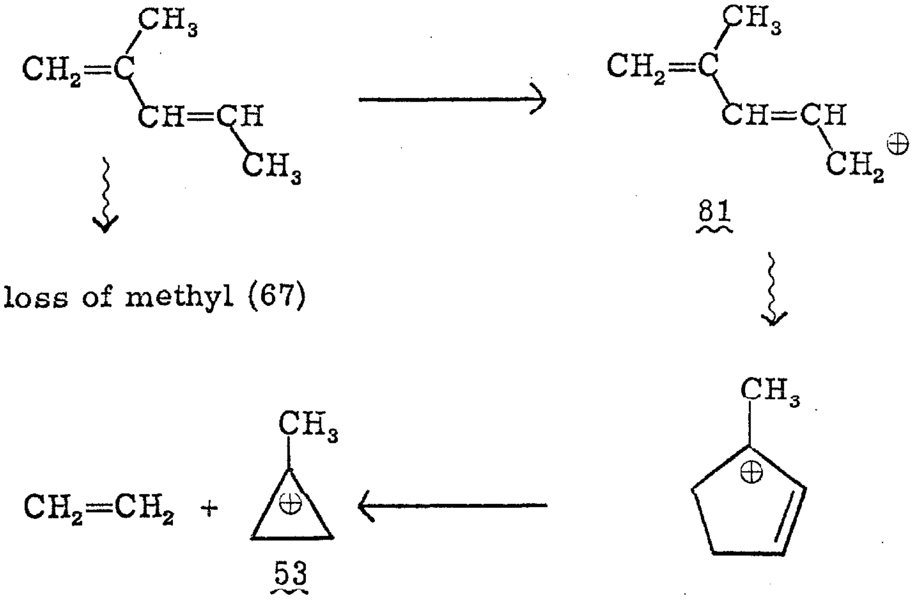


The mass spectrum of 2, 4-hexadiene shows the following encouraging results:

m/e	82	81	67	53	39
intensity	44	12. 3	100	2. 5	44

The evidence seems to point to the fact that the loss of C_2H_5 from pentadiene involves removal of the two terminal carbon atoms as the mechanism implies. Two final examples support this view.

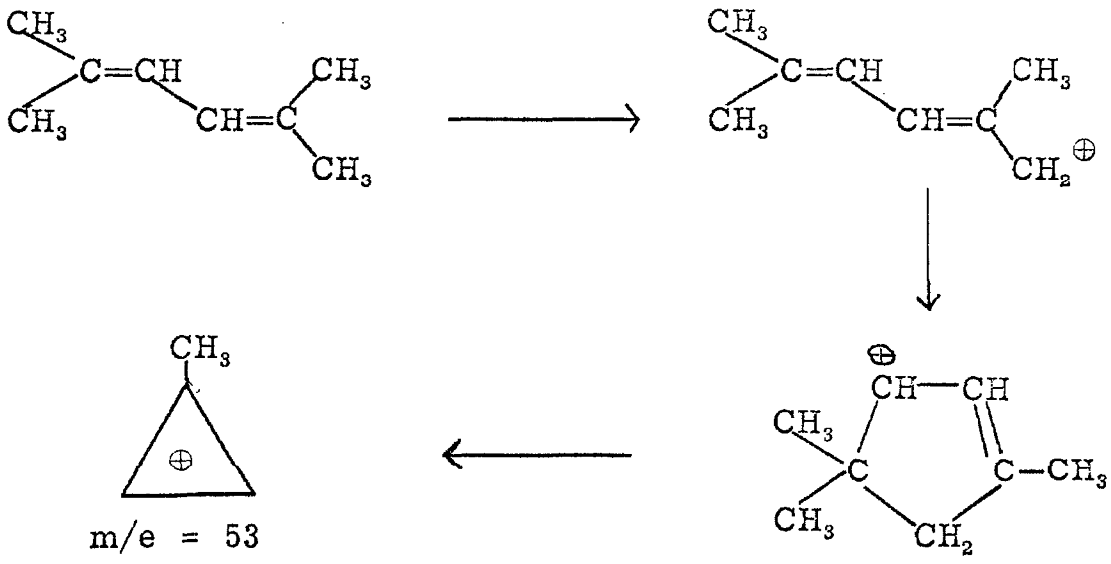
2-Methyl-1, 3-pentadiene is expected to show the fragments below.



The mass spectrum of 2-methyl-1, 3-pentadiene shows considerably larger m/e = 53 fragment than does 2, 4-hexadiene.

m/e	82	81	67	53	41	39
intensity	47	12	100	17	54	61

The mass spectrum of 2, 5-dimethyl-2, 4-hexadiene though quite complex also supports the mechanism. One would here predict strong ions of mass 53 and perhaps also 55 (symmetrical split) and 95 (loss of methyl).

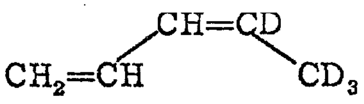


The pattern is displayed below

m/e	110	109	95	81	68
intensity	57.1	2.3	100	4.7	11.7

m/e	67	55	53	39
intensity	4.7	35	22	40

Partial confirmation of the mechanism proposed could be obtained by a study of deuterated compounds such as the pentadiene shown below, whose synthesis would be expected to proceed smoothly *via* the appropriate Wittig reagents.



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1. American Petroleum Institute Research Project # 44.
2. M. J. O'Neal and T. P. Wier, Anal. Chem., **23**, 830 (1951).
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PROPOSITION IV

When absolute configurations of several β-amino ethanols are determined by the method of Prelog incorrect results are obtained. An explanation of these effects is given.

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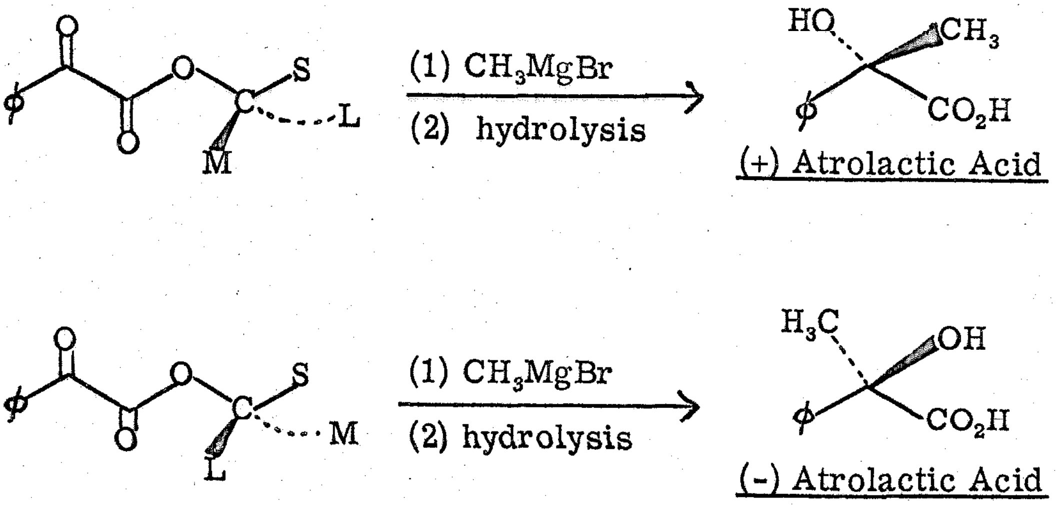
The results primarily of A. McKenzie (1) in his studies of asymmetric induction in phenylglyoxalate esters led Prelog (2) to state an empirical relationship between the arrangement of the groups in the alcohol moiety and the configuration of the hydroxy acid resulting from Grignard reactions on these compounds, followed by hydrolysis.

Prelog's Rule (2) is summarized in Figure 1, below.

Figure 1

Relationships predicted by Prelog's Rule



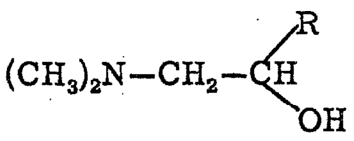
By convention, the molecule is so oriented that the two carbonyl groups are antiparallel, and the smallest group, -S, eclipses the ketone carbonyl. The methyl (R) magnesium halide will then approach from the side offering least hindrance; that is, from the side of the medium-sized group, -M, as shown.

Clearly the absolute configuration of potentially any alcohol can be determined by examination of the sign of rotation of the atrolactic acid produced whose absolute configuration is known (3). (See Figure 1).

This method has been applied successfully in many cases: The determination of the absolute configuration at C_{17} in androstan-17β-ol, in 7 α-, and 7β-cholestanol (4), α-amyrin, dihydrolanosterol, euphol, and in the flavonals (5) catechin and epicatechin, to name several. See Table I.

Examples of failure of this system to predict correct configurations are rare, and can for the most part be traced to incomplete hydrolysis of the ester (since one isomer may hydrolyze more rapidly than the other).

Recently there has been brought to our attention a group of experiments involving β-amino ethanols of the type shown below (6, 7).

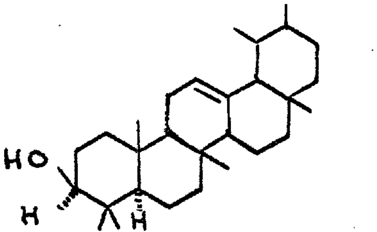
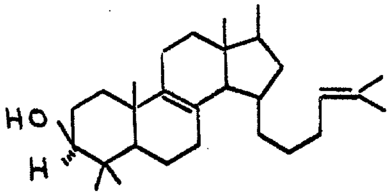
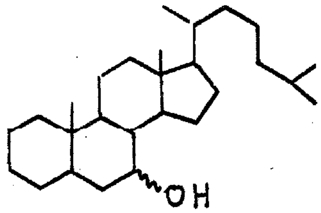


$(CH_3)_2N-CH_2-CH(R)(OH)$

R = $-CH_3$

= $-CH_2CH_3$

Table I

Alcohol	Atrolactic Acid		
	yield	α_D*	% activity
 α-amyrin	71%	3.66	10
 euphol	58%	13.0	34.5
androstanol (17β)	69.4%	6.2	16.5
 cholestanol (7α)	86%	26	69
cholestanol (7β)	45.5%	-4.8	13

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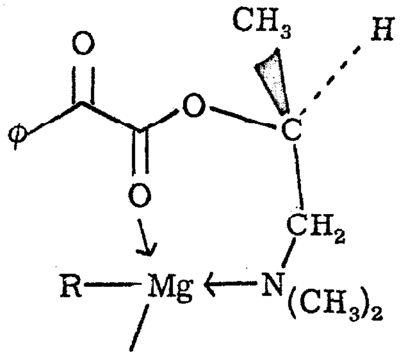
*max = + 37.5° in alcohol.

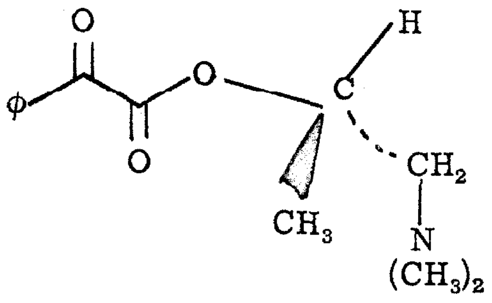
When subjected to the method of Prelog these compounds gave consistently incorrect results. Limited investigations have demonstrated the apparent generality of these results.

Two alternate reaction configurations are proposed to account for these findings, both of which are based on the ability of nitrogen to coordinate with Grignard reagents (8).

The first proposal involves the nitrogen and the ester carbonyl in a chelation complex about the magnesium. As can be seen below this now forces the incoming reagent to choose between methyl and hydrogen nonbonded repulsions in approaching the ketone carbonyl. Attack from below the plane of the page conforms with experimental findings; see conformationA. Conformation B, in accord with the Prelog rule predicts (incorrectly) attack from above the plane of the page.



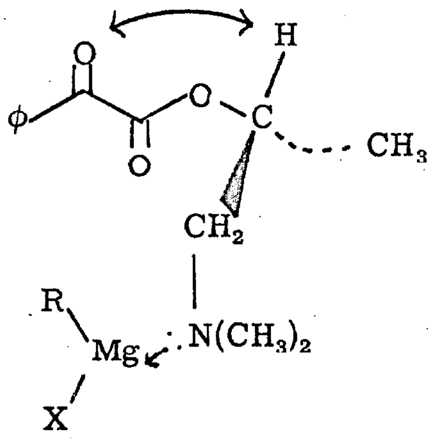
A

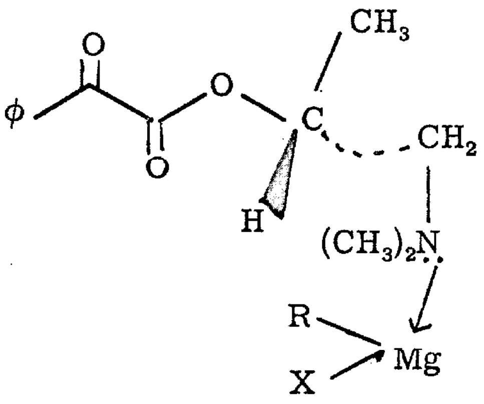


B

This model possesses several disadvantages. The formation of a seven-membered ring is unattractive as is the use of ester carbonyls in complex formation.

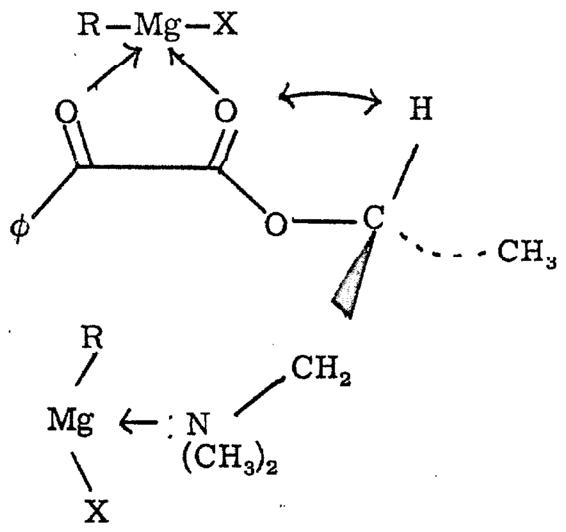
An alternate model uses an amine-Grignard reagent complex to attack the carbonyl. This is pictured as below.





It is seen that if the reagent attacks from above the plane of the page, the repulsion between -H and carbonyl (which is probably also complexed with RMgX increasing its effective bulk) is much less than that between $-CH_3$ and carbonyl which results if the reagent attacks from below the plane of the page.

Prelog's conformation involving a transoid arrangement of carbonyl oxygen has been retained throughout this discussion. It seems likely that the coordination efffct of magnesium could easily overcome the dipolar and steric repulsions of these carbonyls to form a cis chelate. Although not subject to obvious experimental tests the arrangement seems much more compatible with asymmetric induction over such large distances. The model would now include the following features, illustrated for the β-amino alcohol case. It should be



noted that this configuration also provides rationalizations for directions of attack with normal substrates.

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PROPOSITION V

Experiments designed to confirm the energy level assignments in the diazines are proposed.

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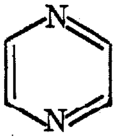
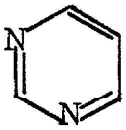
Goodman and Cohen have recently suggested (1) that the weak fluorescence from the diazines involves internal conversion to a lower long-lived forbidden singlet state, rather than a rapid intersystem crossing process. Their data dealing with yields of fluorescence and phosphorescence, together with intersystem crossing measurements performed in Professor Hammond's laboratories by the author, are consistent with the El-Sayed—Robinson (2) assignment of the diazine excited state levels. The level diagrams are shown schematically below. The states are denoted as singlet (S)



∼∼∼ $S(n,\pi^*)$ A 30610

∼∼∼ $S(n,\pi^*)$ F 30175

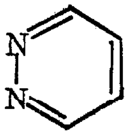
∼∼∼ $T(n,\pi^*)$ 26545



∼∼∼ $S(n,\pi^*)$ A 30930

∼∼∼ $S(n,\pi^*)$ F 30090

∼∼∼ $T(n,\pi^*)$ 28300



∼∼∼ $S(n,\pi^*)$ A 26624

∼∼∼ $T(n,\pi^*)$ 24850

∼∼∼ $S(n,\pi^*)$ F 17760

or triplet (T) of either allowed (A) or forbidden (F) nature; the energies associated with the levels are given in cm^{-1}. Goodman and Cohen were able to demonstrate that the weak fluorescence from the diazines, $\phi_f < 0.01$, originates from an allowed $S(n,\pi^*)$ state and that in general $\phi_f + \phi_{ic} < 0.30$, implying a relatively rapid decay of the singlet state, $S(n,\pi^*)$ A, presumably to $S(n,\pi^*)$ F. Additionally, no phosphorescence could be observed from pyridazine, although pyrimidine and pyrazine phosphoresced strongly with yields comparable to the measured intersystem crossing efficiencies. This result was felt to be due to the existence of the singlet state $S(n,\pi^*)$ F below the triplet level which provides a pathway for the relatively rapid non-radiative deactivation of the $T(n,\pi^*)$ state in pyridazine.

The validity of Goodman's arguments rest primarily on the correctness of the assignments given by El-Sayed and Robinson. Because of the highly interesting and potentially controversial nature of these results, it is felt that an independent confirmation of the energy level scheme with respect of the singlet states would be valuable. A variant of the "chemical spectroscopic" methods discussed by Hammond and co-workers (3) is proposed to accomplish this goal.

The rate of quenching of excited states via energy transfer is expected to follow a definite pattern dependent primarily on the relative excited state energy levels of donor and acceptor. It has been noted (3, 4) that accurate (± 2 kcal/mole) estimates of triplet energies of electronic energy acceptors such as the stilbenes and 1,3-pentadienes can be obtained by utilizing a series of compounds as energy donors which possess a range of triplet energies and by noting the point (on the donor energy scale) at which energy transfer begins to decrease rapidly. A more sophisticated approach makes use again of a series of compounds with a range of triplet energies but in this case employs two energy acceptors both capable of photochemical change. Energy levels of both acceptors are now obtainable by noting that point (again on the donor energy scale) at which an abrupt change in the photochemical response of the systems occurs. These methods provide an extremely valuable supplement to energy level assignments obtained through observation of highly forbidden absorption bands. Of particular appeal is the apparent relative insensitivity to trace levels of impurities.

It is proposed therefore that the fluorescence quenching rates of a series of compounds representing a spectrum of excited singlet state energies be obtained using the diazines as quenchers. Pyridazine (ortho-diazine) seems particularly well suited for this purpose since a large $S(n,\pi)A - S(n,\pi)F$ splitting is indicated and competitive absorption by the allowed singlet level would not provide a complication.

Aromatic hydrocarbons suitable for this study might include (with singlet energies, in cm^{-1}, taken from absorption data): naphthacene (21,180), 5,6,11-triphenylnaphthacene (19,800), rubrene (18,850), benz[a]pentacene (18,160), pentacene (17,390). A large number of dyes of appropriately low singlet energy are also known.

It is anticipated that the quenching rate constants will maintain a high level, approximately diffusion controlled, until the energy of the donor reaches that of the acceptor, pyridazine. A sharp decrease in rate constant is then expected with the endothermicity appearing as an energy of activation in complete analogy with the results obtained by Hammond and co-workers (3) (with slight modifications) in the triplet transfer experiments. It is hoped that, in this way an independent confirmation of the low-lying singlet level in pyridazine can be obtained.

A similar study of the meta- and para-diazines is also possible. Because of the slight $S(n,\pi^*)A$ - $S(n,\pi^*)F$ splitting, however, many experimental difficulties would be anticipated. An additional facet of Goodman's argument suggests a different type of quenching experiment in this case.

According to Goodman, a large fraction of the intersystem crossing from the singlet manifold of pyrazine and pyrimidine occurs from the forbidden singlet states, $S(n,\pi^*)F$, as one might expect by considering the very long natural lifetimes. By using typical triplet quenchers (cis or trans-1, 3-pentadiene) these intersystem crossing efficiencies were determined in these laboratories as 0. 33 (pyrazine) and 0. 12 (pyrimidine). It is further proposed that appropriate singlet quenchers be introduced in the triplet counting experiments, and their effect on intersystem crossing yields determined.

Amines (such as triethylamine) are rapid and relatively indiscriminate singlet quenchers, and are expected to strongly quench the fluorescence of the diazines (5). The extent of this fluorescence quenching can be determined, and the extent to which intersystem crossing from this allowed state $S(n,\pi)$ A would be reduced, could then be calculated. Any additional diminution of the intersystem crossing yield could be attributable to amine quenching of the long-lived and non-fluorescing forbidden state $S(n,\pi^*)F$. In this way a qualitative confirmation of the existence of the lower energy state could be obtained. Unfortunately, no information concerning its energy content or its relative susceptibility to quenching could be obtained, since no information regarding the lifetime of this state is available.

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5. It is recognized that the diazines are amines themselves. However, because of their high ionization potentials they are not expected to quench fluorescence efficiently, if at all. In the author's experience 5M pyridine has no effect on naphthalene or anthracene fluorescence. The appropriate ionization potentials are ~ 9.7 (pyridine), ~ 10.0 (pyrazine). It has previously been determined that conjugated dienes have little or no effect on diazine fluorescence. In addition, measured intersystem crossing efficiencies (using 1,3-pentadiene as a counter) seemed invariant with diene concentrating, implying the $S(n,\pi^*)F$ is not diene quenched either.