COMPLICATIONS IN THE SYSTEMATIC STUDY
OF PHOTOCHEMICAL MECHANISMS

Thesis by
George Francis Vesley Jr.

In Partial Fulfillment of the Requirements
For the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California
1968
(Submitted September 6, 1967)

ACKNOWLEDGEMENTS

To Professor G. S. Hammond, I wish to express my sincere appreciation. His guidance and enthusiasm have been a constant inspiration.

Thanks are due many members of the department and the Hammond group for their helpful discussions. In particular, I wish to thank Drs. S. Murov, J. M. King, W. G. Herkstroeter, L. M. Stephenson, D. H. Valentine and D. G. Whitten. Some of the experiments reported in this work were performed by Dr. L. M. Stephenson and Mr. C. C. Wamser, Mr. K. S. Kamm and Mr. S. M. Pokras. Their help is gratefully acknowledged. Drs. J. Vinograd and N. Davidson are thanked for the use of their Programa 101. I am grateful to Dr. J. A. Magnuson for decoupling the nmr spectra and for valuable discussions concerning these spectra.

Sincere thanks go to my wife Joan, for her typing of this thesis.

Financial assistance in the form of graduate fellowships provided by the National Institute of Health (1965-1967) and the National Science Foundation is gratefully acknowledged. The California Institute of Technology is thanked for the graduate teaching assistantships (1964-1967).

ABSTRACT

The rate constants for energy transfer have been measured by flash spectroscopic techniques. These results show that 1,3-cyclohexadiene undergoes a nonvertical transition when low energy sensitizers are used.

The quantum yields for the high energy sensitized dimerization of 1,3-cyclohexadiene are consistant with the simple mechanism proposed.

The use of 1,2-benzanthracene, a low energy sensitizer, to sensitize the dimerization of 1,3-cyclohexadiene has been studied in detail. The results show that in addition to energy transfer from donor to acceptor, other steps such as reversible energy transfer, adduct formation, singlet quenching of aromatic hydrocarbons by dienes and sensitizer-sensitizer interactions are important.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

The study of photochemistry has advanced greatly in recent years. This has primarily been due to the usefulness of the triplet state and triplet energy transfer.

Terenin and Ermolaev (1,2) were the first to observe triplet energy transfer. In this process the donor, D, in its triplet state, transferred energy to the acceptor, A, yielding A in its triplet state according to equation 1.

$$D\ (T_1) + A\ (S_0) \longrightarrow D\ (S_0) + A\ (T_1) \qquad (1)$$

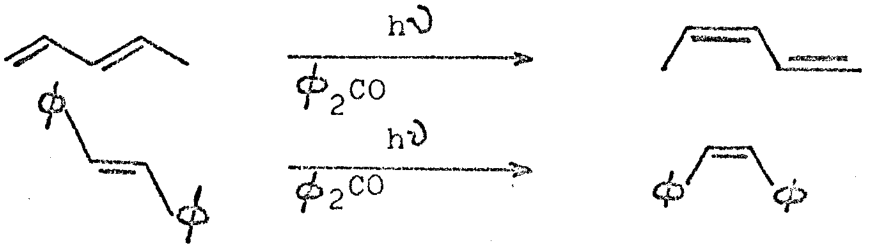
In these experiments the phosphorescence of aromatic hydrocarbons (such as naphthalene) was observed when donor compounds such as benzophenone, which absorb lower excitation energy were excited. These experiments were performed in rigid glasses at 77°K. The spectra obtained in these experiments were identical to those obtained by direct excitation of the acceptor molecule.

Bäckström and Sandros (3) demonstrated a similar phenomenon by quenching the phosphorescence of biacetyl in solution. Later these authors demonstrated that benzophenone, whose triplet lies above that of biacetyl, sensitized the phosphorescence of biacetyl in solution (4).

This was the first evidence for triplet energy transfer in solution.

Since that time there have been many reports, too numerous to mention all of them here, of triplet energy transfer in solution. Hammond and co-workers (5) have presented an abundance of chemical evidence for this type of process. Representative reactions are shown below.

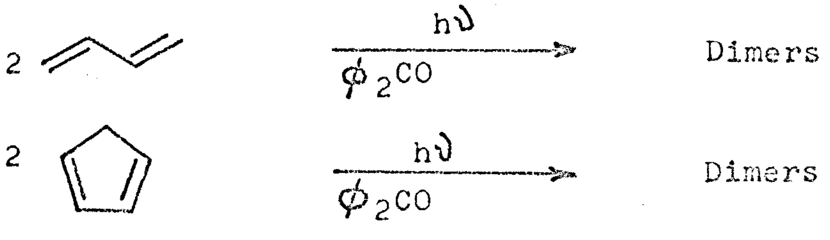
Isomerizations:



(2)

(3)

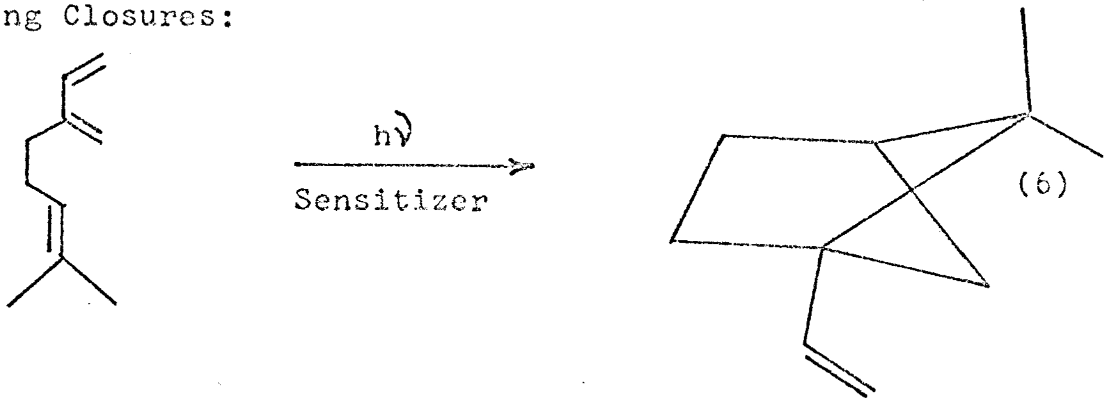
Dimerizations:



(4)

(5)

Ring Closures:



(6)

In general, a donor or sensitizer, absorbs radiation, and transfers this energy to the acceptor in an exothermic process. For this process to be useful the sensitizer must be stable under irradiation conditions; it must be an efficient producer of triplets; and the singlet-triplet splitting must be smaller than that of the acceptor. Fortunately, this often is the case with both aromatic hydrocarbons and carbonyl containing compounds when the acceptor is a diene, or olefin.

Olefins are one of the most frequently used classes of acceptors in organic photochemistry. This is due to the large splitting between the singlet and triplet states in olefins, which allows energy to be put selectively into the sensitizer which is promoted to its singlet state. The excited singlet state of the sensitizer undergoes a process called intersystem crossing by which the triplet state of the sensitizer is produced. If the triplet state of the sensitizer is higher in energy than the triplet state of the acceptor, exothermic energy transfer can occur producing the acceptor triplet. The following general mechanism is typical of such processes;

$$D^{(1)} \xrightarrow{h\nu} D^{*}(1) \qquad (7)$$

$$D^{*}(1) \longrightarrow D^{*}(3) \qquad (8)$$

$$D^{*}(3) + A^{(1)} \longrightarrow D^{(1)} + A^{*}(3) \qquad (9)$$

$$A^{*}(3) \longrightarrow \text{Chemistry} \qquad (10)$$

The superscripts represent the multiplicity of the electronic states. This type of process is called high-energy photosensitization. The above mechanism is extremely simplified but sufficient to explain the basic processes in much organic photochemistry. For a more detailed description of the pathways available to excited states the reader is directed to the article by Leermakers and Vesley (6a) or the text by Calvert and Pitts (6b).

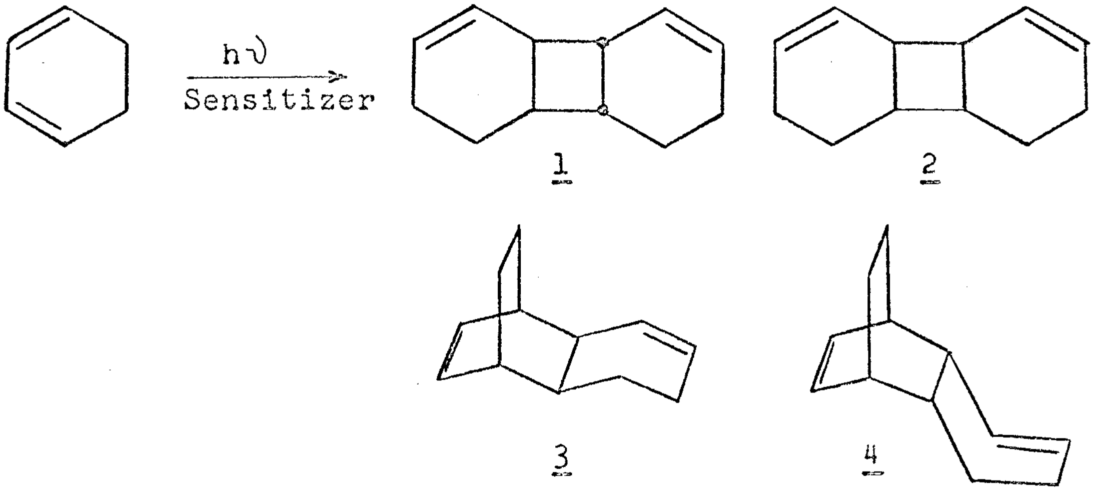
During the course of an extensive investigation of the photosensitized *cis/trans* isomerization of olefins, Hammond and co-workers discovered several unusual features (7) of the energy transfer processes. It was found that isomerizations are effected by sensitizers which apparently have too little excitation energy to promote the chemically active substrates to any known electronically excited states. Similar results obtained in the sensitized dimerization of butadiene and isoprene (8) showed that dimers were formed when low energy sensitizers were used.

Although rate constants for energy transfer from low energy sensitizers have been measured for some photoreactions (9), no detailed study of such processes has been attempted. It has been suggested, however, that the quantum yields for such reactions are very small (8). The original concept of the research reported in this thesis was to measure quantum yields and rate constants for a photoreaction using various low energy sensitizers in order to determine the efficiency and mechanism of a low energy sensitization process, and to determine when such an apparently endothermic process began to develop activation energies.

The dimerization of 1,3-cyclohexadiene (10,11) was chosen as the reaction to be studied under conditions of low-energy sensitization. This choice was made because the 1,3-cyclohexadiene system has been investigated with high energy sensitizers; it appeared to be a clean system (10) of high efficiency (10,12); and preliminary results (10,11) indicated that 1,3-cyclohexadiene underwent non-spectroscopic transitions.

There are reports of dimers formed by the direct irradiation of 1,3-cyclohexadiene (11) and by sensitization (10,11). Three dimers are formed as major products with a fourth formed in only trace amounts from both processes.

(11)



1 2 3 4

Table I gives the relative amounts of these dimers under different irradiation conditions. The total yield of dimers is approximately 90% when high-energy sensitizers are used (10), and considerably less by direct irradiation.

TABLE I

Ratio of 1,3-Cyclohexadiene Dimers Under Different Conditions

%1	%2	%3	Condition	Reference
60	15	25	ϕ_2CO 3660Å	11
44	10	23	direct irradiation 3300Å	11
10	10	10	2537Å*	11
61	17	22	ϕ_2CO 3660Å	12
60	16	24	Fluorenone 3660Å	12
58	19	23	1-Naphthyl phenyl ketone 3660Å	12

* 5% unchanged diene, 11% cleavage, 84% disproportion.

The fact that the ratio of dimers is independent of sensitizer energy indicates that the same intermediate, presumably the diene triplet, yields all three isomers.

This is in contrast to data obtained with acyclic dienes (8). The data from butadiene and isoprene indicate that trans-triplets give mostly cyclohexenes. The following mechanism has been proposed for diene dimerizations (8,10).

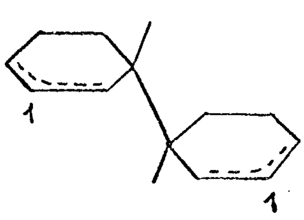
$$S \xrightarrow{h\nu} S^1 \longrightarrow S^3 \qquad (12)$$

$$S^3 + C=C-C=C \longrightarrow S + C=C-C=C^3 \qquad (13)$$

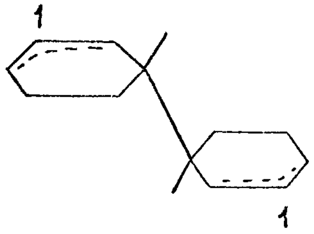
$$C=C-C=C^3 + C=C-C=C \longrightarrow \begin{array}{l} C-\overset{1}{C}-C=C \\ | \\ C-\underset{1}{C}-C=C \end{array} \qquad (14)$$

$$\begin{array}{l} C-\overset{1}{C}-C=C \\ | \\ C-\underset{1}{C}-C=C \end{array} \xrightarrow[\text{inversion}]{\text{Spin}} \xrightarrow{\text{Cyclization}} \text{dimers} \qquad (15)$$

Applying this mechanism to the dimerization of 1,3-cyclohexadiene, two biradical intermediates would be formed.



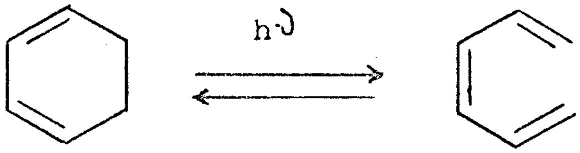
5



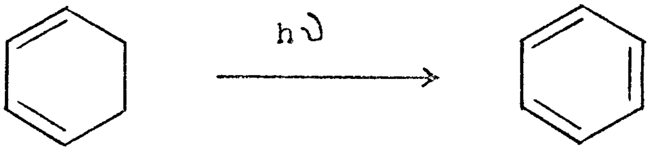
6

It can be seen that dimers 1 and 4 are formed from 5 and 2 and 3 are formed from 6.

In addition, 1,3-cyclohexadiene undergoes several unsensitized reactions in the vapor phase (13,14). 1,3-Cyclohexadiene is found in the vapor phase to be in photochemical equilibrium with 1,3,5-hexatriene (15). The stereochemistry of this reaction is not known since the triene absorption is very similar to that of the cyclic diene (16). The other modes of reactions in the vapor phase are dehydrogenation (17):



(16)



$+H_2$ (17)

and decomposition:

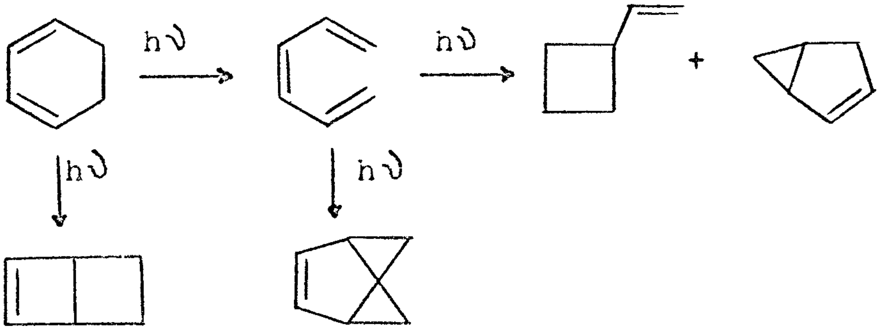
$2C_2H_2 + C_2H_4$. (18)

A hydrogen migration to give the 1,2,4-hexatriene is also observed (18). The products formed in equations 22 and 23 are believed to arise from vibrationally excited ground

$$CH_2 = CH - CH = CH - CH = CH_2 \xrightarrow{h\nu} \qquad (19)$$
$$CH_2 = C = CH - CH = CH - CH_3$$

state molecules since they do not occur in solution and are quenched by an increase in pressure in the vapor phase (16). The reverse of reaction 16 reportedly has the same origin (19). The formation of the triene (15) and hydrogen migration, equation 19 are the primary unsensitized processes in solution (20), the former being the major. In these reactions some dimer and polymer are also formed.

Several other reactions of 1,3-cyclohexadiene have been observed in ether solution (21,22,23).



(20)

α-Phellandrene, a substituted 1,3-cyclohexadiene undergoes analogous reactions in solution (24,25).

RESULTS AND DISCUSSION

The problem of studying low energy sensitization was approached from three main paths: measurement of quenching rates by flash spectroscopic techniques, measurement of quantum yields using high energy sensitizers, and measurement of quantum yields using low energy sensitizers.

In the remainder of this work S represents sensitizer, D represents 1,3-cyclohexadiene and the superscripts show the multiplicity of the excited state. The following is the simplest mechanism that can be written for the dimerization reaction.

$$S \xrightarrow{h\nu} S^1 \qquad (21)$$

$$S^1 \xrightarrow{k_{ds}} S \qquad (22)$$

$$S^1 \xrightarrow{k_f} S + h \qquad (23)$$

$$S^1 \xrightarrow{k_{ic}} S^3 \qquad (24)$$

$$S^3 \xrightarrow{k_{dt}} S \qquad (25)$$

$$S^3 + D \xrightarrow{k_Q} S + D^3 \qquad (26)$$

$$D^3 \xrightarrow{k_d} D \qquad (27)$$

$$D^3 + D \xrightarrow{k_r} D_2 \qquad (28)$$

The one symbol, D_2, is used to represent the mixture of four dimeric products (page 5). If the mechanism is correct, the ratio of the dimers formed should be constant with respect to the sensitizer energy. The relative yields of the three principal products were measured using sensitizers whose lowest triplet energies ranged from 68.5 to 40.2 kcal./mole at various diene concentrations. These results, which appear in Table II, agree with those previously reported (10,11,12).

Rate Constant for Triplet Energy Transfer to 1,3-Cyclohexadiene.

In order to understand the energy transfer step, the effect of 1,3-cyclohexadiene on the decay rates of the triplet states of various sensitizers was studied by flash spectroscopic techniques. The method used for determining k_Q, the rate of quenching of the sensitizer triplet by 1,3-cyclohexadiene, and the kinetics involved have been considered in the experimental section. The rate constant, k_Q, was measured using sensitizers having energies ranging from 68.5 to 40.2 kcal./mole.

$$S^3 + D \xrightarrow{k_Q} D^3 + S \qquad (26)$$

TABLE II

Ratio of Dimers[a]

Sensitizer	E_T[b] (kcal./mole)	% 1	% 2	% 3	$[D]_I$
Benzophenone (12)	68.5	61	22	17	
Fluorenone (12)		60	24	16	
1-Naphthyl phenyl ketone (12)	57.5	58	23	19	
Benzophenone	68.5	61	23	16	10.5
Benzophenone	68.5	62	22	16	0.21
Benzophenone	68.5	58	25	17	0.105
Benzophenone	68.5	57	24	19	0.021
Benzophenone	68.5	62	21	17	0.021
p-Diacetylbenzene	67.7	58	24	18	0.21
Phenanthrene	61.8	55	22	21	0.21
1,2-Benzanthracene	47.2	56	25	19	0.21
Acridine	45.3	60	25	15	0.21
9,10-Dimethyl-1,2-benzanthracene	44.3	50	22	28	0.21
Anthracene	42.6	56	23	21	0.21
3,4,9,10-Dibenzpyrene	40.2	65	21	14	0.21
9,10-Dibromoanthracene	40.2	53	24	23	0.21

[a] These numbers are accurate to ± 5%.

[b] See Appendix I.

The triplet energy of 1,3-cyclohexadiene has been determined to be 53.5 kcal./mole by Evans (26), using the oxygen perturbation method. This was later remeasured by Kellogg and Simpson (27), who found 52.5 kcal./mole. Therefore k_Q would be expected to approach the diffusion controlled rate for sensitizers with energies above 55 kcal./mole (28), which is observed in the present case. (See Table III). The rates for phenanthrene and triphenylene (29) are slightly lower than would have been expected, but this could have been due to quenching by impurities in the solvent, diene, or sensitizer. As the energy of the sensitizer decreases below that of 1,3-cyclohexadiene the quenching rate drops off. If the quenching is considered "classical", as was observed by Herkstroeter with trans-stilbene (9), and by Sandros with another "classical" acceptor biacetyl (30), the decrease in transfer efficiency as a function of the excitation energy of the sensitizer should be given by

$$\frac{\Delta \log k_Q}{\Delta E_T} = -\frac{1}{2.303\ RT} \quad . \qquad (29)$$

Figure I shows a plot of the rate constants for triplet energy transfer from various sensitizers to the stilbene isomers. The straight line drawn in Figure I has the slope indicated by equation 29.

TABLE III

Rate Constants for Triplet Energy Transfer

from Photosensitizers to 1,3-Cyclohexadiene

Sensitizer[a]	E_T kcal.[b]	α_f(sec.$^{-1}$)	β_f(sec.$^{-1}$)	[D]	λ	k_QM.$^{-1}$ sec.$^{-1}$
Triphenylene[c]	66.6					$1.3x10^9$
Phenanthrene[c]	61.8					$2.3x10^9$
2-Acetonaphthone	59.3	$2.6\pm0.1x10^4$	$1.3\pm0.3x10^4$	$5.25x10^{-6}$	4358	$4.6x10^9$
		$1.5\pm0.5x10^3$	$3.0\pm0.5x10^4$	0	4358	
		$4.4\pm0.1x10^4$	$3.4\pm0.6x10^4$	$1.05x10^{-5}$	4358	$3.9x10^9$
		$3.1\pm0.4x10^3$	$3.3\pm0.6x10^4$	0	4358	
2-Acetonaphthone[d]	59.3	$2.1\pm0.8x10^3$	$1.9\pm0.2x10^4$	0	4358	
		$1.0\pm0.2x10^4$	$2.8\pm0.8x10^4$	$5.25x10^{-6}$	4358	$1.5x10^9$
		$2.5\pm0.5x10^4$	$7.1\pm1.5x10^4$	$1.05x10^{-5}$	4358	$2.2x10^9$

TABLE III (cont'd.)

Sensitizer[a]	E_T kcal.[b]	α_f(sec.$^{-1}$)	β_f(sec.$^{-1}$)	[D]	λ	k_QM.$^{-1}$ sec.$^{-1}$
-Naphthyl phenyl ketone	57.5	$2.4\pm0.2\times10^{2}$	$6.5\pm0.2\times10^{4}$	0	4358	
		$2.4\pm0.2\times10^{4}$	$4.0\pm0.5\times10^{4}$	5.25×10^{-6}	4358	4.6×10^{9}
		$3.8\pm0.2\times10^{4}$	$4.3\pm0.2\times10^{4}$	1.05×10^{-5}	4358	3.6×10^{9}
Fluorenone	53.3	$4.5\pm0.6\times10^{3}$	$3.1\pm0.6\times10^{4}$	0	4358	
		$1.2\pm0.1\times10^{4}$	$4.2\pm0.5\times10^{4}$	1.05×10^{-5}	4358	7.1×10^{8}
		$1.5\pm0.0\times10^{4}$	$2.0\pm0.1\times10^{5}$	2.10×10^{-5}	4358	5.0×10^{8}
1,2,7,8-Dibenzanthracene	52.9	$2.9\pm0.6\times10^{3}$	$2.8\pm0.3\times10^{4}$	0	5460	
		$3.5\pm0.3\times10^{4}$	$7.8\pm1.0\times10^{4}$	8.40×10^{-5}	5460	3.9×10^{8}
		$2.9\pm0.3\times10^{4}$	$3.3\pm0.1\times10^{4}$	3.15×10^{-5}	5460	8.1×10^{8}
1,2,5,6-Dibenzanthracene	52.2	$1.1\pm0.1\times10^{3}$	$1.5\pm0.1\times10^{4}$	0	5460	
		$2.1\pm0.3\times10^{4}$	$1.6\pm0.3\times10^{4}$	4.20×10^{-5}	5460	4.8×10^{8}
		$8.3\pm0.7\times10^{2}$	$1.4\pm0.1\times10^{4}$	0	5460	
		$1.5\pm0.1\times10^{4}$	$1.9\pm0.1\times10^{4}$	4.20×10^{-5}	5460	3.3×10^{8}

TABLE III (cont'd.)

Sensitizer[a]	E_T kcal.[b]	α_f(sec.$^{-1}$)	β_f(sec.$^{-1}$)	[D]	λ	k_QM.$^{-1}$ sec.$^{-1}$
1,2,3,4-Dibenz-anthracene	50.8	$8.7 \pm 0.5 \times 10^{2}$	$1.7 \pm 0.0 \times 10^{4}$	0	4358	
		$1.2 \pm 0.0 \times 10^{4}$	$2.2 \pm 0.3 \times 10^{4}$	8.40×10^{-5}	4358	1.3×10^{8}
		$3.8 \pm 0.1 \times 10^{4}$	$2.3 \pm 0.1 \times 10^{4}$	3.15×10^{-5}	4358	9.4×10^{7}
Pyrene[e]	48.7	$2.4 \pm 0.1 \times 10^{3}$	$4.7 \pm 0.4 \times 10^{4}$	0	4358	
		$3.9 \pm 1.0 \times 10^{3}$	$5.3 \pm 1.0 \times 10^{4}$	8.40×10^{-5}	4358	1.8×10^{7}
		$5.3 \pm 0.3 \times 10^{3}$	$4.9 \pm 0.7 \times 10^{4}$	1.05×10^{-5}	4358	2.8×10^{7}
1,2-Benz-anthracene[f]	47.2	$2.4 \pm 0.8 \times 10^{3}$	$5.8 \pm 3. \times 10^{4}$	0	4358	
		$2.5 \pm 0.2 \times 10^{3}$	$5.6 \pm 3. \times 10^{4}$	1.00×10^{-4}	4358	1.7×10^{6}
		$3.4 \pm 1.2 \times 10^{3}$	$1.3 \pm 1. \times 10^{5}$	2.00×10^{-4}	4358	5.1×10^{6}
Acridine	45.2	$1.4 \quad \times 10^{3}$	$1.7 \quad \times 10^{4}$	0	4358	
		$8.6 \pm 0.3 \times 10^{3}$	$3.0 \pm 0.4 \times 10^{4}$	2.00×10^{-3}	4358	1.4×10^{6}
		$1.3 \quad \times 10^{3}$	$2.8 \quad \times 10^{4}$	4.00×10^{-3}	4358	3.0×10^{6}

TABLE III (cont'd.)

Sensitizer[a]	E_T kcal.[b]	α_f(sec.$^{-1}$)	β_f(sec.$^{-1}$)	[D]	λ	k_QM.$^{-1}$ sec.$^{-1}$
Anthracene	42.6	$1.1 \pm 0.1 \times 10^{3}$	$7.0 \pm 0.5 \times 10^{3}$	0	4358	
		$3.8 \pm 0.6 \times 10^{3}$	$8.8 \pm 3.0 \times 10^{3}$	3.15×10^{-2}	4358	8.7×10^{4}
		$2.0 \pm 0.3 \times 10^{3}$	$8.8 \pm 1.0 \times 10^{3}$	2.63×10^{-2}	4358	3.5×10^{4}
3,4-Benzpyrene	41.9	$7.6 \pm 0.4 \times 10^{3}$	$1.4 \pm 0.1 \times 10^{4}$	0	4358	
		$1.1 \pm 0.3 \times 10^{3}$	$1.4 \pm 0.2 \times 10^{4}$	2.10×10^{-2}	4358	1.8×10^{4}
		$2.3 \pm 0.1 \times 10^{3}$	$1.2 \pm 0.1 \times 10^{4}$	2.94×10^{-2}	4358	5.1×10^{4}
9,10-Dibromo-anthracene	40.2	$2.7 \pm 0.9 \times 10^{4}$	$1.3 \pm 0.5 \times 10^{4}$	0	4358	
		$3.3 \pm 0.1 \times 10^{4}$	$1.2 \pm 0.1 \times 10^{4}$	1.05×10^{-5}	4358	5.3×10^{8}
		$3.4 \pm 0.3 \times 10^{4}$		2.10×10^{-5}	4358	3.1×10^{8}

TABLE III (cont'd.)

[a] 4×10^{-4}M. unless otherwise indicated.

[b] See Appendix I.

[c] See Reference 29.

[d] Zone refined 2-acetonaphthone.

[e] 1.05×10^{-4}M.

[f] 1.50×10^{-4}M.

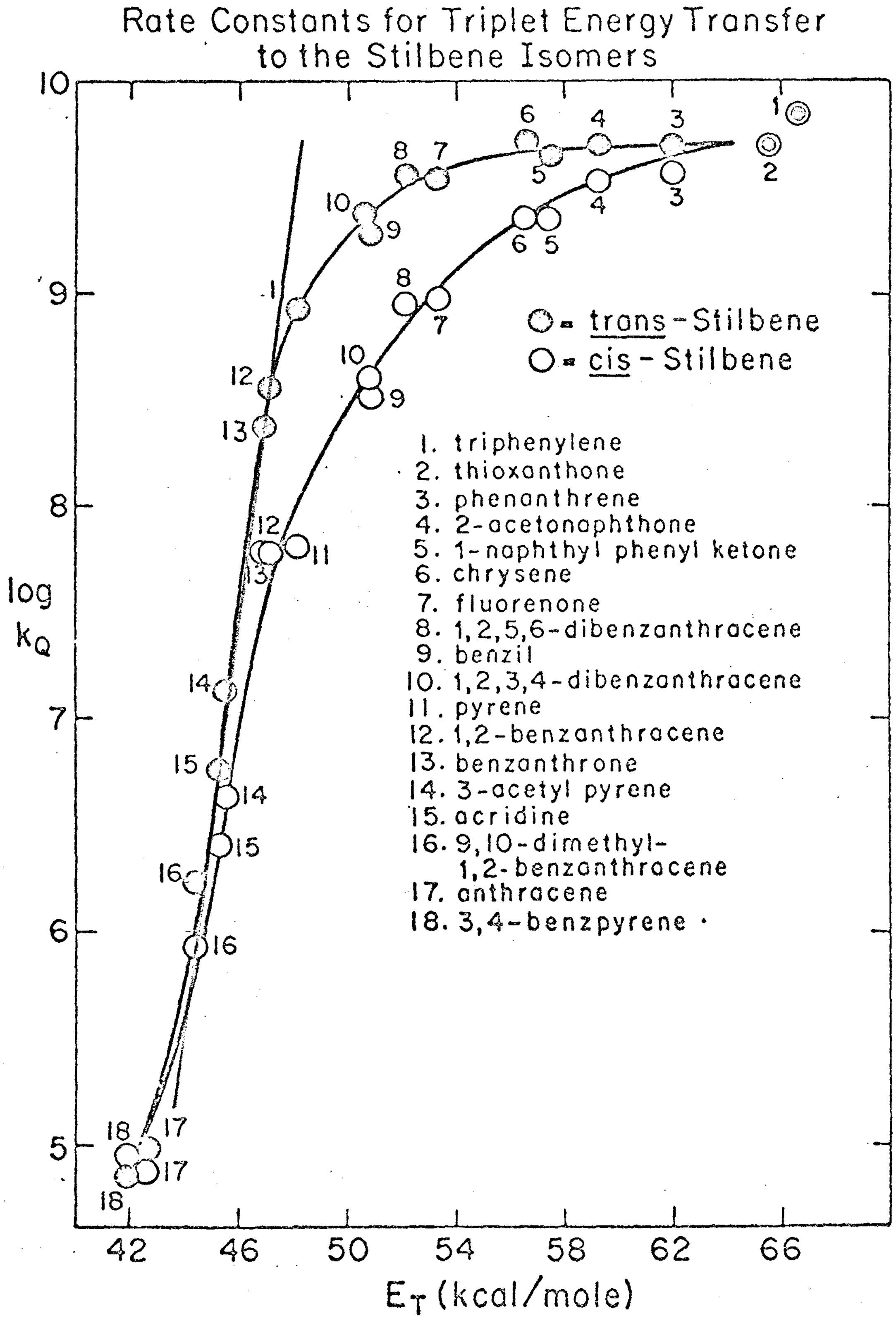

Rate Constants for Triplet Energy Transfer to the Stilbene Isomers
10
9
8
7
6
5
log k_Q
42
46
50
54
58
62
66
E_T (kcal/mole)
○ = trans-Stilbene
○ = cis-Stilbene
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
1. triphenylene
2. thioxanthone
3. phenanthrene
4. 2-acetonaphthone
5. 1-naphthyl phenyl ketone
6. chrysene
7. fluorenone
8. 1,2,5,6-dibenzanthracene
9. benzil
10. 1,2,3,4-dibenzanthracene
11. pyrene
12. 1,2-benzanthracene
13. benzanthrone
14. 3-acetyl pyrene
15. acridine
16. 9,10-dimethyl-1,2-benzanthracene
17. anthracene
18. 3,4-benzpyrene

FIGURE I

However when 1,3-cyclohexadiene is the acceptor, the slope does not fit equation 29. (Figure II). These data were similar to those which were obtained for <u>cis</u>-stilbene and 1,2-diphenylpropene. The quenching remains efficient with sensitizers whose energy is below that of 1,3-cyclohexadiene by 10 kcal./mole. Therefore, we conclude that 1,3-cyclohexadiene undergoes non-Franck-Condon transitions to a relaxed triplet when low energy sensitizers are employed (31).

<u>Quantum Yield Measurements Using High Energy Sensitizers.</u>

If the mechanism, equations 21 to 28, is valid, the quantum yield for the production of dimers is given by equation 30.

$$\frac{1}{\varphi} = \frac{1}{\phi} \alpha \beta \qquad (30)$$

$$\alpha = 1 + \frac{k_{dt}}{k_Q[D]} \qquad (31)$$

$$\beta = 1 + \frac{k_d}{k_r[D]} \qquad (32)$$

$$\phi = \frac{k_{ic}}{k_{ds} + k_f + k_{ic}} \qquad (33)$$

Rate Constants for Triplet Energy Transfer to 1,3-Cyclohexadiene

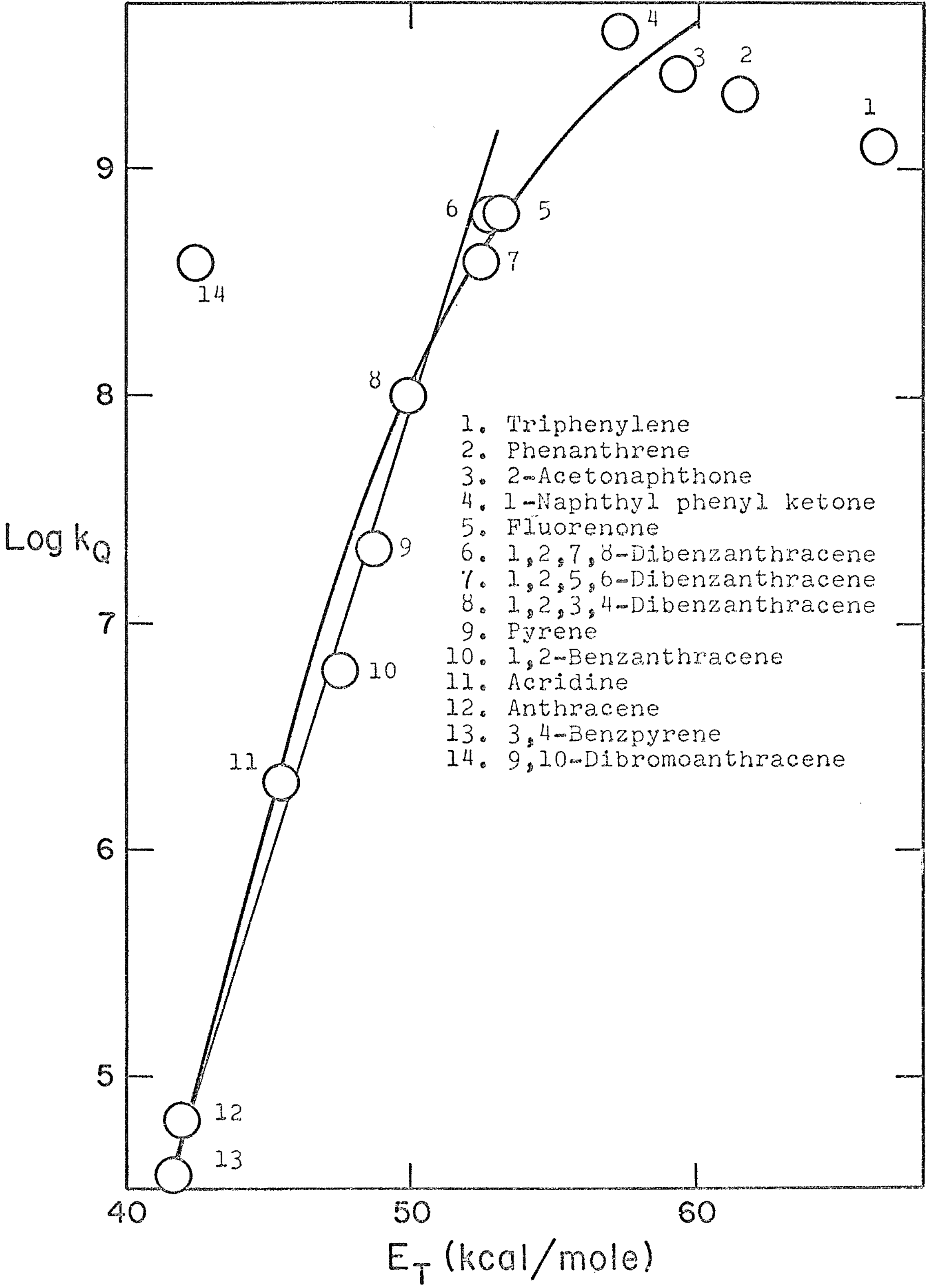


FIGURE II

In this equation α is a measure of the efficiency of the energy transfer step. It is dependent on the rate of unimolecular decay of the sensitizer and the rate of energy transfer k_Q. For exothermic reactions, when k_Q is diffusion controlled (30), α is approximately unity for reasonable diene concentration. The function β is a measure of the efficiency of the diene triplet reactions. It depends on the rate constants for unimolecular decay of the diene triplet and for reactions of diene triplets with diene ground state. Since α is approximately unity for high energy sensitizers such as benzophenone, β can be determined by separate measurements.

Before β was determined, several preliminary experiments were performed. These experiments consisted of determining the benzophenone sensitized quantum yield at 0.2M. diene using various actinometers at two wavelengths. (Table IV).

Each value of ϕ_{D_2} is the average of three identical tubes run simultaneously. The average of all measurements at 0.20M. diene is 0.87 ± .03. The values are identical at both irradiation wavelengths.

Since appearance of dimers is easy to determine accurately, most ϕ's in this work are quantum yields for the appearance of dimers. With benzophenone the

TABLE IV

Benzophenone Sensitized Quantum Yields at 0.2M.
1,3-Cyclohexadiene at 25°

Å	ϕ_{D_2}	[D]ave.	Actinometer*
3660	0.84±.02	0.210	1
	0.89±.01	0.206	1
	0.85±.02	0.205	2
	0.88±.02	0.203	1
	0.82±.02	0.201	1
	0.87±.01	0.196	1
	0.90±.01	0.192	3
	0.87±.01	0.192	1
	0.88±.02	0.190	1
3130	0.87±.01	0.204	1
	0.88±.01	0.207	1

*Actinometer 1 is potassium ferrioxalate, 2 is 1,2-diphenylpropene ϕ = 0.55 (7), 3 is trans-stilbene ϕ = 0.55 (32).

quantum yield for disappearance of diene relative to that of formation of dimers has been measured. Both quantum yields were determined from the same tube.

$$\phi_{-D} = 2.03 \pm .03\phi_{D_2}$$

This measurement is in agreement with the above mechanism.

The variation of the quantum yield with diene concentration appears in Table V. Since benzophenone is a high energy sensitizer, and α is approximately unity, the slope of a reciprocal plot should give the ratio k_d/k_r, which determines β. Figure III is a plot of these data.

Analysis of these data yielded the following parameters for benzophenone:

$$\phi_{ic} = 0.99 \pm 0.6 \qquad k_d/k_r = 0.029 \pm .005.^{*}$$

The reciprocal of the intercept is a measurement of the intersystem crossing efficiency. The value obtained is in excellent agreement with that obtained by Lamola for benzophenone, $\phi_{ic} = 0.99 \pm .02$ (33). Since β is a function only of the particular diene reaction, it should remain constant with any sensitizer. Similar data (Table VI) for other high energy sensitizers are plotted in Figure IV.

---

[*] For analysis of the errors in these calculations see Appendix II.

TABLE V

Benzophenone Sensitized Dimerization Quantum Yields as a Function of 1,3-Cyclohexadiene Concentration at 25°

ϕ_{D_2}	[D]ave.	$1/\phi_{D_2}$	1/[D]ave.
0.97±.02	0.994	1.03	1.01
0.94±.01	0.519	1.06	1.93
0.84±.02	0.210	1.19	4.85
0.89±.01	0.206	1.13	4.85
0.85±.02	0.205	1.18	4.87
0.88±.02	0.203	1.14	4.92
0.82±.02	0.201	1.22	4.97
0.87±.01	0.196	1.15	5.10
0.90±.01	0.192	1.11	5.21
0.87±.01	0.191	1.15	5.23
0.86±.01	0.140	1.16	5.26
0.84±.02	0.121	1.19	8.30
0.76±.02	0.101	1.31	9.90
0.64±.02	0.084	1.56	11.90
0.70±.02	0.040	1.43	25.00
0.52±.02	0.032	1.92	31.50
0.42±.04	0.020	2.32	50.00
0.32±.04	0.015	3.12	67.00

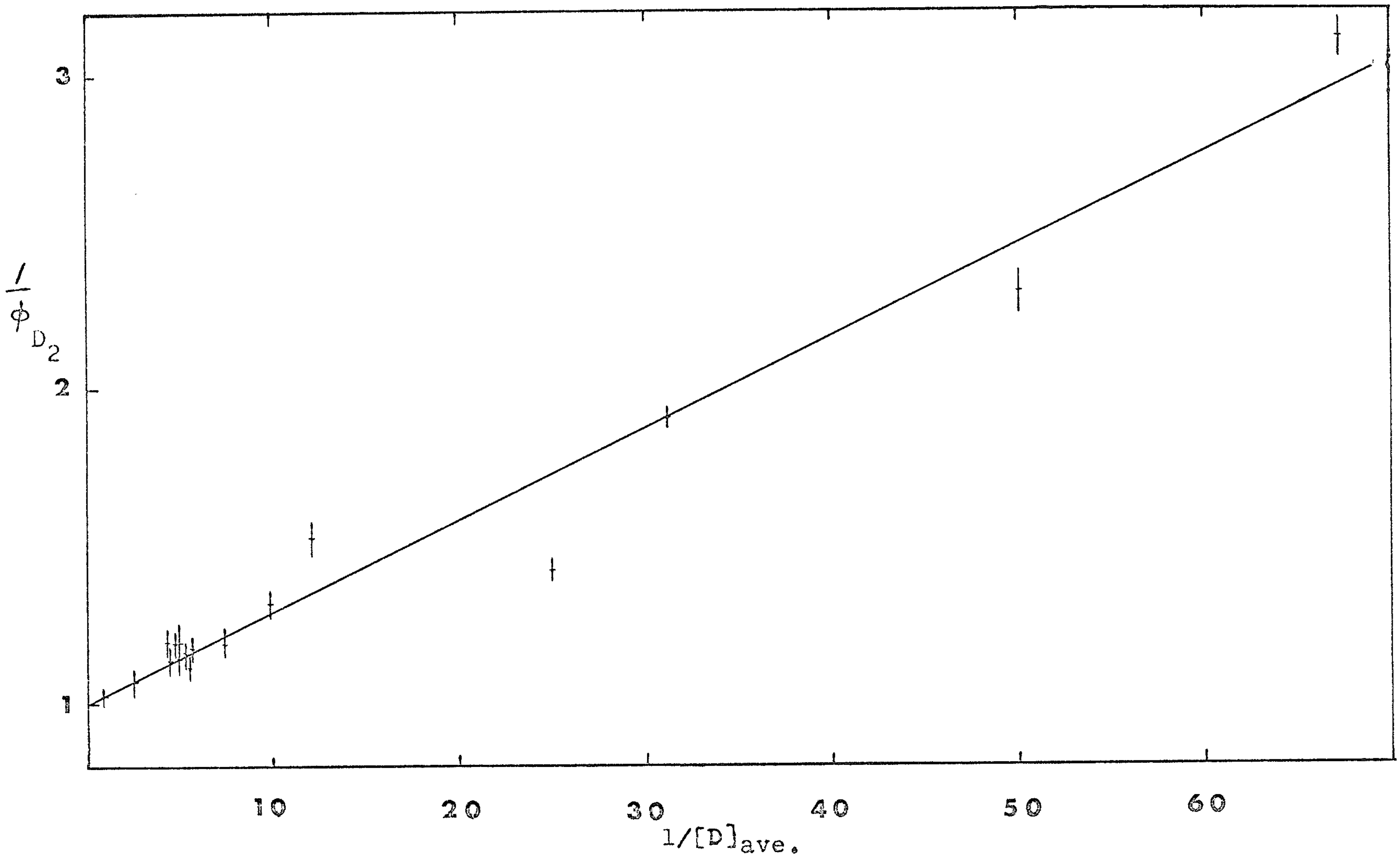


FIGURE III Quantum Yields for the Benzophenone Sensitized Dimerization with Varying Concentrations of 1,3-Cyclohexadiene

TABLE VI

Quantum Yields for Dimerization with Varying Concentrations of 1,3-Cyclohexadiene at 25°

Sensitizer	E_T^* (kcal./mole)	ϕ_{D_2}	[D]ave.	$1/\phi_{D_2}$	1/[D]ave.
Phenanthrene	61.8	0.72±.03	0.21	1.39	4.76
		0.71±.02	0.205	1.41	4.87
		0.62±.01	0.102	1.64	9.70
		0.58±.02	0.080	1.72	12.50
		0.53±.03	0.059	1.89	17.20
		0.45±.02	0.039	2.22	25.60
Chrysene	56.6	0.73±.01	0.21	1.37	4.75
		0.66±.01	0.105	1.52	9.50
		0.68±.06	0.105	1.48	9.50
		0.55±.05	0.049	1.82	20.40
		0.48±.05	0.030	2.08	33.30
		0.43±.04	0.020	2.31	50.00

TABLE VI (cont'd.)

Sensitizer	E_T^* (kcal./mole)	ϕ_{D_2}	[D]ave.	$1/\phi_{D_2}$	1/[D]ave.
1,2,5,6-Dibenzanthracene	52.2	0.88±.02	1.03	1.14	0.97
		0.83±.01	0.507	1.20	1.97
		0.86±.01	0.40	1.16	2.50
		0.75±.02	0.20	1.33	5.00
		0.82±.01	0.19	1.22	5.26
		0.77±.01	0.14	1.30	7.15
		0.62±.01	0.099	1.62	10.10
		0.58±.02	0.079	1.72	12.80
		0.43±.02	0.037	2.32	27.00
		0.58±.02	0.031	1.72	32.00
		0.37±.01	0.019	2.70	52.60
		0.33±.02	0.018	3.04	54.00

---

[*] See Appendix I for Triplet State Energies.

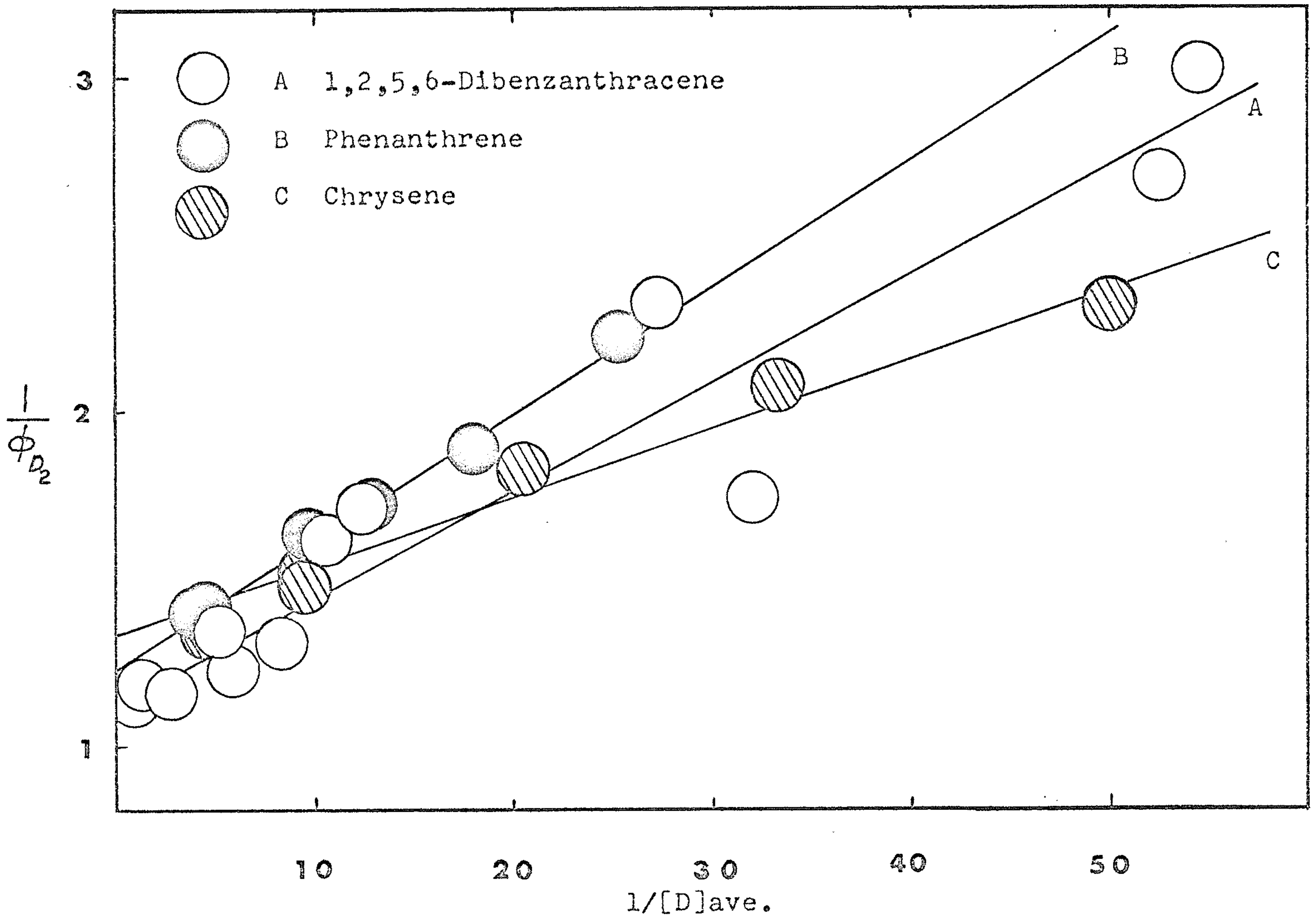


FIGURE IV Quantum Yields for Dimerization Using High Energy Sensitizers with Varying Concentrations of 1,3-Cyclohexadiene

A summary of the parameters is given in Table VII. The ratio k_d/k_r appears to be constant except when chrysene is used as the sensitizer.

The surprising feature about the data of Table VII is the excellent agreement between k_d/k_r determined from the benzophenone data and the 1,2,5,6-dibenzanthracene data. With benzophenone α was assumed to be unity. Since 1,2,5,6-dibenzanthracene is approximately isoenergetic with 1,3-cyclohexadiene, the rate of energy transfer would be expected to be less than diffusion controlled (9), and this decrease in rate would be expected to be reflected in the quantum yield for dimerization. Since k_d/k_r is the same for the sensitizers, α must be unity for 1,2,5,6-dibenzanthracene also. This can be confirmed by consideration of the rate constants for energy transfer obtained by flash spectroscopy for the 1,2,5,6-dibenzanthracene 1,3-cyclohexadiene system. Inspection of Table VIII shows that a diene concentration of 10^{-4}M. or less is needed to make α large enough to affect ϕ_{D_2}.

The quantum yield for several other high energy sensitizers have been measured, (see Table IX).

The results obtained using 1-naphthyl phenyl ketone and p-diacetylbenzene are identical to those found with benzophenone. This is not surprising since the inter-

TABLE VII

Parameters Obtained from High Energy Sensitizers

Sensitizer	E_T[a] (kcal./mole)	ϕ_{ic}[b]	k_d/k_r[b]
Benzophenone	68.5	0.99±.06	0.029±.005
Phenanthrene	61.8	0.81±.01	0.031±.001
Chrysene	56.6	0.76±.03	0.016±.005
1,2,5,6-Dibenzanthracene	52.2	0.87±.07	0.028±.005

[a] See Appendix I for triplet energies.

[b] See Appendix II for discussion of errors.

TABLE VIII

Rate Constants for Energy Transfer

from 1,2,5,6-Dibenzanthracene

k_{d_t}	k_Q	k_{d_t}/k_Q
9.7×10^2 sec.$^{-1}$	4.1×10^8 M.$^{-1}$ sec.$^{-1}$	2.3×10^{-6} M.

TABLE IX

Quantum Yields for Dimerization Using High Energy Sensitizers at 25°[a]

Sensitizer	E_T[b] (kcal./mole)	Φ_{D_2}
p-Diacetylbenzene	67.7	0.84±.05
2-Acetonaphthone	59.3	0.62±.03
		0.63±.01
		0.64±.01
		0.67±.01
		0.61±.01
1-Naphthyl phenyl ketone	57.5	0.86±.05
2,3-Benzofluorene	57.5	0.58±.01
1,2,7,8-Dibenzanthracene	52.9	0.29±.01

[a] The diene concentration in all runs was approximately 0.2M.

[b] See Appendix I.

system crossing efficiencies would be expected to be close to unity (33). It is puzzling that the value for 2-acetonaphthone is lower than would be expected (see Table X). This could be due to several factors, chemical reaction between sensitizer and diene or radiationless quenching of the singlet state (vide infra). These possibilities are reasonable, since the lowest triplet of 2-acetonaphthone is $\pi \rightarrow \pi^*$ (34,35,36), it may resemble an aromatic hydrocarbon and adducts between dienes and aromatic hydrocarbons have been isolated. The value obtained for 2,3-benzofluorene is reasonable but no comparison can be made since the intersystem crossing efficiency is not known.

The values obtained (Table VII) are in good agreement with the literature values for ϕ_{ic}. (Table X). Recent workers have shown that for aromatic hydrocarbons, radiationless decay of the first excited singlet state is unimportant (33,37,38,39,40,41,42). These workers have shown for a variety of compounds that $\phi_{ic} + \phi_f = 1$. Table X gives some representative data of ϕ_{ic} and ϕ_f in solution (33,37,40,42,43,44,45,46,47,48,49,50). Inspection of these data shows the validity of this relationship.

TABLE X[a]

Triplet and Fluorescence Yields in Solution

Compound	ϕ_{ic}	Reference	ϕ_f	Reference
Naphthalene	0.75	37	0.23	40
	0.67	43	0.39	42
Benzophenone	0.99±.02	33		
Phenanthrene	0.76±.01	33	0.14	46
	0.85	37		
Chrysene	0.67	33	0.14	40
	0.85	37		
1,2,5,6-Dibenzanthracene	0.89	33		
2-Acetonaphthone	0.84	33		
Anthracene	0.72	37	0.28	47
			0.29	48
Acridine	0.70	37		
1,2-Benzanthracene	0.55±.1	44	0.20	49
			0.19	50

TABLE X[a] (cont'd.)

Compound	ϕ_{ic}	Reference	ϕ_f	Reference
1,2,3,4-Dibenz-anthracene	0.71	45		
1,2,7,8-Dibenz-anthracene	0.80	45		
Pyrene			0.32	40

[a] Although benzene was used as the solvent for most of these measurements, cyclohexane and ethanol were used in some cases. The values obtained in these solvents are several percent higher than those in benzene (37). This is still within the accuracy of the experiments reported here.

Quenching by Azulene.

The fact that azulene has a triplet state of very low energy (51) makes it an excellent triplet quencher. It has been shown that azulene quenches benzophenone and anthracene triplets at diffusion controlled rates (52). There also have been several reports of azulene quenching the triplet states of dienes (7,8). Conveniently, azulene has a low extinction coefficient between 3500 and 4200Å (< 50) (8). Quenching experiments can therefore be performed, in which all of the light is absorbed by the sensitizer. The azulene quenching data appear in Table XI.

If equation 34 were included in the mechanism represented by equations 21-28 the quantum yield would be predicted by equation 35.

$$D^3 + A_z \xrightarrow{k_{Q'}} A_z{}^3 + D \qquad (34)$$

$$\frac{1}{\phi_{D_2}} = \frac{1}{\phi_{ic}} \left(1 + \frac{k_d}{k_r[D]} + \frac{k'_Q\,[A_z]}{k_r[D]} \right) \qquad (35)$$

If benzophenone is used as a sensitizer, ϕ_{ic} and α are unity. Since the concentration of azulene is very small relative to the diene concentration, and transfer to the diene and azulene, from benzophenone

TABLE XI

Quantum Yields for Dimerization with Various Concentrations of Azulene [D] = 0.21[a]

Φ_{D_2}	$[Az] \times 10^5$	$1/\Phi_{D_2}$
0.65±.03	3	1.55
0.73±.01	3	1.40
0.55±.01	5	1.83
0.61±.01	5	1.64
0.46±.02	7	2.20
0.42±.01	8	2.41
0.52±.03	10	1.94
0.38±.02	10	2.64

[a] The intercept and slope of a plot of these data (Figure V) are 1.13±.08 and $1.30 \pm 1.7 \times 10^4$ respectively. The intercept calculated from the previous benzophenone data is 1.11.

triplets, is diffusion controlled, essentially none of the benzophenone triplets are quenched by the azulene. A plot of these data appears in Figure V. According to equation 35 the intercept of such a plot should be identical with that obtained from the previous benzophenone data. Excellent agreement was found. This agreement supports the argument that benzophenone triplets are not quenched by the azulene. If k_Q is assumed to be 5×10^9M. sec.$^{-1*}$, then k_r equals at least 1.8±1 x 10^6M.$^{-1}$ sec.$^{-1}$. From this a lifetime for the diene triplet of at least 2.5±1 x 10^{-5} sec. is obtained. This is a long lifetime for a diene triplet compared to previously measured values of 10^{-8} sec. (7) and 5 x 10^{-6} sec. (8) for stilbene and isoprene triplets, respectively. Potts (53) has suggested that the cyclic triplet would have an increased lifetime compared to the acyclic triplet. In the ground state, the configuration of 1,3-cyclohexadiene is nonplaner. The methylene protons are not eclipsed as would be

---

*This assumption may not be valid since the 1,3-cyclohexadiene triplet is considered to be a relaxed state. Therefore the quenching of the diene triplet must involve deexcitation of the non-spectroscopic triplet. The rate constant for quenching of diene triplets by azulene could be less than the diffusion-controlled rate and the lifetime of the diene triplet may be longer (8).

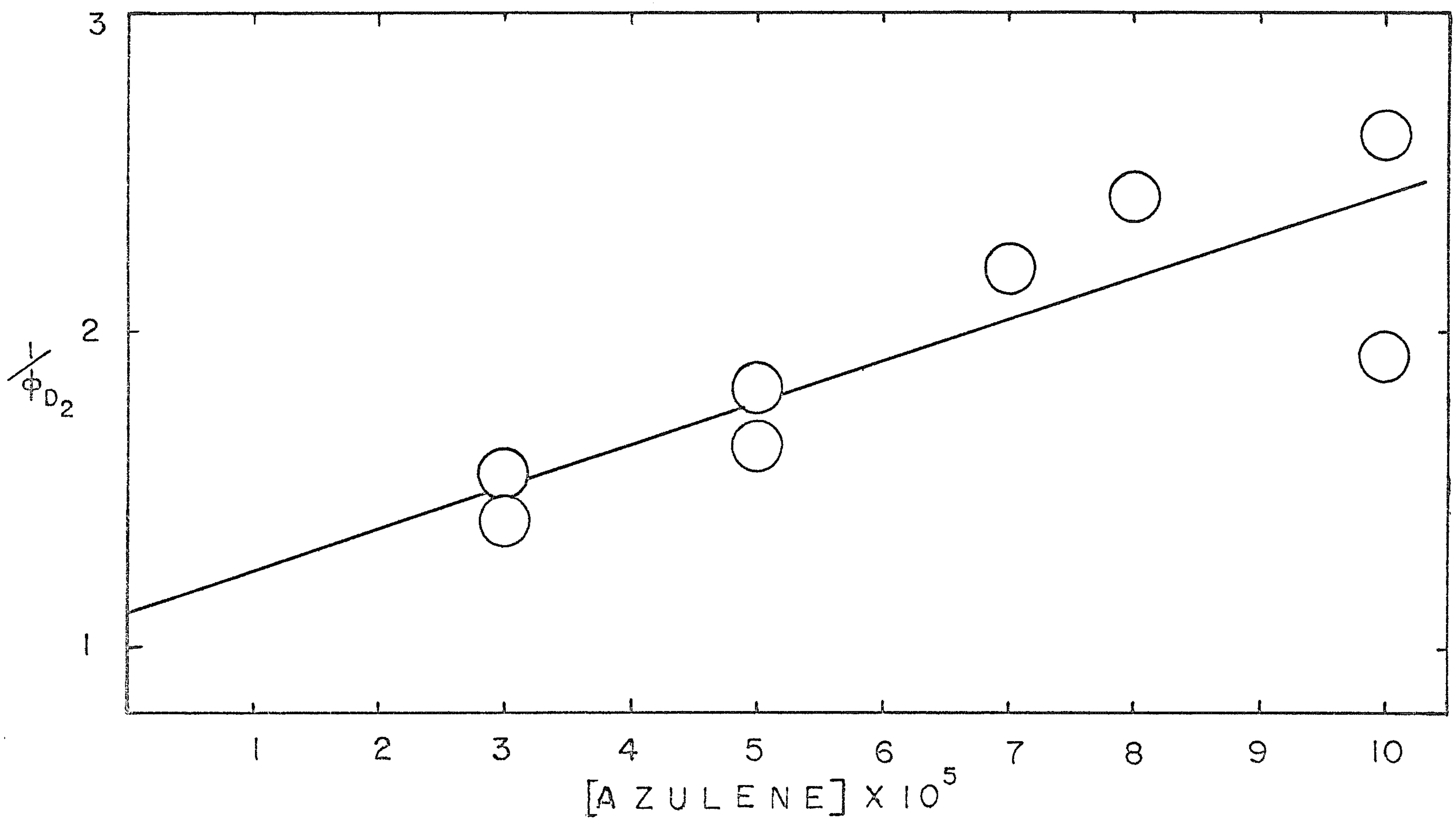


FIGURE V Quantum Yields for Dimerization with Varying Concentrations of Azulene [D] = 0.21M.

expected in a planer configuration. The 1,3-cyclohexadiene triplet, having less double bond character than the ground state, probably has a configuration between the ground state diene and cyclohexene relieving ring strain and decreasing electron-electron repulsion.

Since 1,3-cyclohexadiene has a long lifetime, detection of this triplet by flash spectroscopy would be expected to be possible. Experiments using acetone and phenanthrene as sensitizers were designed to detect triplet-triplet absorption of 1,3-cyclohexadiene (54). In these experiments transients were looked for using the procedure used in flash kinetics. Additionally, full absorption spectra were obtained using a spectrograph and photographic plate. These experiments were performed at 20° and 77°K but no transients were detected.

Temperature Effect on High Energy Sensitization.

At the outset of this work it was thought that an activation energy for the nonvertical energy transfer process would be reflected in the quantum yield for dimerization. To determine the effect of temperature on the energy transfer step it was intended to measure the quantum yields as a function of temperature. Before this could be accomplished the effect of temperature on the dimerization reaction was studied using a well understood high energy sensitizer, benzophenone. The data are tabulated in Table XII and plotted in Figure VI. The parameters from these plots appear in Table XIII. Similar data using 1,2,5,6-dibenzanthracene were obtained at 60° only, and these data appear in Table XIV and Figure VII.

It is important to notice that the ϕ_{ic}'s (Table XIII) are in close agreement and the k_d/k_r ratios are apparently temperature independent. The average of these values yields a k_d/k_r of $0.022 \pm .007$. This is probably the best value for this ratio and is used throughout this work.

The fact that k_d/k_r remains constant is rather puzzling, since both rate constants are less than diffusion controlled. This means that both k_d and k_r are changing at the same rate or are temperature independent. If we assume k_d to be temperature independent (55) then the temperature independence of k_r can be rationalized if $\Delta H^{\ddagger}$ is negligibly small and $T\Delta S^{\ddagger}$ is large ($k = [RT/Nh]e^{-\Delta H^{\ddagger}/RT}e^{\Delta S^{\ddagger}/R}$). These conditions give a rate that is less than diffusion controlled but is still insensitive to temperature.

TABLE XII

Quantum Yields for Benzophenone Sensitized Dimerization at Various Temperatures

41±1°

ϕ_{D_2}	[D]ave.	$1/\phi_{D_2}$	1/[D]ave.
0.98±.02	1.025	1.02	0.975
0.97±.01	0.820	1.03	1.22
0.97±.01	0.810	1.03	1.23
1.00±.03	0.810	1.00	1.23
0.93±.02	0.420	1.09	2.40
0.97±.01	0.420	1.03	2.40
0.90±.02	0.210	1.12	4.75
0.88±.01	0.210	1.14	4.75
0.92±.04	0.210	1.09	4.75
0.90±.03	0.200	1.11	5.00
0.87±.02	0.200	1.15	5.00
0.93±.01	0.187	1.07	5.35
0.79±.01	0.167	1.26	6.00
0.84±.01	0.125	1.19	8.00
0.88±.01	0.123	1.14	7.90
0.83±.01	0.093	1.20	10.40
0.84±.02	0.092	1.19	10.90

TABLE XII (cont'd).

ϕ_{D_2}	[D]ave.	$1/\phi_{D_2}$	1/[D]ave.
51±1°			
0.97±.01	0.830	1.03	1.20
0.86±.01	0.205	1.16	4.87
0.96±.01	0.205	1.04	4.87
0.87±.03	0.200	1.15	5.00
0.87±.02	0.200	1.16	5.00
0.78±.03	0.167	1.28	6.00
0.87±.01	0.165	1.15	6.05
0.87±.01	0.124	1.16	8.10
0.89±.01	0.082	1.23	12.20
0.69±.01	0.040	1.45	23.80
59±1°			
0.89±.01	0.210	1.13	4.75
0.91±.02	0.210	1.11	4.75
0.89±.02	0.210	1.12	4.75
0.81±.01	0.167	1.23	6.00
0.84±.01	0.160	1.19	6.25
0.88±.01	0.165	1.14	6.06
0.81±.01	0.124	1.23	8.05
0.78±.01	0.082	1.28	12.20

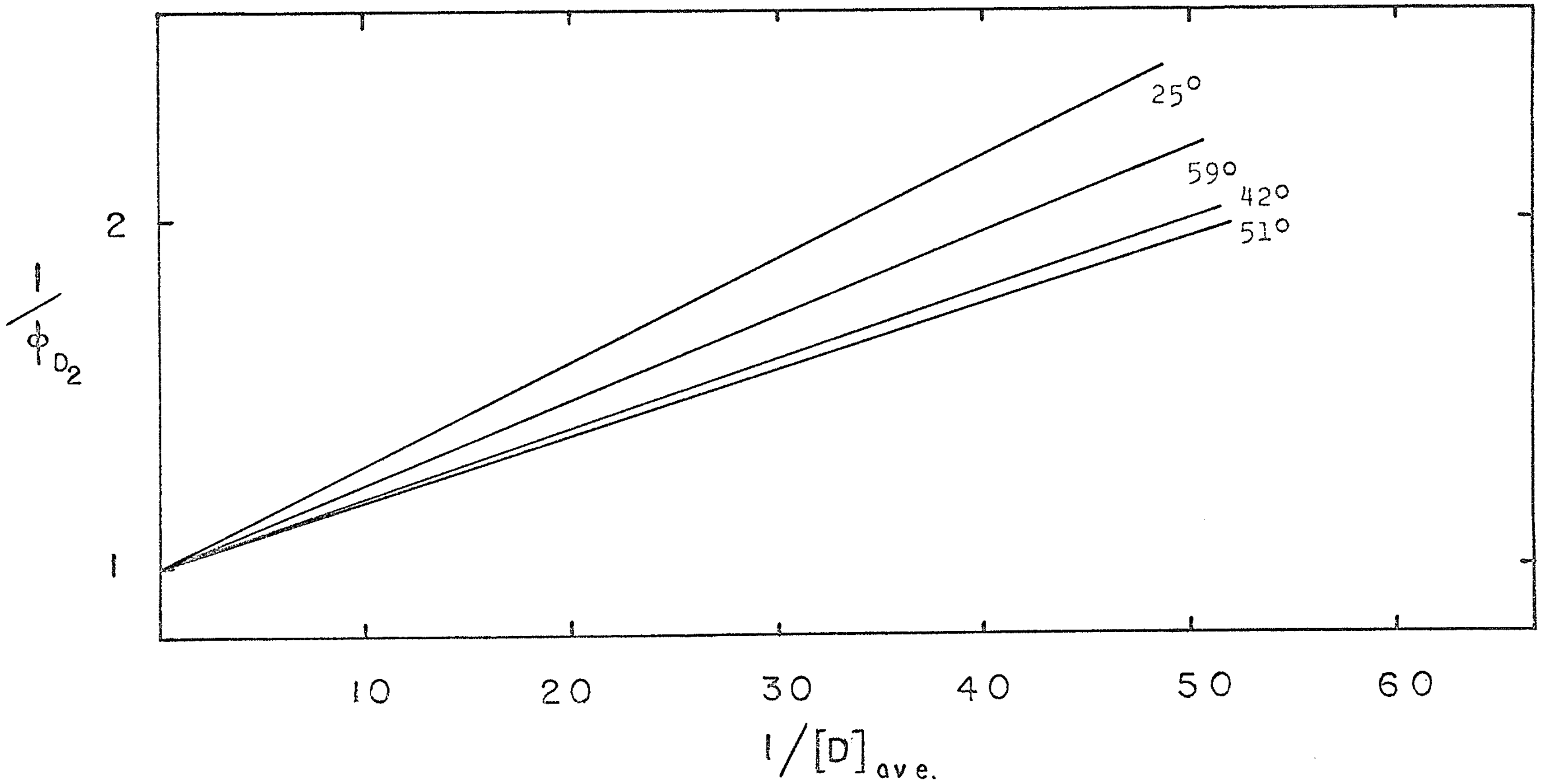


FIGURE VI Quantum Yields for Benzophenone Sensitized Dimerization with Various Concentrations of 1,3-Cyclohexadiene at Different Temperatures

TABLE XIII

Parameters Obtained from the Benzophenone Data at Various Temperatures

Temperature	ϕ_{ic}	k_d/k_r
25±1	0.99±.06	0.029±.005
42±1	0.99±.03	0.020±.005
51±1	0.97±.05	0.017±.007
59±1	0.98±.08	0.023±.007

TABLE XIV

Quantum Yields for 1,2,5,6-Dibenzanthracene Sensitized Dimerization at 60°

ϕ_{D_2}	[D]ave.	$1/\phi_{D_2}$	1/[D]ave.
0.83±.02	0.49	1.21	2.04
0.77±.02	0.27	1.30	3.80
0.79±.02	0.20	1.26	5.00
0.84±.01	0.095	1.19	10.50
0.62±.01	0.061	1.61	16.40

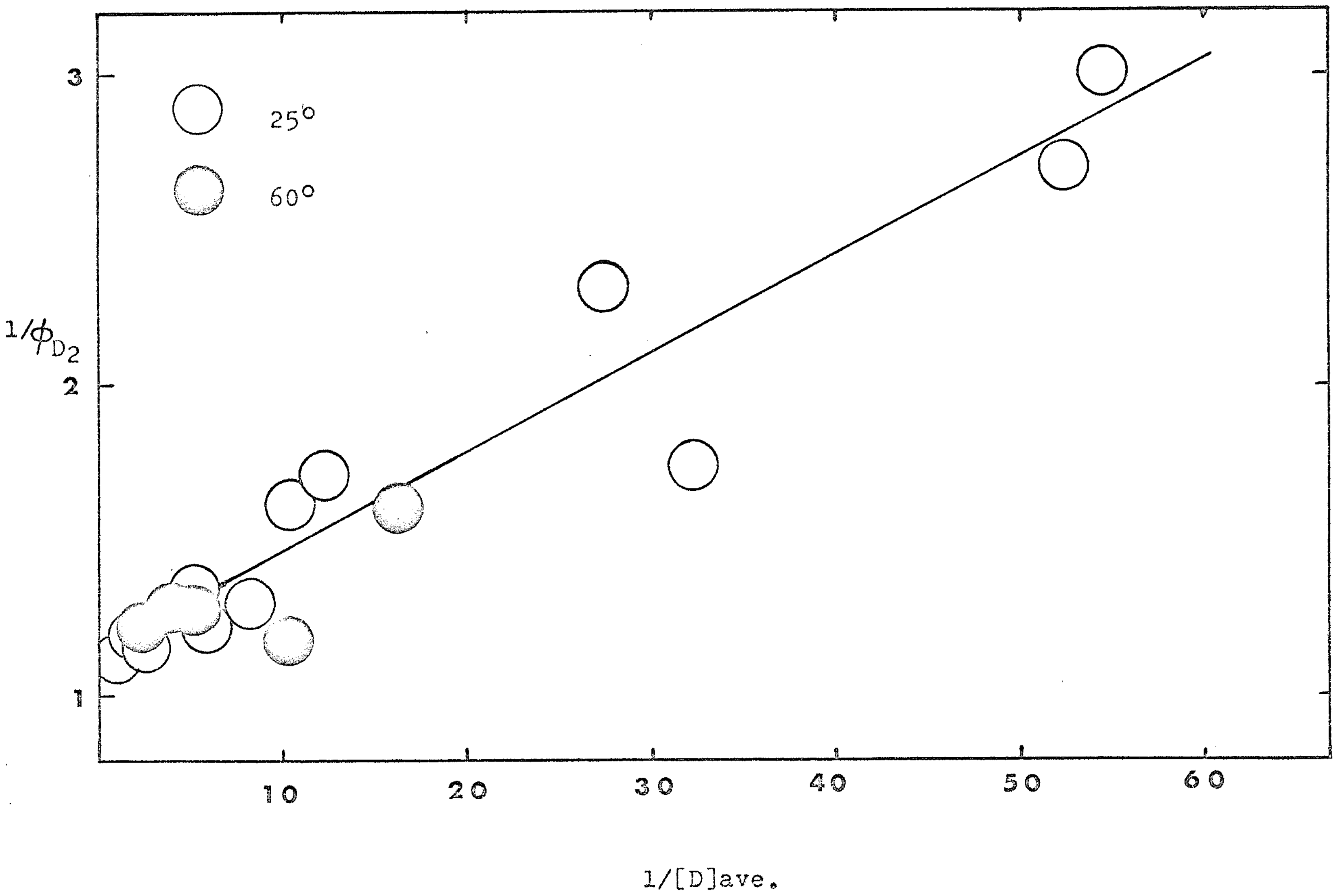


FIGURE VII Quantum Yields for 1,2,5,6-Dibenzanthracene Sensitized Dimerization with Varying 1,3-Cyclohexadiene Concentrations at Different Temperatures

1,3-Cyclohexadiene as an Actinometer.

Since the benzophenone sensitized dimerization of 1,3-cyclohexadiene is straightforward and analysis is relatively simple this system has been used in the Hammond group as a chemical actinometer (56,57). The advantage of this system is that it can be run for long periods. If the average diene concentration is substituted in equation 30 using $k_d/k_r = 0.022$, the intensity can be calculated. At high diene concentrations this value is more accurate than the 90% confidence limit shows. The error in the slope arises from large deviations in the low concentration range.

For example: if 1M. initial diene concentration was used and run to 25% conversion, the average diene concentration would be 0.875M. This would give a quantum yield of 0.975, 50% conversion would yield $\phi_{D_2} = 0.970$. Therefore under these conditions, the quantum yield for dimerization is relatively insensitive to changes in the diene concentration.

Quantum Yields Using Low Energy Sensitizers.

Measurement of dimerization quantum yields using low energy sensitizers confirmed the previous predictions (See page 4) (8). (Table XV). Although these data were obtained at 0.21M. diene, by comparison with Table X,

TABLE XV

Quantum Yields Using Low Energy Sensitizers. [D]=0.20.

Sensitizer	E_T (kcal./mole)	Φ_{D_2}
1,2,3,4-Dibenzanthracene	50.8	0.38± .01
Pyrene	48.7	4.1 ± .4x10^{-3}
1,2-Benzanthracene	47.2	6.6 ± .1x10^{-2}
3-Acetylpyrene	45.5	0.53± .02
Acridine	45.3	6.3 ± .06x10^{-3}
9,10-Dimethyl-1,2-benzanthracene	44.3	6.2 ± .2x10^{-2}
Anthracene	42.6	5.0 ± .3x10^{-2}
3,4-Benzpyrene	41.9	5.7 ±1.5x10^{-4}
3,4,9,10-Dibenzpyrene	40.2	1.7 ± .1x10^{-3}
9,10-Dibromoanthracene	40.2	8.0 ± .1x10^{-3}

it can be seen that these numbers are lower than those which would have been expected from the intersystem crossing yield. This loss in energy could be accounted for by inefficient energy transfer, but it has already been shown in the case of 1,2,5,6-dibenzanthracene, whose rate constant for energy transfer was less than diffusion controlled, that the efficiency of transfer (α) remains nearly unity at the concentrations used. It might be argued that this is also the case here. In the case of 1,2-benzanthracene at 0.2M. diene, β is calculated to be 1.11 and α to be 1.0035. Substitution of these in equation 41 predicts a quantum yield of 0.72. This is considerably higher than what was found. The fluorescence quantum yield ϕ_f has been measured by several workers (49,50) as 0.20±.01 and appears to be a reliable number. This would indicate that ϕ_{ic} should be 0.80, or if the value of ϕ_{ic} is (0.55) correct it appears that approximately 25% of the molecules undergo the radiationless transition $S_1^* \rightarrow S_0$. This loss could also be accounted for by excimer formation followed by radiative or nonradiative decay, (50) or chemical reaction of the sensitizer (58,59). In this work it is assumed that for 1,2-benzanthracene $\phi_{ic} = 0.80$.

The only low energy sensitizer used which has a high quantum yield is 3-acetylpyrene. The reasons for this high quantum yield are unknown at this time. Due to the fact that the fluorescence spectra of 3-acetylpyrene show unusual concentration and solvent dependences and that no phosphorescence could be detected in glasses at 77°K (60), it is difficult to put much meaning in the values.

The quantum yields for the 1,2-benzanthracene sensitized dimerization were measured as a function of diene concentration. These data appear in Table XVI and Figure VIII. Inspection of these data show that the quantum yield has a maximum. This unexpected phenomenon was believed to be caused by a competition between intersystem crossing and quenching of the singlet states of the 1,2-benzanthracene by the diene. Considerable work has been done in these laboratories on this quenching phenomenon (43,61).

A brief discussion of singlet quenching and its implications to this work will now be presented.

It was found that the fluorescence of aromatic hydrocarbons was quenched by conjugated dienes. Considering the destruction of sensitizer singlets by interaction with dienes, the following equations can be obtained.

TABLE XVI[a]

Dimerization Quantum Yields Using 1,2-Benzanthracene at 25°

ϕ_{D_2}	$[D]$ave.	$1/[D]$ave.	$1/\phi_{D_2}$	%D used
0.041±.001	0.490	2.02	24.4	1.4
0.044±.001	0.395	3.47	22.7	2.
0.066±.001	0.209	4.80	15.2	11.
0.066±.001	0.199	5.10	15.2	11.
0.093±.004	0.139	7.17	10.7	11.
0.16 ±.01	0.087	11.5	6.25	33.
0.19 ±.01	0.040	25.0	5.25	59.
0.21 ±.01	0.035	28.6	4.75	7.5
0.18 ±.01	0.028	35.7	5.55	8.2
0.17 ±.01	0.021	48.8	5.90	7.2
0.14 ±.01	0.0170	58.8	7.15	63.
0.092±.003	0.0101	99.0	10.8	31.
0.067±.005	0.0089	112.	14.9	30.
0.073±.003	0.0078	128.	13.7	35.
0.052±.001	0.0070	143.	19.2	35.

[a] 1,2-Benzanthracene concentration was 1×10^{-3}M.

1,2-Benzanthracene Sensitized Quantum Yields
with Varying 1,3-Cyclohexadiene Concentrations

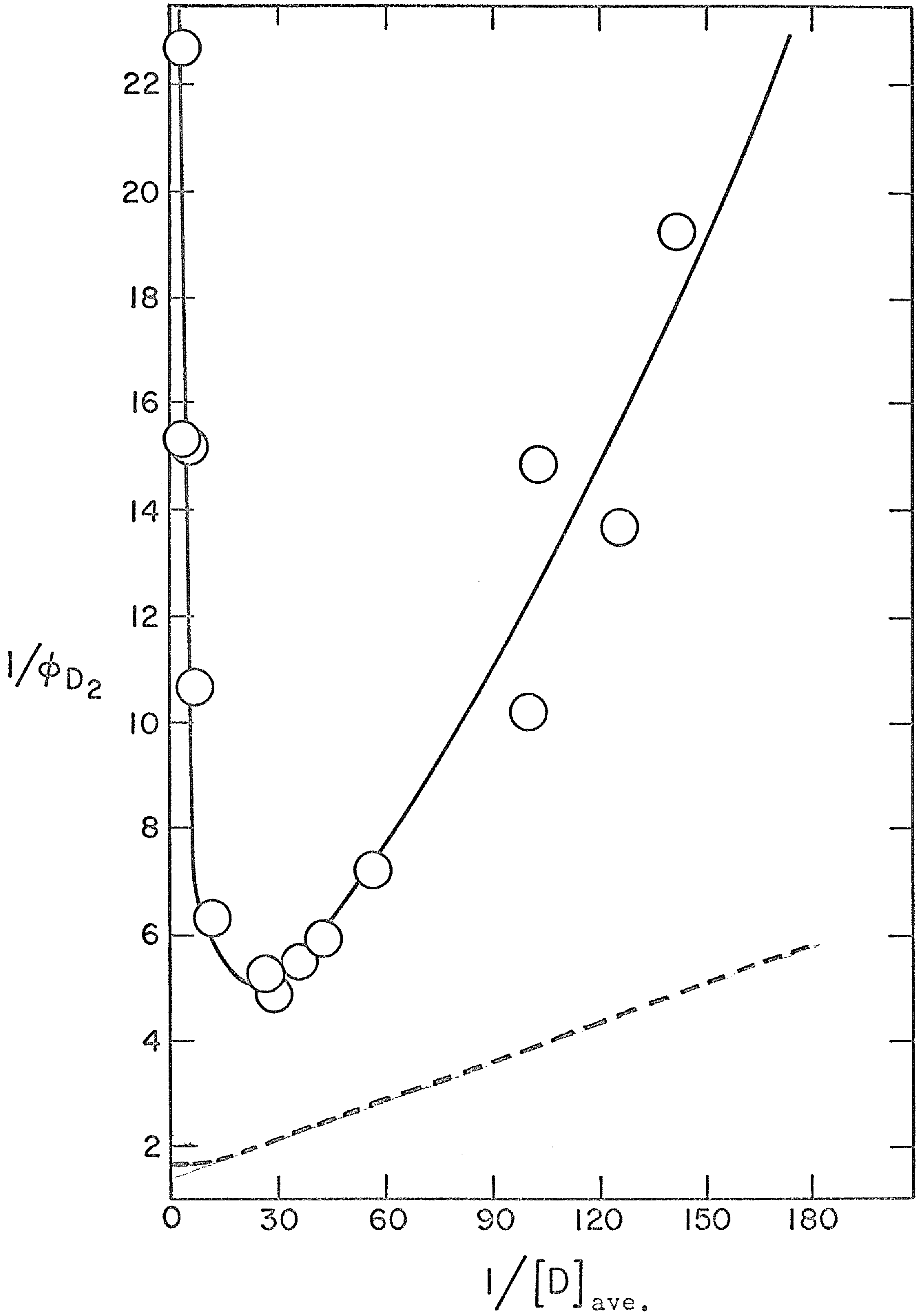


FIGURE VIII

$$S^1 + D \xrightarrow{k_q} S + D \qquad (36)$$

$$\phi_{f_o} = \frac{k_f}{k_f + k_{ic} + k_{d_s}} = \text{fluorescence quantum yield without quencher} \qquad (37)$$

$$\phi_f = k_f/(k_f + k_{ic} + k_{ds} + k_q\,[D]) = \text{fluorescence quantum yield with added quencher} \qquad (38)$$

$$\phi_{f_o}/\phi_f = 1 + k_q\,\tau_s\,[D] \qquad (39)$$

$$\tau_s = 1/(k_f + k_{ic} + k_{ds}) \qquad (40)$$

A plot of ϕ_{f_o}/ϕ_f is linear with diene concentration, as is predicted by equation 39 (see Figure IX). If the singlet lifetime is known, k_q can be determined. Table XVII shows the k_q's obtained for various sensitizers with 1,3-cyclohexadiene.

Since no chemistry is observed from the quenching process, (isomerization or dimerization of the diene) the excited states that are intermediates in usual photosensitized reactions are not involved. Quenching could be accomplished through a complex as pictured below.

$$Ar^* + D \longrightarrow (Ar^* \text{- - - -} D \longleftrightarrow Ar \text{- - - -} D^*) \qquad (41)$$

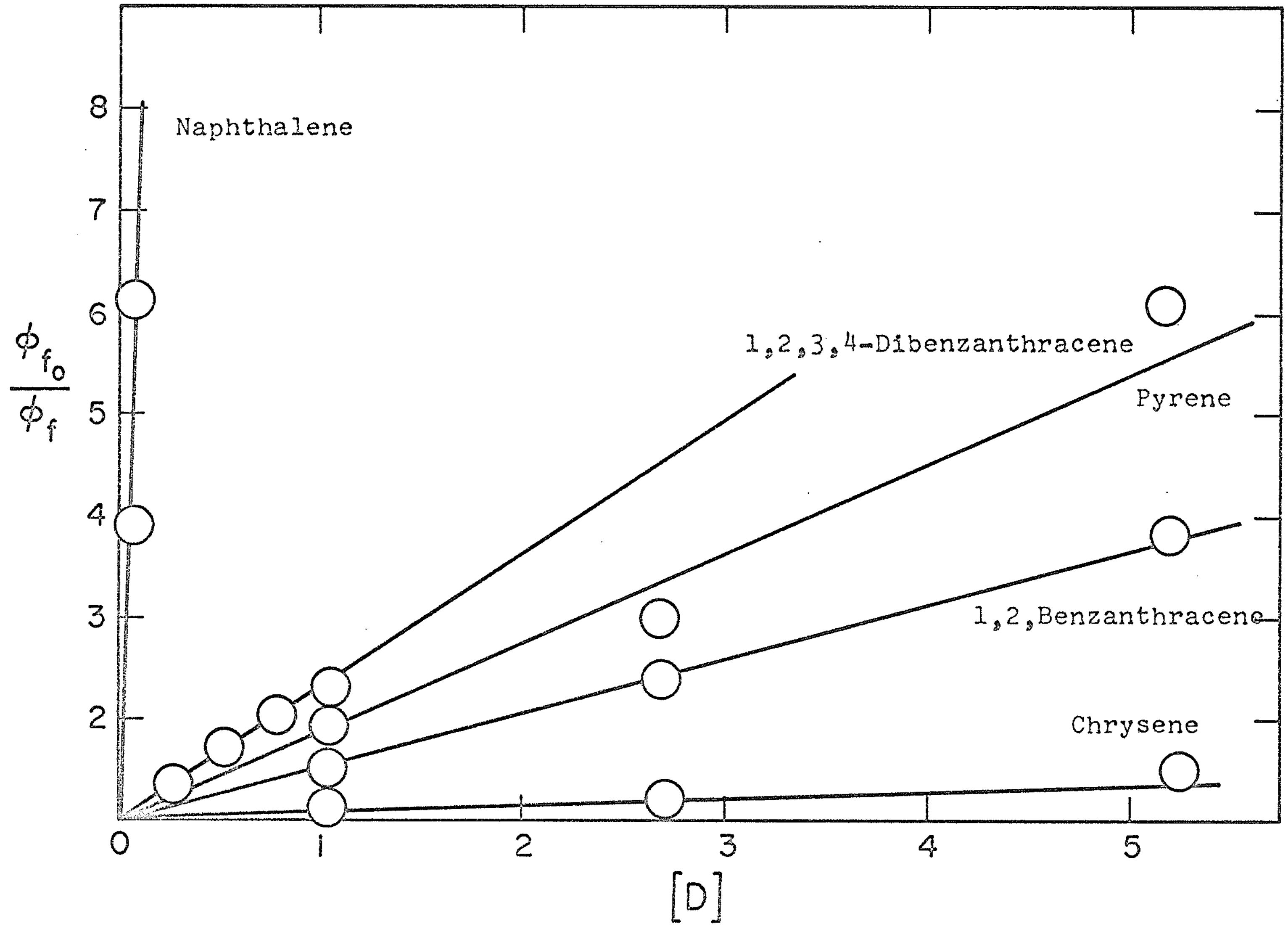


FIGURE IX Quenching of Fluorescence of Aromatic Hydrocarbons by 1,3-Cyclohexadiene

TABLE XVII

Quenching of Fluorescence by 1,3-Cyclohexadiene

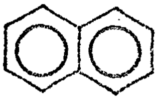
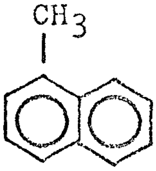
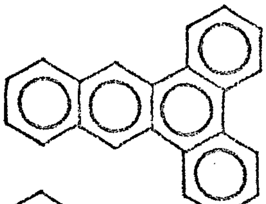
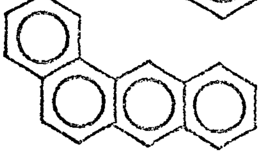
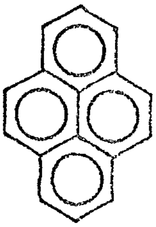
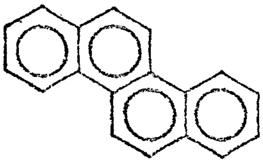
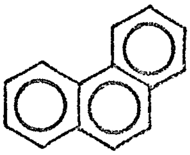
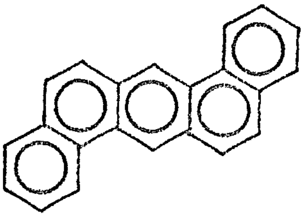
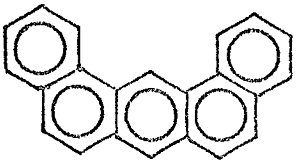
Sensitizer	$(I-S_1)$/eV.(62)	$\tau \times 10^9$ sec.[a]	$k_q \times 10^{-8}$ M.$^{-1}$ sec.$^{-1}$
	4.22	96	25[b]
	4.05	4.9	25[b]
		76	14
	4.31	38	4.6
	4.23	42	1.3
	4.21	445(63)	0.405
	4.38	49	0.3

TABLE XVII (cont'd).

Sensitizer	$(I-S_1)$/eV.(62)	τ x10^9 sec.[a]	k_qx10^{-8} $M.^{-1}$ $sec.^{-1}$
	4.51	63	no quenching
	4.66	20	no quenching
	4.54	78	no quenching

[a] See the experimental section (page 103) for discussion of singlet lifetime.

[b] These data were run in cyclohexane, (see reference 43). Other data were run in benzene.

Such a complex borrows from the diene the property of rapid nonradiative decay. Rates of nonradiative decay can be estimated to be about $10^{10} - 10^{11}$ sec. This complex may possess charge transfer character such as that proposed for aromatic hydrocarbon excimers (64). In this picture the frequency of emission of the excimer is related to other parameters by equation 42.

$$h\nu = (I - S_1) - E_A - \Delta \qquad (42)$$

In equation 42, I is the ionization potential of the electron donor, E_A is the electron affinity of the acceptor, Δ represents the other interaction terms and S_1 the singlet energy (62). In this view $(I-S_1)$ is the ionization potential of the excited state. It is interesting to note that aromatic hydrocarbons that have values of $(I - S_1)$ less than 4.36eV form excimers and those above 4.36eV do not form excimers in solution.

Since the electron affinities of dienes are not accurately known, an exact analogy can not be made. Values of $(I - S_1)$ for the aromatic hydrocarbons are reported in Table XVII. There is a correlation between these values and the tendency of these hydrocarbons to be quenched. If this is the case, the charge transfer complex would be formed between the excited states of the hydrocarbon and diene. Considering the molecular orbitals of the excited states of the diene and hydrocarbon, there are certain positions in which overlap is more favorable. Although there are some data concerning the steric requirements of the aromatic hydrocarbons and dimers (43), it is not sufficient to determine exactly the geometry of this complex.

The singlet quenching data are consistant with the quantum yields measured for high energy sensitizers. Of the high energy sensitizers, only chrysene showed this quenching effect, but due to the small quenching rate the quantum yields are not appreciably reduced. The fact that naphthalene is quenched efficiently explains the previously disturbing result that the dimerization of 1,3-cyclohexadiene could not be effectively sensitized by naphthalene.

With the available quenching data, the quantum yields can be adjusted to account for the quenching of singlets. Adjusting equation 30 for this effect we have

$$\frac{1}{\phi_{D_2}} = \frac{\phi_{fo}}{\phi_f} \frac{1}{\phi_{ic}} \alpha \beta \qquad (43)$$

This type of correction was first applied to 1-methylnaphthalene-1,3-cyclohexadiene (61). Here ϕ_{D_2} is calculated to be 0.028 and $\phi_{D_2} = 0.027$ is observed. Singer (65) has proposed singlet quenching to explain a similarly shaped curve for a different system. The above type of calculation has also been successful in explaining naphthalene sensitized *cis* ⟶ *trans* isomerizations of piperylenes (43).

Applying this technique to the 1,2-benzanthracene data, the dotted curve in Figure VIII is obtained. It can be seen that this does not account for the observation. This calculation assumes that k_q is the only energy wasting step involved and that $\phi_{ic} = 0.80$.

Since singlet quenching did not completely account for the decrease in quantum yield at high diene concentration, processes such as reversible energy transfer or reaction between diene or sensitizer were considered. It was found that sensitizer was consumed in the reaction. The effect of sensitizer and diene concentration on various quantum yields is shown in Table XVIII, Table XIX and Table XX and Figures X, XI, XII and XIII.

Examination of the data shows that, at constant diene concentration, the yield of dimers decreases as the sensitizer concentration increases and the quantum yield for sensitizer disappearance increases as the sensitizer concentration increases. (Table XVIII and XIX). At a constant initial sensitizer concentration both the quantum yields for dimer formation and sensitizer disappearance decrease with decreasing diene concentration. (Table XX). There are several possible explanations for

TABLE XVIII

Quantum Yields at Various 1,2-Benzanthracene

Concentrations [D] = 0.21

$[S]_I x10^3$	ϕ_{D_2}	$1/\phi_{D_2}$	ϕ_{-s}	$1/\phi_{-s}$	$1/[S]_I x10^{-2}$	%D used	%S used
1.92	0.36±.01	2.78				10.2	
1.92	0.37±.01	2.70	0.042	23.8	5.2	8.0	49
2.88	0.34±.01	3.06	0.048	20.8	3.47	9.5	50
4.80	0.20±.01	3.85	0.069	14.5	2.08	7.4	43
6.72	0.21±.01	4.75	0.057	17.5	1.49	5.9	25
8.64	0.18±.01	5.87	0.088	11.4	1.16	4.9	30

TABLE XIX

Quantum Yields at Various 1,2-Benzanthracene

Concentrations [D] = 0.021

$[S]_I \times 10^3$	ϕ_{D_2}	$1/\phi_{D_2}$	$1/[S]_I \times 10^{-2}$	%D used
0.878	0.17±.01	5.9	11.2	22
1.750	0.12±.01	8.3	5.72	14
2.634	0.10±.02	10.0	3.80	13
4.39	0.053±.005	18.8	2.28	7
6.05	0.0335±.001	29.8	1.65	4.5
7.80	0.0155±.001	64.5	1.28	2

TABLE XX[a]

Quantum Yields as a Function of 1,3-Cyclohexadiene Concentration

[D]	1/[D]	ϕ_{-s}	$1/\phi_{-s}$	ϕ_{D_2}	$1/\phi_{D_2}$	%D used	%S used
0.42	2.39	0.081	12.4	0.23	4.35	0.6	14.2
0.21	4.75	0.071	14.2	0.17	5.89	0.8	12.4
0.105	9.52	0.065	15.4	0.17	5.89	0.8	11.4
0.042	23.9	0.060	16.6	0.092	10.9	1.0	10.6
0.021	47.5	0.057	17.5	0.045	22.1	2.0	10.0

[a] $[S]_I = 2.9\text{x}10^{-3}$M.

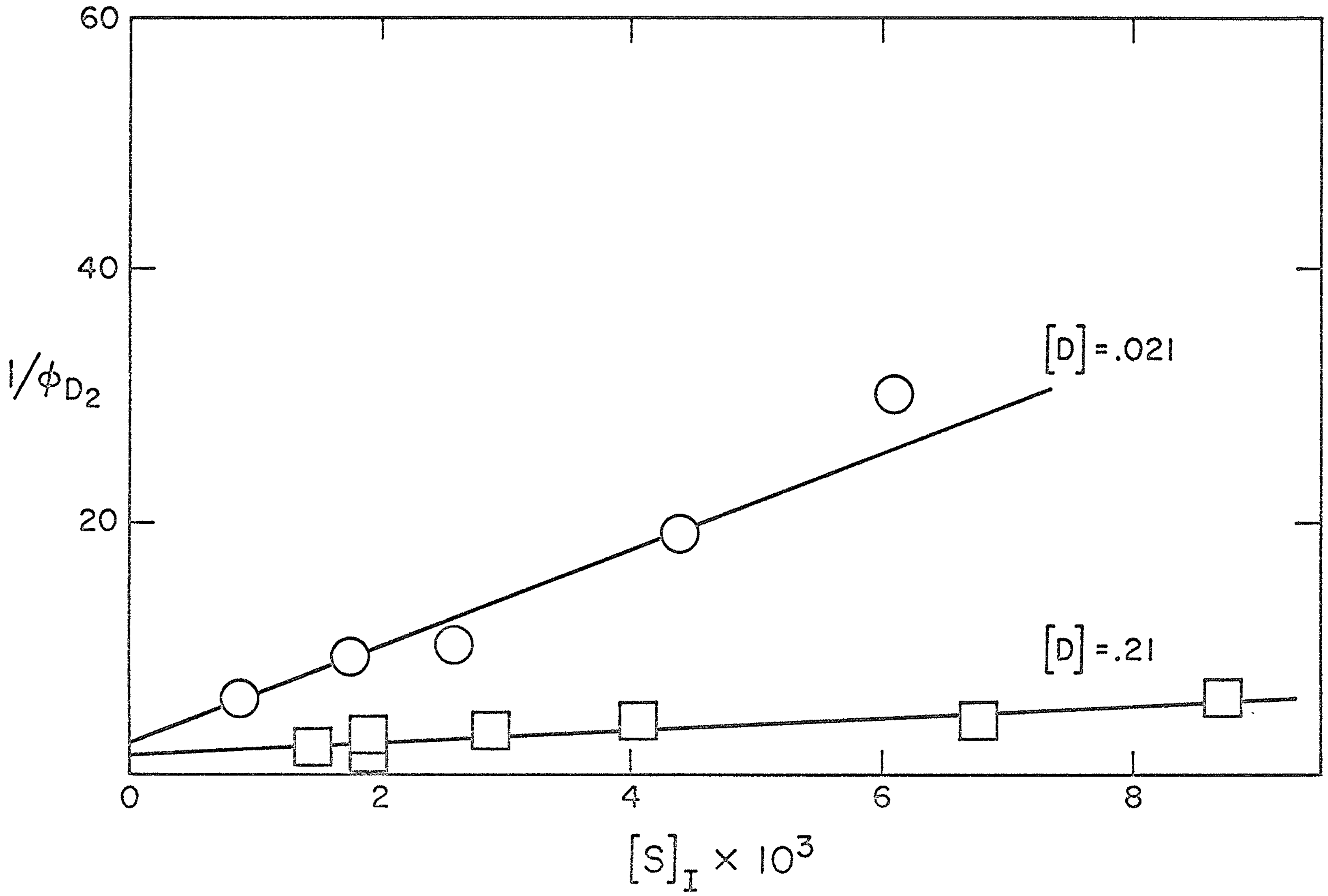


FIGURE X Effect of 1,2-Benzanthracene Concentration on the Quantum Yield for Dimerization

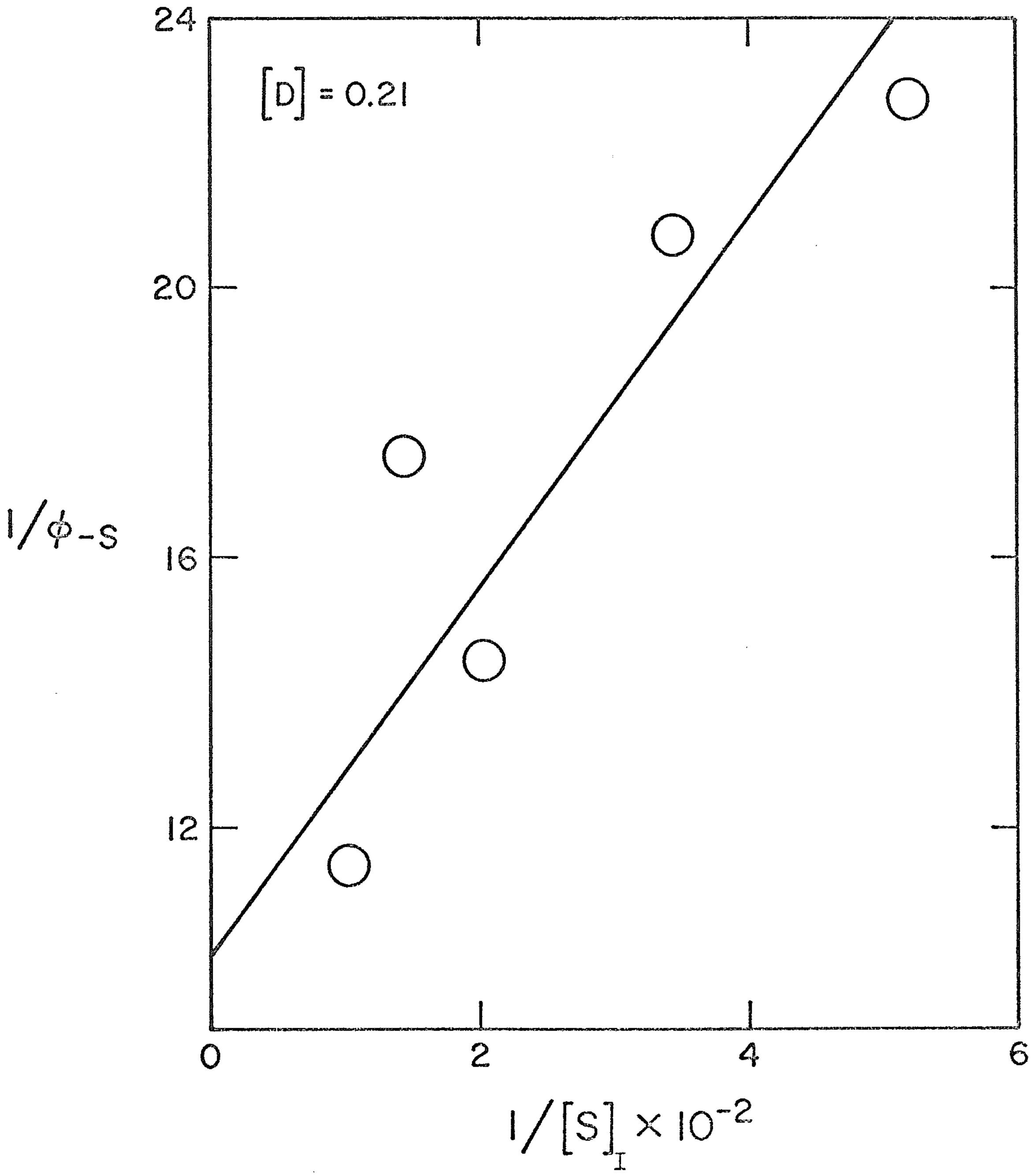


FIGURE XI Effect of 1,2-Benzanthracene Concentration on the Quantum Yield for 1,2-Benzanthracene Disappearance

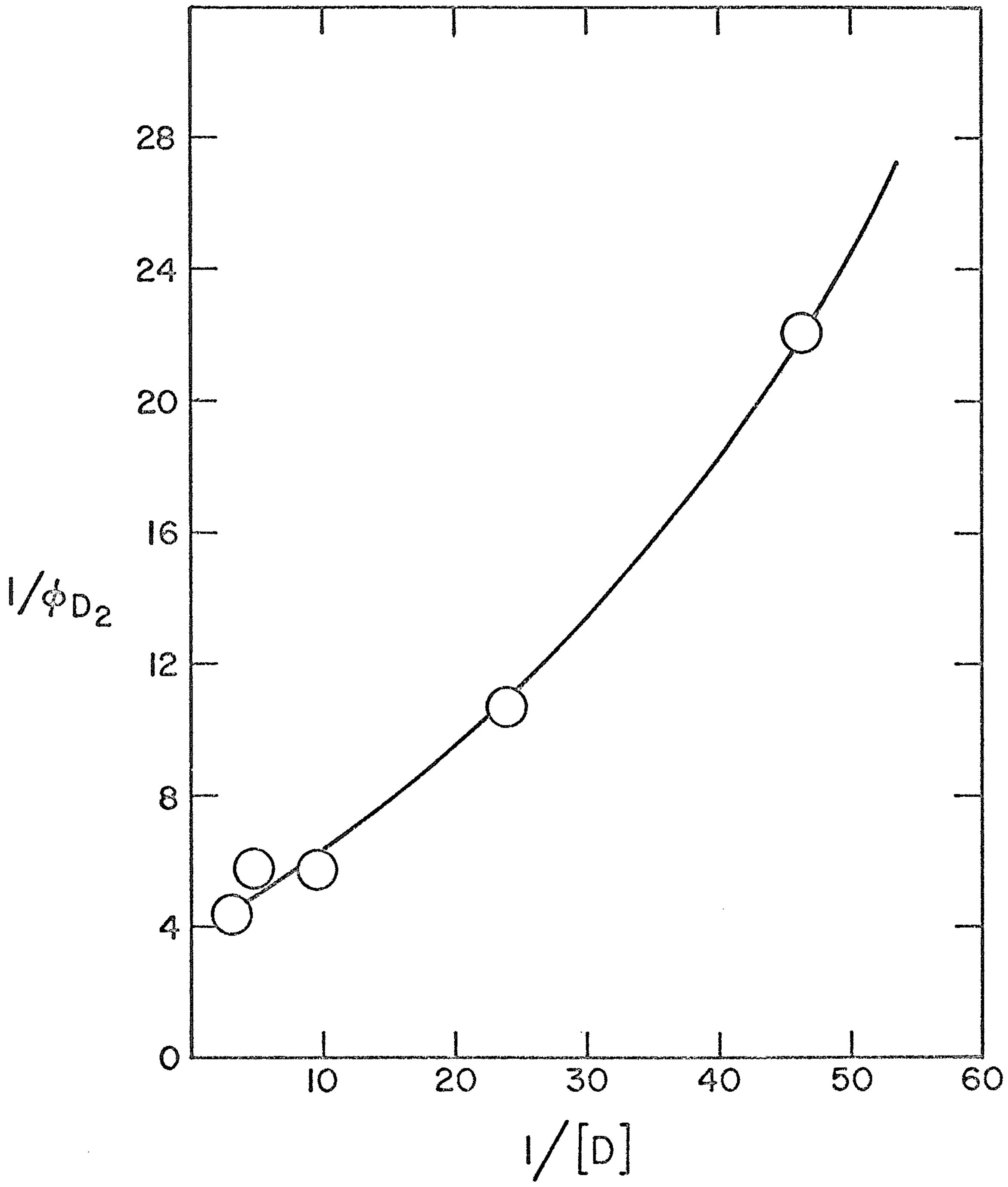


FIGURE XII Dependence of the Dimerization Quantum Yields on the 1,3-Cyclohexadiene Concentration

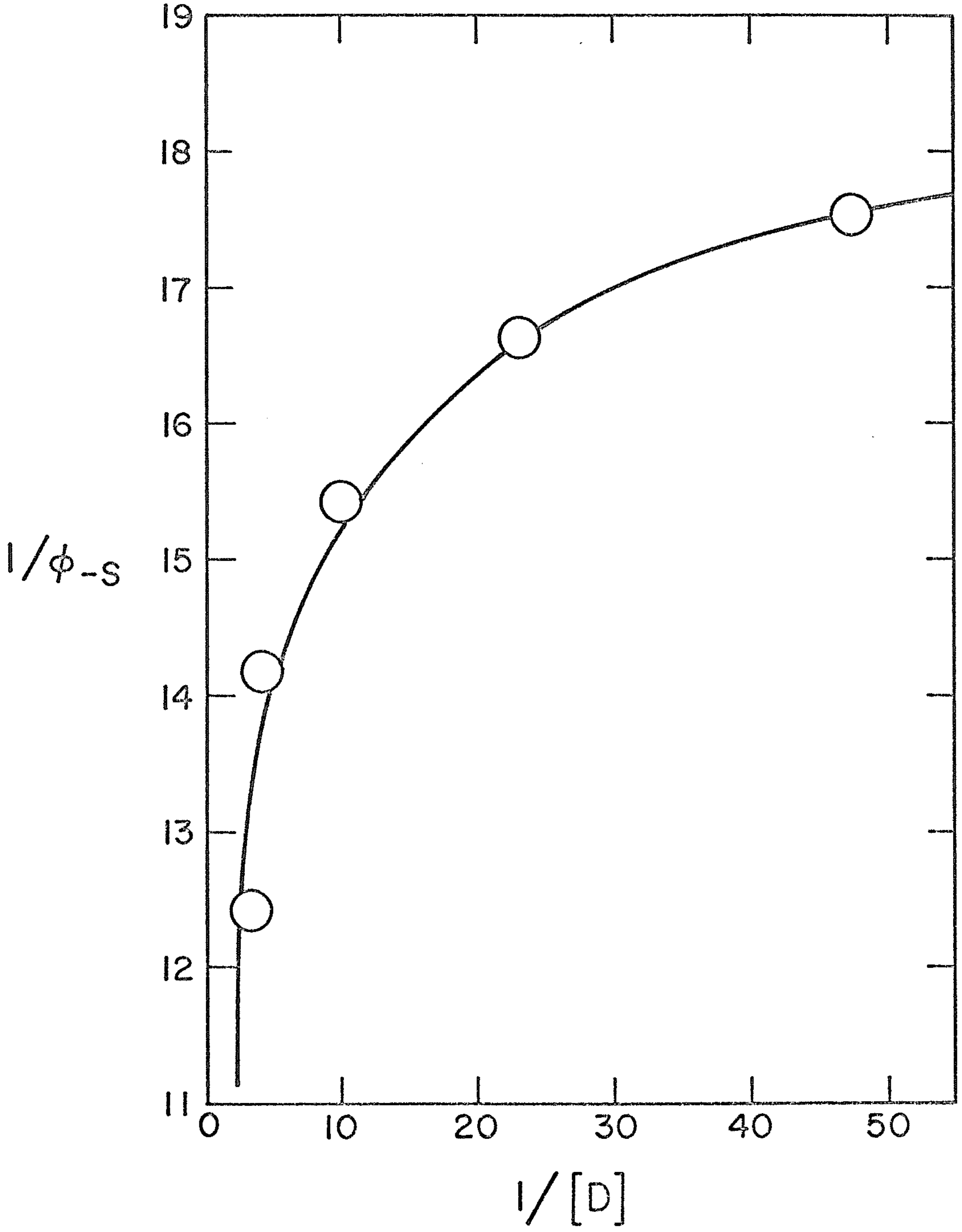


FIGURE XIII Dependence of the Quantum Yields for Sensitizer Disappearance on the 1,3-Cyclohexadiene Concentration the decrease in the yield of D^3 with increasing 1,2-benzanthracene concentration: self quenching of 1,2-benzanthracene singlets (equation 44), or triplets (equation 45); reversible energy transfer (equation 46) with rate of decay of $S^3(k_{dt})$ competing with the rate of decay of $D^3(k_d)$; reaction between diene and 1,2-benzanthracene to form a stable adduct (equation 47,48); and quenching of S^3 by impurities (equation (49).

$$S^1 + S \longrightarrow 2S \qquad (44)$$

$$S^3 + S \longrightarrow 2S \qquad (45)$$

$$S^3 + D \underset{k_{-Q}}{\overset{k_Q}{\rightleftharpoons}} D^3 + S \qquad (46)$$

$$S^{1,3} + D \xrightarrow{k_p} SD \qquad (47)$$

$$S + D^3 \xrightarrow{k_p} SD \qquad (48)$$

$$\text{Impurity} + S^3 \longrightarrow S + \text{Impurity} \qquad (49)$$

Self quenching of sensitizer (equation 45) triplets has been shown to be usually negligible in solution at the concentrations used in this work (9), so this energy wasting step can be neglected.

The reaction of 1,3-cyclohexadiene with 1,2-benzanthracene to form a stable adduct accounts for the disappearance of the sensitizer. The structure of this adduct is considered at a later part of this thesis, (see page 81). From the data available, it can not be rigorously determined whether the excited diene triplet (D^3) reacts with ground state sensitizer or if the excited sensitizer ($S^{1,3}$, singlet or triplet) reacts with ground state diene. Solutions of fluorenone(10^{-2}M.), 1,2-benzanthracene(10^{-3}M.) and 1,3-cyclohexadiene(0.5M.) were irradiated using a 1,2-benzanthracene filter so only light > 4000Å was absorbed by the solution. It was hoped that the fluorenone would produce diene triplets which would then add to the 1,2-benzanthracene. Only 1,2-benzanthracene was recovered. The failure of this experiment to produce the desired adduct does not absolutely rule out the possibility that diene triplets are involved in the formation of this adduct. In this experiment a large amount of 1,3-cyclohexadiene dimers were observed as well as a side reaction of diene with fluorenone. The amount of dimers formed in the presence of 1,2-benzanthracene was less than in the control. This seems to indicate that the adduct probably arises from reaction of excited sensitizer with ground state diene. Since the variation of ϕ_{-S} with diene concentration is small (Table XX) the adduct may be the result of singlet quenching.

The reaction of dienes with sensitizers should be further investigated to determine the generality of this adduct formation. The use of acyclic dienes as well as cyclic dienes and various sensitizers could lead to information concerning the mechanism of this adduct formation.

In the isolation of this 1,3-cyclohexadiene 1,2-benzanthracene adduct, another product was obtained, which is believed to be the 1,2-benzanthracene dimer (vide infra) (58,59).

Further inspection of the data in Table XVIII shows that the decrease in ϕ_{D_2} at higher 1,2-benzanthracene concentrations can not be accounted for by the increase in ϕ_{-S}. The leveling off of the quantum yield ϕ_{-S} at low diene concentration shows that the sensitizer is disappearing by steps other than adduct formation (Table XX). Considering these facts, a singlet self quenching step should be added to the mechanism (equations 49,50,51).

$$S^1 + S \underset{k_{DiM}}{\overset{k_{MDi}}{\rightleftharpoons}} S_2^1 \qquad (49)$$

$$S_2^1 \xrightarrow{k_{fDi}} 2S + h\nu' \qquad (50)$$

$$S_2^1 \xrightarrow{k_{S_2}} S_2 \qquad (51)$$

Birks (50) has studied the fluorescence and excimer formation of 1,2-benzanthracene by phase and modulation fluorometer measurements, and by pulsed light source measurements. A summary of Birks' data appears in Table XXI.

From Birks' data the formation of the 1,2-benzanthracene excimer at $3x10^{-3}$M. is 10 times slower than its dissociation. Therefore only a small amount of energy is lost by this path. At 10^{-2}M. 1,2-benzanthracene concentration, the rate of formation of the 1,2-benzanthracene excimer competes with the rate for its dissociation. Therefore, at high 1,2-benzanthracene concentration, loss of energy by excimer formation and decay becomes very important.

Reviewing the original data in Figure VIII in light of these complications, a considerable amount of sensitizer could have been consumed under the conditions of these original experiments. Therefore the low quantum yields obtained at high diene concentrations are now explainable.

The possibility of reversible energy transfer must still be considered (equation 46). A detailed discussion of reversible energy has been presented by Sandros and Bäckström (28,30). Sandros (30) has shown that k_Q

TABLE XXI

Rate Constants for the 1,2-Benzanthracene System (50)

$k_M = 2.2\mathrm{x}10^{-7}$ sec.$^{-1}$

$k_{Di} = 2.4\mathrm{x}10^{-7}$ sec.$^{-1}$

$\phi_{fM} = 0.19$

$\phi_{fDi} = 0.47$

$k_{fM} = k_M \phi_{fM}$

$k_{fDi} = k_{Di} \phi_{fDi}$

$k_{fM} = 0.42\mathrm{x}10^{7}$ sec.$^{-1}$

$k_{fDi} = 1.13\mathrm{x}10^{7}$ sec.$^{-1}$

$k_{MDi} = 2.85\mathrm{x}10^{9}$ M.$^{-1}$ sec.$^{-1}$

$k_{DiM} = 10.1\ \mathrm{x}10^{7}$ sec.$^{-1}$

k_M = monomer fluorescence and internal quenching

k_{Di} = excimer fluorescence and internal quenching

---

and k_{-Q} for exothermic energy transfer are related by equation 52. For endothermic energy transfer, the expression is valid in the reverse direction (equation 53).

$$k_{-Q} = k_Q \exp(-\Delta E_T/kT) \tag{52}$$

$$k_Q = k_{-Q} \exp(-\Delta E_T/kT) \tag{53}$$

In these equations ΔE_T is the difference in the triplet state energies of the donor and acceptor and k is Boltzman's constant. Application of the equation to the 1,2-benzanthracene data yields $k_{-Q} = 2\times10^{10}$ M.$^{-1}$ sec.$^{-1}$. This equation may not be valid in this case since 1,3-cyclohexadiene has a nonspectroscopic triplet state. The rate constants obtained by flash spectroscopy should be considered in light of possible reversible energy transfer. Without reversible energy transfer, analysis of the kinetic data yields two parameters with the following significance.

$$\alpha_f = k_{dt} + k_Q[D] + k_3[S] \tag{54}$$

$$\beta_f = \frac{1}{\epsilon^*_1}(k_2 - k_3) \tag{55}$$

For an explanation of the origin of these terms see the experimental section (see page 99).

The following mechanism is assumed considering the reversible energy transfer in the analysis of the values obtained by flash spectroscopy (30).

$$S^* \xrightarrow{k_{dt}} S \qquad (56)$$

$$D^* \xrightarrow{k_d} D \qquad (57)$$

$$D^* + D \xrightarrow{k_r} D_2 \qquad (58)$$

$$S^* + D^* \underset{k_{-Q}}{\overset{k_Q}{\rightleftharpoons}} S + D^* \qquad (59)$$

$$D^* + D^* \xrightarrow{k_{2Q}} D^* + D \qquad (60)$$

$$S^* + S^* \xrightarrow{k_{2S}} S^* + S \qquad (61)$$

$$S^* + D^* \xrightarrow{k_{2SD}} S^* + D \qquad (62)$$

$$S^* + D^* \xrightarrow{k_{2DS}} S + D^* \qquad (63)$$

The decay of $[S^*]$ and $[D^*]$ with respect to time is given by equations 64 and 65.

$$-\frac{d[S^*]}{dt} = k_{dt}[S^*] + k_Q[S^*][D] - k_{-Q}[S][D^*] + k_{2S}[S^*]^2 + k_{2QS}[S^*][D^*] \qquad (64)$$

$$
\begin{aligned}
-\frac{d[D^*]}{dt} = {} & k_d[D^*] + k_{-Q}[S][D^*] - k_Q[D][S^*] \\
& + k_{2Q}[D^*]^2 + k_{2SQ}[D^*][S^*] + k_r[D][D^*]
\end{aligned}
\tag{65}
$$

If [D*] and [S*] are assumed to reach steady state concentrations, then

$$
[S^*] = \frac{k_{-Q}[D^*][S]}{k_Q[D] + k_{dt}} \tag{66}
$$

and

$$
[D^*] = \frac{k_Q[S^*][D]}{k_{-Q}[S] + k_d + k_r[D]} \tag{67}
$$

ignoring second order terms. Sandros and Bäckström (28) have pointed out that the steady state assumption for [D*] is valid for the quencher when k_d is greater than k_{dt}. Substitution of equation 67 into equation 64 yields:

$$
\begin{aligned}
-\frac{d[S^*]}{dt} = {} & k_{dt}[S^*] + k_Q[D][S^*] - k_{-Q}[S]\,\frac{k_Q[S^*][D]}{k_{-Q}[S] + k_d + k[D]} \\
& + k_{2S}[S^*]^2 + k_{2QS}[S^*]\,\frac{k_Q[S^*][D]}{k_{-Q}[S] + k_d + k_r[D]}
\end{aligned}
\tag{68}
$$

According to the derivation in the experimental section (page 99), the parameters α_f and β_f have the following meaning:

$$\alpha_f = k_{dt} + \frac{k_Q[D]\ (k_d + k_r\ [D])}{k_{-Q}[S] + k_d + k_r[D]} \qquad (69)$$

$$\beta_f = \frac{1}{*1} \quad k_{2S} + \frac{k_{2SQ}k_Q[D]}{k_{-Q}[S] + k_d + k_r[D]} \qquad (70)$$

Therefore the previously determined k_Q's are actually a lower limit of the true value. The ratio $(k_d + k_r[D])/(k_{-Q}[S] + k_d + k_r[D])$ is always less than, or equal to unity, so the larger $(k_{-Q}[S] + k_d + k_r[D])$ becomes, the greater the error in k_Q. Since a lower limit on k_Q is obtained, the postulation of nonvertical excitation is still valid. Equations 69 and 70 can be simplified since $k_d > k_r[D]$. Therefore reversible energy transfer becomes important when $k_{-Q}[S]$ is of the same magnitude or greater than k_d.

The importance of k_{-Q} could be determined experimentally by studying the effect of sensitizer concentration on the rate constants obtained by flash spectroscopy. It may be recalled that reversible energy transfer requires a sensitizer concentration dependence (see equation 69). This experiment may be difficult due to absorption problems.

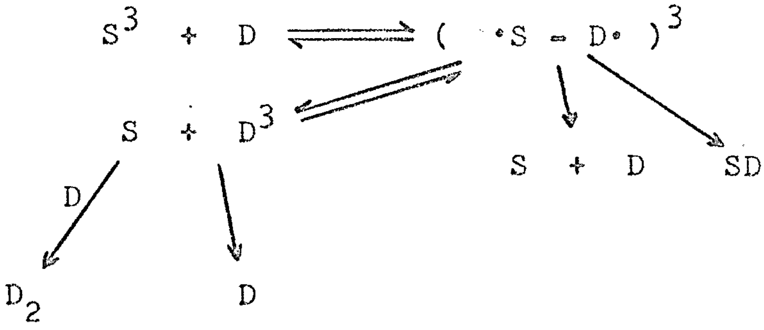
In conclusion it should be mentioned that 0.1% impurity in the solvent, sensitizer or diene, which can quench at a diffusion controlled rate can significantly reduce the quantum yield for dimerization. The data in Table XIX and Table XX are not consistant with each other. This discrepancy is attributed to impurities which may not be consistant from run to run.

Due to the complexity of this system, a kinetic expression for the desired quantum yields has not been obtained. This system could be simplified by using a sensitizer whose singlet is of lower energy than the 1,2-benzanthracene singlet, and whose triplet is higher than the 1,3-cyclohexadiene triplet. Fluorenone possesses these properties but it has been shown that sensitizer reacts with diene. Other likely candidates are anthraquinone or naphthaquinone.

The data in Table XVIII, Birks' data (50), and the known rate constants seem to indicate that most of the decrease in ϕ_{D_2} can be attributed to sensitizer-sensitizer interactions.

Addition Elimination Mechanism.

Schenck (66) has been advocating a mechanism in which the sensitizer forms a bond with the acceptor during the energy transfer process. If the 1,2-benzanthracene 1,3-cyclohexadiene system is considered in the light of a Schenck complex, the following mechanism would hold.



(71)

Although this mechanism seems attractive to explain the formation of the adduct, excitation transfer is preferred. There is no evidence against the Schenck mechanism at this time.

Temperature Dependence on the 1,2-Benzanthracene Sensitized Dimerization.

At the outset of this work it was believed that a temperature dependence on k_Q would be reflected in the quantum yields for dimerization. Preliminary results of this type of experiment appear in Table XXII. These experiments were performed before the later discovered complications had been observed, therefore data on the disappearance of 1,2-benzanthracene were not obtained. In general the conversion of diene was small, but without knowledge of the fate of the sensitizer not much quantitative information can be obtained from these data.

It was originally thought that α (equation 31) would reflect the temperature dependence of k_Q, but since α is approximately unity, an increase in k_Q would not be detected by this function. A temperature effect was sought in this manner rather than by flash spectroscopic methods, since quantum yields can be measured more accurately.

Comparison of the data in Table XXII to that in Table XVI shows that the dimerization seems to become more efficient at elevated temperatures. The fact that ϕ_{D_2} measured with benzophenone is constant indicates that no significant temperature effect is associated with the reaction between diene triplets and diene ground state molecules. The increase in the quantum yields could be explained if there were a large effect of variation in temperature on the singlet quenching process. This was shown not to be the case. Samples of solutions containing 1,2-benzanthracene and the diene were warmed to about 60°, rapidly placed in the fluorometer and

TABLE XXII

1,2-Benzanthracene Quantum Yields at Various Temperatures

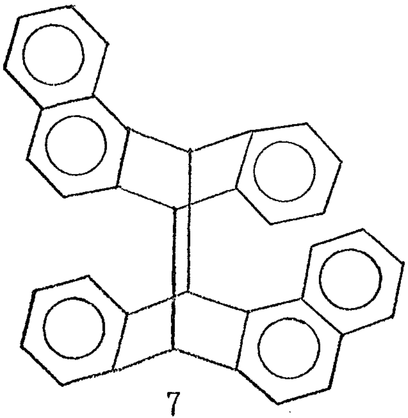
[D]		ϕ_{D_2}	
	42°	51°	59°
0.61	0.14 ±.01	0.25 ±.01	
0.50			0.50±.03
0.31			0.81±.03
0.20	0.32 ±.01	0.53 ±.01	0.83±.03
0.095		0.53 ±.01	0.89±.01
0.087	0.55 ±.01		
0.040	0.41 ±.01	0.43 ±.01	
0.020	0.24 ±.01	0.29 ±.01	0.40±.02
0.012	0.25 ±.01	0.22 ±.02	
0.008	0.074±.001	0.085±.005	

the fluorescence spectrum monitored as the solution cooled. There was no detectable change in the intensity of emission, indicating that there is no significant change in the singlet quenching rate with changes of temperature.

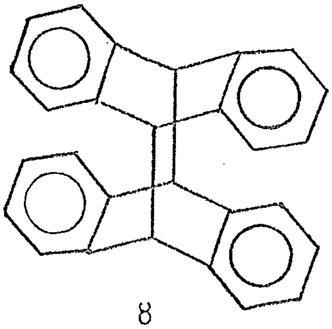
Due to the uncertainties in these data and the complexity of the kinetics, it is not possible to determine which step has been activated.

Identification of 1,3-Cyclohexadiene 1,2-Benzanthracene Photoadduct.

As previously shown in the irradiation of benzene solution of 1,3-cyclohexadiene 1,2-benzanthracene, the benzanthracene disappeared with a measurable quantum yield. Preliminary experiments conducted under quantum yield conditions ([S] = $3\text{x}10^{-3}$M., [D] = 0.21M.) showed that after prolonged irradiation no 1,2-benzanthracene fluorescence could be detected and a new fluorescence appeared. Enough product was isolated by preparative thin layer chromatography to obtain nmr and ultraviolet spectra. To obtain more of this product, 1,3-cyclohexadiene saturated with 1,2-benzanthracene was irradiated. During irradiation a product separated from solution. This product was assigned the structure of the 1,2-benzanthracene dimer <u>7</u>, on the basis of insolubility, melting point and reports that 1,2-benzanthracene, (58,59) like anthracene (67) dimerizes, 8. The dimer is probably a mixture of the isomers.

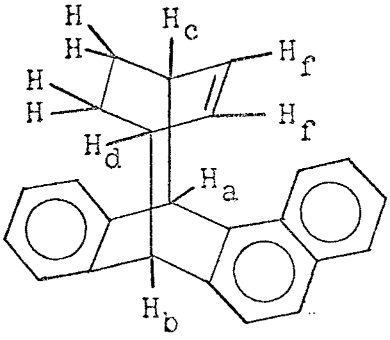


7



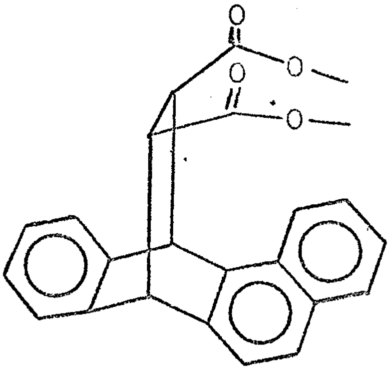
8

Evaporation of the solvent and preparative TLC of the remaining oil yielded hydrocarbon 9. Hydrocarbon 9 was assigned the structure of a 1,4 adduct on the basis of the ultraviolet and nmr spectra. The ultraviolet



9

spectra of hydrocarbon 9, naphthalene, 1,2-benzanthracene and the dimethyl-ester prepared from the maleic anhydride 1,2-benzanthracene Diels-Alder adduct 10 appear in Figure XIV. Adduct 10 is probably a mixture of both



10

cis-isomers. It can be seen that both hydrocarbons 9 and 10 have the first absorption band characteristic of the naphthalene nucleus. This transition is red shifted from unsubstituted naphthalene which is expected.(68). The ultraviolet spectrum shows that the 1,2-benzanthracene nucleus is destroyed and if an anthracene or phenanthrene nucleus remained, the first transition would be at longer wavelengths.

The nmr spectrum appears in Figure XV. The ten aromatic protons appear between 6.7 and 8.4ppm. The multiplet centered at 5.45 ppm is assigned to the two non-equivalent vinyl protons. The bridgehead protons H_a and H_b are assigned to the two doublets at 4.2 and

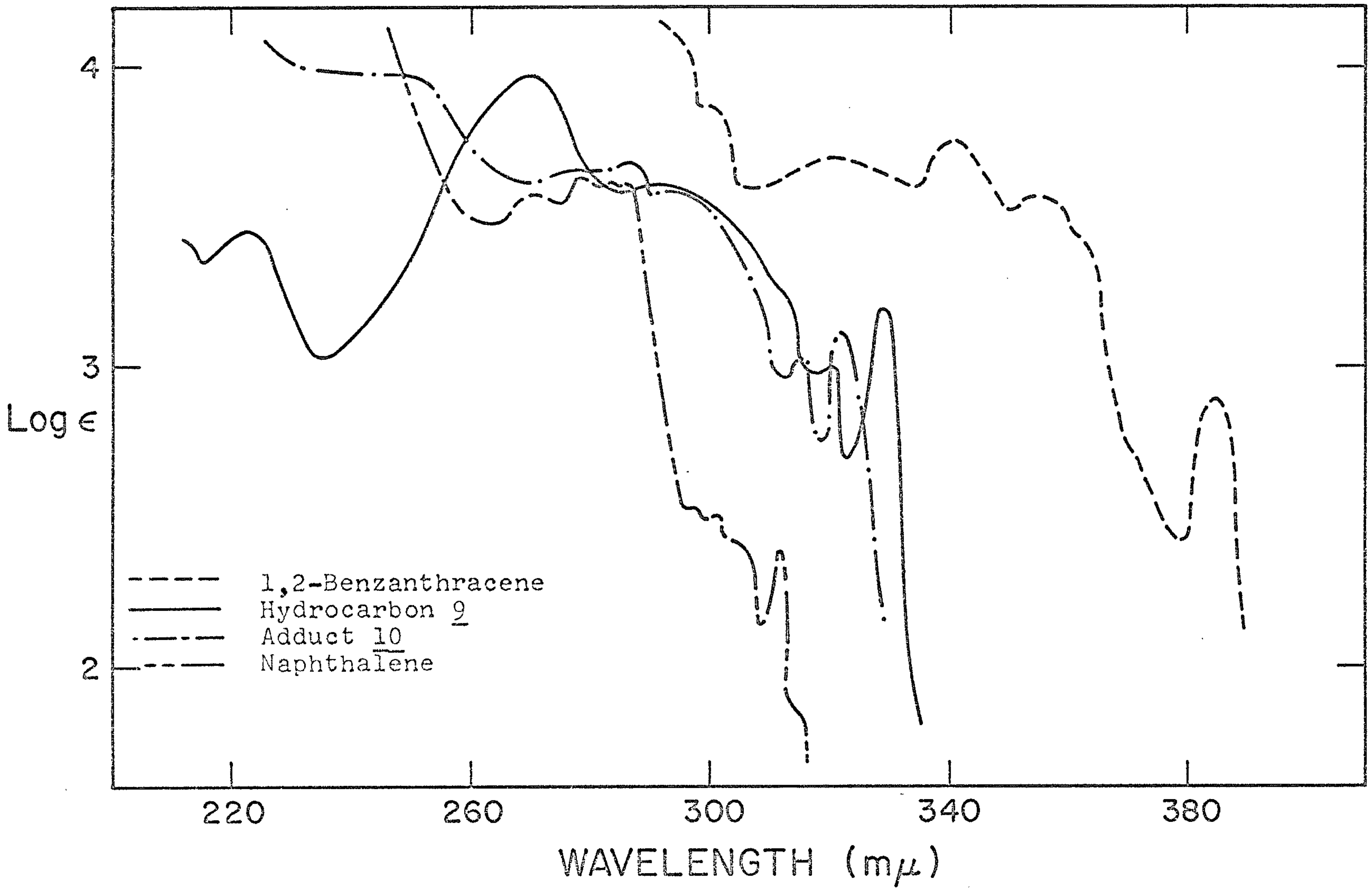


FIGURE XIV Ultraviolet Spectra

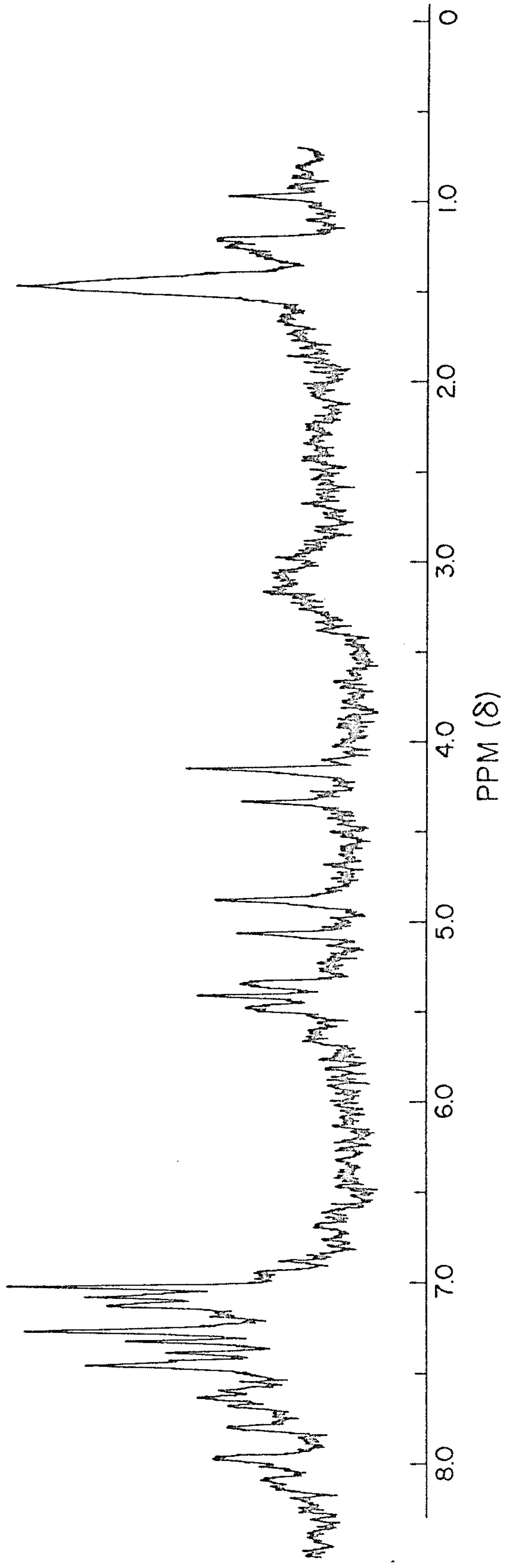


FIGURE XV Nuclear Magnetic Resonance Spectrum of Hydrocarbon 9

5.0 ppm. The bridgehead protons H_c and H_d are coupled to the aliphatic protons H_e, the vinyl protons and the bridgehead H_a, H_b. Therefore they should present a complicated splitting pattern. The broad peak at 3.1 ppm is assigned to these protons. The aliphatic protons appear at 1.5 ppm. Other peaks are impurities.

The protons were decoupled on a Varian HA-100 spectrometer. Irradiation at 3.1 ppm collapsed the doublet at 4.2 ppm to a singlet, while irradiation at 3.0 ppm collapsed the doublet at 5.0 ppm to a singlet.

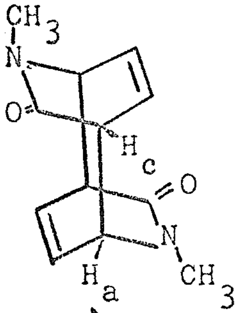
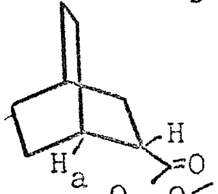
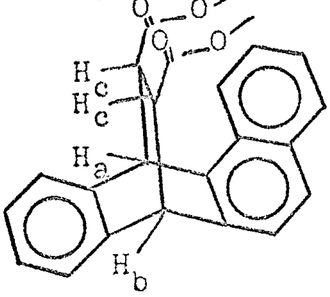
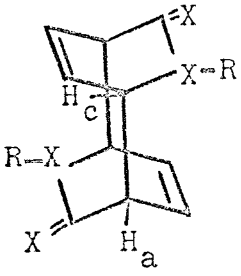
Irradiation at both of these frequencies collapsed the multiplet at 5.45 ppm. The coupling constant for the bridgehead protons was found to be very large, $J_{ac} = J_{bd} =$ 11 cps. Reference to the Karplus curve shows that for dihedral angles of 0° the coupling constant is of the order of 10 - 11 cps. (70).

Several examples of 1,4 adducts with their coupling constants are shown in Table XXIII.

Compound 9 apparently undergoes a retro Diels-Alder in the mass spectrometer since no parent peak m/e = 308 could be detected at 20 eV. Only mass ions, m/e = 228, for 1,2-benzanthracene were detected. Analysis of the cracking pattern in the m/e = 80 range (1,3-cyclohexadiene m/e = 80) shows ratios inconsistant with

TABLE XXIII

Coupling Constants of 1,4 - Adducts

Compound	δ(ppm)		J_{ac}/cps	Reference
	$H_{a,b}$	H_c		
9	4.2,5.0	3.2	11	This work
	3.70 multiplet		10	71
	3.0			72
	5.5,4.9	3.3	1.5-2	72
			9.5-10	73

that of pure benzanthracene. It was therefore concluded that the spectrum of hydrocarbon 9 was a mixture of diene and benzanthracene. A sample of 9 from the same source gave an excellent carbon hydrogen analysis for the structure 9.

There is no real proof of the position of the double bond. It is assigned in 9 on the basis of maximum accumulation of unsaturated centers (74).

CONCLUSION

In conclusion, the complexity of the 1,3-cyclohexadiene 1,2-benzanthracene system has hindered our attempts to solve the original problem. However, the data obtained with high energy sensitizers are consistant with the proposed mechanism. With low energy sensitization several additional steps complicate the kinetics. Although destruction of excited singlet states by a quenching mechanism can be compensated for, adduct formation, reversible energy transfer and sensitizer-sensitizer interactions must also be considered. There are insufficient data to determine if the temperature effect on the 1,2-benzanthracene sensitization is real. It should also be pointed out that with low energy sensitizers 0.1% impurities can compete with energy transfer. In spite of these complications the existence of a nonvertical 1,3-cyclohexadiene triplet is confirmed, and the apparently low quantum yields obtained with low energy sensitizers are not due to the slow rate of energy transfer, but other competing reactions.

The complications that have frustrated, at least in part, the original objective of the study, have led to the use of an unusually large number of the tools available for study of photochemical mechanisms. Coordination of a variety of experimental methods to form a methodology, may well be the most useful product of the study of an unexpectedly complex system. In addition, we have been rewarded by the discovery of a new reaction, the photocyclic addition of 1,3-cyclohexadiene to 1,2-benzanthracene.

EXPERIMENTAL

Purification of Sensitizers.

2-Acetonaphthone (Matheson, Coleman, and Bell) was recrystallized several times from petroleum ether (60-70° b.p.) and zone refined by Dr. W. G. Herkstroeter.

3-Acetylpyrene was prepared by the method of Vollmann (75). Purification consisted of recrystallization from methanol, treatment with Norite and sublimation. m.p. 89° (lit. 90°). m/e = 244.

Acridine (Eastman, Practical Grade) was chromatographed on aluminum oxide and sublimed.

Anthracene (Matheson, Coleman, and Bell, Fluorescent Grade) was recrystallized from a benzene ethanol mixture.

1,2-Benzanthracene (Eastman, White Label) was chromatographed several times on silica gel.

Benzophenone (Matheson, Coleman, and Bell). Zone refined benzophenone was obtained from Dr. W. G. Herkstroeter. Benzophenone purified by this method gave identical results to that purified by recrystallization from petroleum ether (60-70° b.p.).

3,4-Benzpyrene (Eastman, White Label) was recrystallized from a mixture of benzene and methanol.

Chrysene (Matheson, Coleman, and Bell) was recrystallized from ethanol.

p-Diacetylbenzene (Eastman, White Label) was sublimed before use.

1,2,3,4-Dibenzanthracene (Aldrich, Research Grade) was used as received.

1,2,5,6-Dibenzanthracene (Eastman, White Label) was chromatographed on silica gel and sublimed.

1,2,7,8-Dibenzanthracene (Aldrich, Research Grade) was used as received.

9,10-Dibromoanthracene was received from Dr. D. H. Valentine and recrystallized from carbontetrachloride.

3,4,9,10-Dibenzpyrene (Koch Light) was chromatographed on aluminum oxide.

Naphthalene (Matheson, Coleman, and Bell) was recrystallized and zone refined by Dr. W. G. Herkstroeter.

1-Naphthyl phenyl ketone was obtained from Dr. C. D. DeBoer.

Phenanthrene (J. Hinton, Ph.D., Valparaiso, Florida) was used as received.

Pyrene was obtained from Dr. W. G. Herkstroeter.

Purification of Substrates.

Azulene (Aldrich Research Grade) was sublimed twice before use.

trans-1,2-Diphenylpropene was obtained from Dr. D. H. Hunter.

trans-Stilbene was obtained from Dr. D. H. Valentine.

Purification of 1,3-Cyclohexadiene.

1,3-Cyclohexadiene (Aldrich Chemicals Co.) was purified by two methods. The diene was washed with sodium bisulfite solution, dried and distilled through a spinning-band column, or it was refluxed over lithium aluminum hydride and distilled through a spinning-band column. The freshly distilled diene was degassed in a manifold using three freeze-thaw cycles and sealed. The manifold was designed so that quanities of diene could be bulb-to-bulb distilled into small ampules prior to use. The manifold was stored at 0° when not in use. Vapor Phase Chromatographic (VPC) analysis of the diene showed trace amounts of benzene and 0.5-1.5% of cyclohexene depending on the run. No other impurities were detected. A Loenco Model 15B flame ionization detector chromatograph equipped with a 6-foot XE-60 column was used for this analysis.

Purification of Benzene.

Benzene (Matheson, Coleman, and Bell) was stirred over portions of sulfuric acid until the acid layer was not discolored. It was then washed with water, dried over potassium hydroxide pellets, washed with water again and dried over magnesium sulfate. Finally it was distilled from phosphorous pentoxide through a 3-foot column filled with glass helices.

Quantum Yields.

The 1,3-cyclohexadiene was bulb-to-bulb distilled in the manifold prior to use. The desired amount of the diene was added to benzene solutions of the appropriate sensitizer and a weighed amount of hexadecane. Hexadecane was used as an internal standard. The concentration of the sensitizer was such that all of the light was absorbed throughout the experiment. The solutions containing high energy sensitizers were transferred by a constant delivery syringe, into Pyrex culture tubes (13 x 100 mm.), which had a constriction to facilitate sealing. These tubes were degassed using three freeze-pump-thaw cycles to a vacuum between 2 and 5 x 10^{-4} mm. Hg. For the measurement of quantum yields using low energy sensitizers, tubes possessing grease traps and standard taper joints were substituted for the culture tubes. These tubes were degassed on a vacuum line equipped with an oil diffusion pump capable of obtaining a vacuum of 10^{-7} mm. Hg. Two freeze-pump-thaw cycles were performed without the diffusion pump in operation and three cycles using the diffusion pump. All tubes were protected from stray light at all times.

The tubes for the azulene quenching experiments were prepared in the same manner except that 0.1M. benzophenone was used instead of 0.05M. This insured that 99% of the light was absorbed by the benzophenone.

Irradiation of Samples.

All quantum yield tubes were irradiated in the ("merry-go-round") apparatus (35) to insure equal irradiation of all the samples. This apparatus can accommodate several filter systems and a shutter system enabling accurate irradiation times. The light source in the "merry-go-round" was a Hanovia L679A450-W medium pressure mercury lamp. The "merry-go-round" apparatus was operated in a constant temperature bath which could be thermostated to within one degree.

Filters.

a) 3660Å Filter. Corning 7-37 and 0-52 glass filters which fit into the "merry-go-round" were used to isolate the group of mercury lines centered around 3660Å. This filter transmitted about 20% of the incident light with a 100Å band width (33).

b) 3130Å Filter. A 2.62×10^{-3}M. solution of potassium chromate in 1% sodium carbonate was used to isolate the 3130Å line. This solution in a cylindrical filter-cell, having a 0.6 cm. path length, had the properties shown in Table XXIV.

TABLE XXIV

Properties of 3130Å Filter

λ Å	Absorbance
3035	0.966
3130	0.402
3341	2.11
3660	> 2.
4000	> 2.
4358	0.801

A pyrex sleeve was used around the lamp to filter the light below 3000Å. To enable this filter to be used with potassium ferrioxalate actinometry a 1.68M. Cobalt sulfate (1 cm. path length) was placed in a second cylindrical compartment of the filter cell. This absorbed wavelengths above 4000Å.

Actinometry.

Several methods of actinometry were used. The first consisted of measuring numbers relative to the benzophenone sensitized dimerization of 1,3-cyclohexadiene. From the knowledge of k_d/k_r for the diene reaction and the average diene concentration, the absolute quantum yield could be calculated. This method was found to be satisfactory for reactions which require long irradiation time.

In several benzophenone sensitized experiments, trans-1,2-diphenylpropene (ϕ = 0.55) (7) and trans-stilbene (ϕ = 0.55) (32) were used as actinometers.

The most widely used actinometer in this work was potassium ferrioxalate. The procedure of Hatchard and Parker was used (76) with slight modification. This modification was in the preparation of the potassium ferrioxalate solution. Three ml. of a stock 0.2M. ferric alum solution and 3 ml. of a stock 0.2M. potassium oxalate solution were diluted to 100 ml. with a 0.1*N* sulfuric acid. Four ml. of this solution were irradiated for three minutes. Aliquots of the irradiated solution were mixed with phenanthroline to complex the Fe^{+2} formed and analyzed spectrophotometrically at 510mμ. The quantum yield for the potassium ferrioxalate was taken to be 1.21 at 3660Å and 1.24 at 3130Å (76). The extinction coefficient for the complex was measured as 1.103×10^4.

Analysis.

All analyses were done on a Loenco Model 15B or Model 70 flame ionization detector VPC. Cyclohexadiene dimers and hexadecane were separated on a 6-foot 10% Fluorosilicone column or a column containing 2 feet of 10% DEGS, 2 feet of 10% silicone grease and 2 feet of silicone gum rubber.

trans-Stilbene and *trans*-1,2-diphenyl propene were analyzed on a 6-foot 10% Apiezon J Column.

The ratio of the dimers was determined on a 150 foot Apiezon J Golay column. This column cleanly separated the four isomers.

Preparation of 1,3-Cyclohexadiene Dimers.

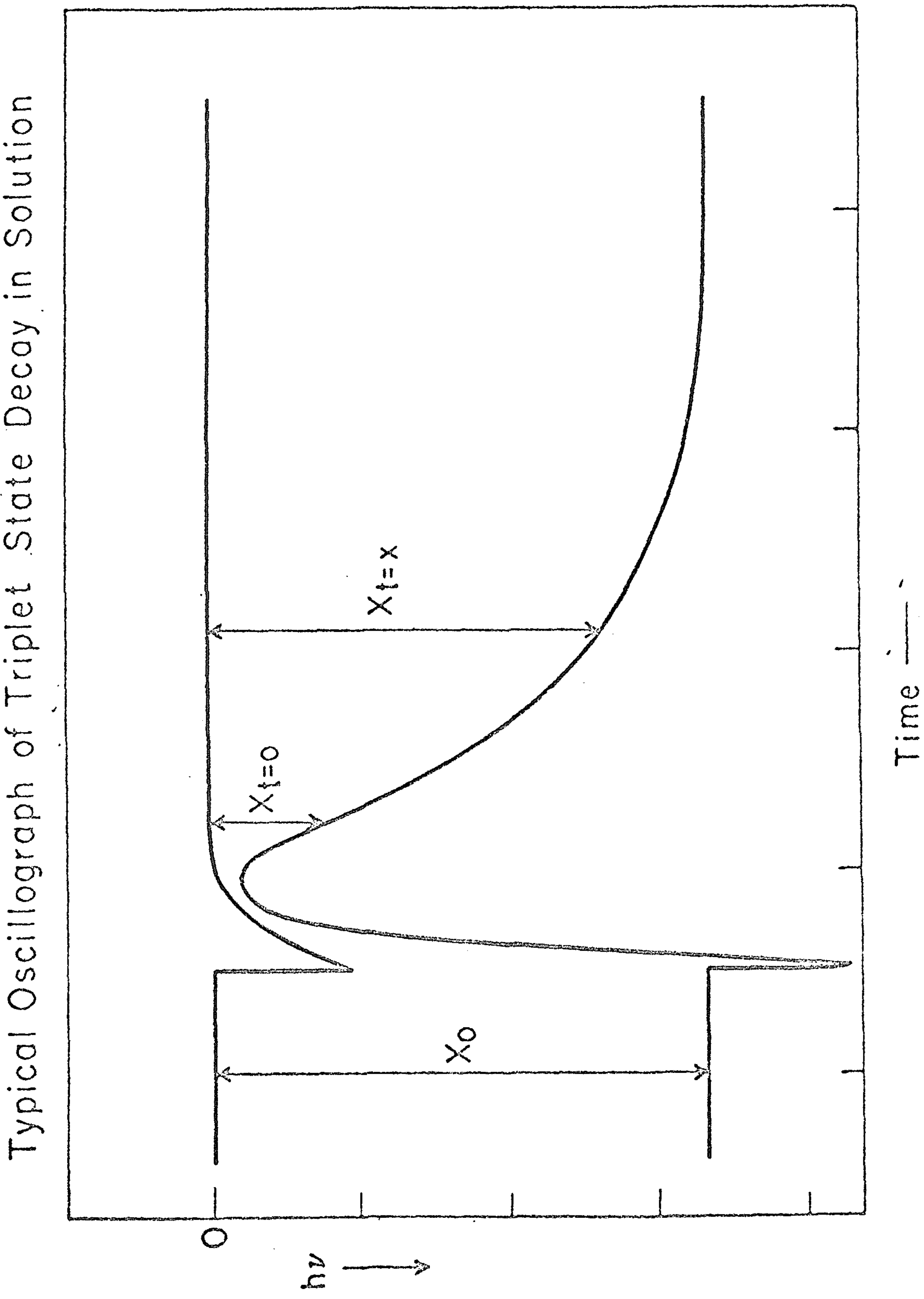
The photo dimers of 1,3-cyclohexadiene have been prepared before (10) and this procedure was used when dimers were needed for identification and VPC standardization.

Flash Photolysis Experiments.

The apparatus and procedure used for the flash spectroscopic experiments has been described in detail (9). Although the kinetic analysis of this type of experiment has been described previously, a brief summary is presented here (77,78).

A typical oscillograph of triplet decay is shown in Figure XVI. Light intensity is plotted vertically and time horizontally. The upper curve represents zero light intensity and the lower curve the decay of the triplets. The sharp downward spike at the beginning of the picture corresponds to stray light from the flash. The arbitrary zero time was chosen at a point where the stray light would not interfere. X_o and X_t at various times were recorded in each case. The kinetic analysis relies on the fact that response of the photoelectric cell is linear with light intensity. Then

$$\frac{X_o}{X_t} \propto \frac{I_o}{I_t} \qquad 72)$$



Typical Oscillograph of Triplet State Decay in Solution

FIGURE XVI

Substitution in Beers Law yields:

$$\log \ (I_o/I_t) = \log \ (X_o/X_t) = \epsilon^* c^* l = A_t, \qquad (73)$$

where A_t is the absorbance at time t, ϵ^* and c^* are the extinction coefficients of the triplet-triplet absorption and concentration of the triplets respectively and l is the path length.

The decay of triplets in solution follows the imperical equation (79,80,81)

$$-(dc^*/dt) = k_f c^* + k_s (c^*)^2, \qquad (74)$$

where k_f and k_s are the first and second order rate constants respectively. Substitution of $c^* = A_t/\epsilon^* l$

$$-dA_t/dt = k_f A_t + k_s/\epsilon^* l \ (A_t)^2 \qquad (75)$$

a plot of

$$\frac{-1}{A_t} \left(\frac{dA_t}{dt}\right)_t = \alpha + \beta A_t \qquad (76)$$

yields values for α (the first order rate constant) and β (the second order term). This analysis was done by an IBM 7090-7094 computer using a program written by Dr. K. W. Jacob of the California Institute of Technology Computing Center.

If we assume the mechanism for triplet decay proposed by Linschitz (78,81) shown below:

$$S^* \xrightarrow{k_{dt}} S \qquad (77)$$

$$S^* + S^* \xrightarrow{k_2} S^* + S \qquad (78)$$

$$S^* + S \xrightarrow{k_3} 2S \qquad (79)$$

$$S^* + Q \xrightarrow{k_Q} S + Q^* \qquad (80)$$

where S denotes sensitizer, Q the added quencher and triplet states by asterisks, α represents the first order coefficients $k_{dt} + k_Q[Q] + k_3[S_o]$ and β the coefficients $(1/\varepsilon^* l)(k_2-k_3)$. The function α depends on the concentration of sensitizer and added quencher, while β only depends on the analysis wavelength. If we assume $k_3[S_o]$ to be small compared to $k_1 + k_Q[Q]$, k_1 and k_Q can be determined.

In order to decrease the error due to impurity quenchers in the solvent, each run consisted of three cells with identical sensitizer concentration, two of them with added quencher. By this procedure, trace impurities would not effect the value of k_Q.

The search for triplet-triplet absorption of 1,3-cyclohexadiene was done in the following manner. The flash apparatus was designed so that a small dewer could be placed between the flash lamps. A small cylindrical quartz cell (1 cm. x 4.5 cm.), containing the sensitizer and 1:1:1 mixture of 1,3-cyclohexadiene, isopentane and methylcyclohexane was degassed by methods previously mentioned. This mixture of diene and hydrocarbon forms a glass at 77°K. The operation of the apparatus was the same as that used for kinetic measurements.

In order to obtain a full absorption spectrum, a prism spectrograph was substituted for the monochromator. Kodak Type 103a-F plates were used.

Fluorescence Quenching Experiments.

Several tubes containing the same sensitizer concentration and various diene concentrations were prepared in precision bore pyrex test tubes (O.D. = 1/2 inch) which were constricted to facilitate sealing. These tubes were degassed by the above mentioned procedure and sealed at the constriction. Relative fluorescence intensities were measured on an Aminco-Bowman spectrophotofluorometer.

Fluorescence Lifetimes.

Due to the short singlet lifetime of aromatic hydrocarbons (10-100 nsec.) good lifetime values are hard to obtain. In this work the values of Berlman were used when available (40). When directly measured lifetimes were not available, an empirical method developed by Berlman was used. The fact that oxygen quenches the fluorescence of aromatic hydrocarbons, (82) is the basis of this method. Bowen (83) has pointed out that the rate of quenching of fluorescence by oxygen was nearly constant for a wide range of compounds ($k_q = 3.4 \times 10^{10} M.^{-1} sec.^{-1}$).

$$S^1 + O_2 \xrightarrow{k_q} S + NO\ h\nu \qquad (81)$$

$$\frac{\phi_{fo}}{\phi_f} = 1 + k_q\ \tau_s[O_2] \qquad (82)$$

Berlman shows that there is a linear relation between the ratio of the quantum yield of fluorescence to the quantum yield of fluorescence in the presence of oxygen in equilibrium with the atmosphere to the singlet lifetime. Figure XVII shows this relation.

Phenanthrene lifetime was measured by a TRW Model 31A Nanosecond pulsing source (84).

Isolation of 1,3-Cyclohexadiene 1,2-Benzanthracene Photoadduct.

1,3-Cyclohexadiene saturated with 1,2-benzanthracene (~ 0.05M.) was irradiated for one week with a uranium glass filtered Hanovia 500W, medium pressure

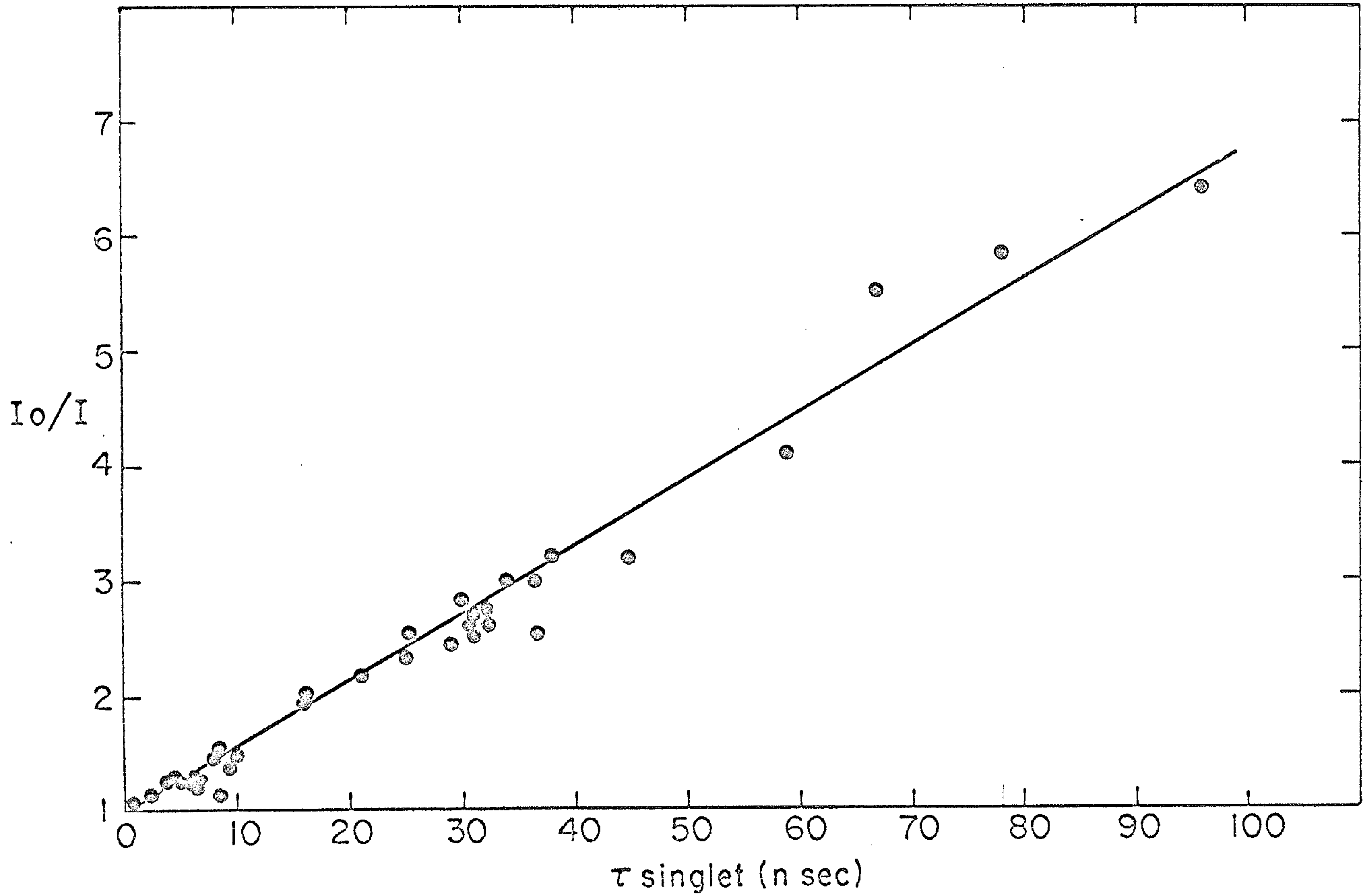


FIGURE XVII The Relation Between Oxygen Quenching and Singlet Lifetimes mercury arc. During irradiation crystals separated hydrocarbon 9. Hydrocarbon 9 was found to be very insoluble in most organic solvents. It was assigned the structure of dibenzanthracene, m.p. 231, lit. 235 (35,36).

The solution was evaporated under a stream of nitrogen and the remaining oil was separated by preparative thin layer chromatography. The TLC plates were made of silica gel 2 mm. thick. Cyclohexadiene dimers, 1,2-benzanthracene and hydrocarbon 9 were separated by this method. The nmr spectrum of hydrocarbon 9 had the following peaks: 1.40 ppm (4 protons); 3.0 ppm broad (2 protons); doublets centered at 4.17 ppm and 4.90 ppm (2 protons); multiplet at 8.34 ppm (2 protons) and aromatic protons at 6.70 ppm to 8.30 ppm (10 protons).

The nmr spectra were taken in carbon tetrachloride with tetramethylsilane as an internal standard. A Varian A-60A spectrometer or A-56/60A spectrometer with a Varian C-1024 Time Averaging Computer was used to record the spectrum. The decoupling experiments were conducted on a Varian HA-100 spectrometer.

Anal. Calcd for $C_{24}H_{20}$: C, 93.51; H, 6.56.
Found: C, 93.34; H, 6.49.

APPENDIX I

Triplet State Energies of Sensitizers

Sensitizer	E_T (kcal./mole)	Reference
Benzophenone	68.5	85
Triphenylene	66.6	85
Phenanthrene	61.8	86
Naphthalene	60.9	85
2-Acetonaphthone	59.3	85
1-Naphthyl phenyl ketone	57.5	85
Chrysene	56.6	87
Fluorenone	53.3	85
1,2,7,8-Dibenzanthracene	52.9	86
1,2,5,6-Dibenzanthracene	52.2	86
1,2,3,4-Dibenzanthracene	50.8	86
Pyrene	48.2	86
1,2-Benzanthracene	47.2	86
3-Acetyl pyrene	45.5	77
Acridine	45.2	88
9,10-Dimethyl-1,2-benzanthracene	44.3	89
Anthracene	42.6	90
3,4-Benzpyrene	41.9	91
9,10-Dibromoanthracene	40.2	88
3,4,9,10-Dibenzpyrene	40.2	92

APPENDIX II[a] (93)

The slopes and intercepts of the plots were calculated from the standard formulas:

$$\text{Slope} = \frac{n \sum yx - \sum x \sum y}{S^2} , \qquad (83)$$

$$\text{Intercept} = \frac{\sum x^2 \sum y - \sum x \sum xy}{S^2} . \qquad (84)$$

The variance of the slope and intercept were calculated from:

$$\text{var(Slope)} = \frac{\sigma^2}{nS^2} , \qquad (85)$$

$$\text{var(Intercept)} = \frac{\sigma^2}{n} [1 + \frac{\bar{x}^2}{S^2}] , \qquad (86)$$

where,

$$S^2 = n \sum x^2 - (\sum x)^2 \qquad (87)$$

and

$$\sigma^2 = \frac{1}{n} \text{ (y actual - y calculated)}^2 . \qquad (88)$$

To obtain a 90% confidence limit of β the following formula was used:

$$\beta \pm 1.65\sqrt{\mathrm{var}(\beta)} \quad . \qquad (89)$$

---

[a] The least squares calculations were done on a Olevette-Underwood 101 Programa desk computer.

REFERENCES

1. a. A. N. Terenin, E. Putzeiko and I. Akimov, Discussions Faraday Soc., 27, 83 (1959).
   b. A. N. Terenin and V. L. Ermolaev, Doklady Acad. Sci. U.S.S.R., 85, 547 (1952).
   c. V. L. Ermolaev and A. N. Terenin, S. I. Vavilow Memorial Volume, ed. by Academy of Science, U.S.S.R., 1952, p. 137.
   d. V. L. Ermolaev, Doklady Acad. Sci. U.S.S.R., 102, 925 (1955).
2. Recent reviews by A. N. Terenin, "Recent Progress in Photobiology", ed. by E. J. Bowen, Blackwells, 1963, p. 3. V. L. Ermolaev, Uspekhi Fiz. Nauk., 80, 3 (1963), English translation; Soviet Phys., Uspekhi, Nov. - Dec. 1963, p. 333.
3. H. L. Bäckström and K. Sandros, Acta Chem. Scand., 12, 823 (1958).
4. H. L. Bäckström and K. Sandros, Acta Chem. Scand., 14, 48 (1960).
5. G. S. Hammond et al., Kagaku to Kogyo (Tokyo) 18, 1464 (1965), and references therein.
6. a. P. A. Leermakers and G. F. Vesley, J. Chem. Ed., 41, 535 (1964).

b. J. G. Calvert and J. N. Pitts Jr., "Photochemistry", J. Wiley and Sons, New York, 1966.

7. G. W. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt and C. Dalton, *J. Am. Chem. Soc.*, *86*, 3197 (1964).

8. R. S. H. Liu, N. J. Turro and G. S. Hammond, *J. Am. Chem. Soc.*, *87*, 3406 (1965).

9. W. G. Herkstroeter and G. S. Hammond, *J. Am. Chem. Soc.*, *88*, 4769 (1966).

10. D. H. Valentine, N. J. Turro and G. S. Hammond, *J. Am. Chem. Soc.*, *86*, 5202 (1964).

11. G. O. Schenck, S. P. Mannsfield, G. Schomburg and C. H. Krauch, *Z. Natarforschz*, *19b*, 18 (1964).

12. N. J. Turro, Ph.D. Thesis, California Institute of Technology, 1963.

13. For a review of the photochemistry of conjugated dienes see R. Srinivasan, "Advances in Photochemistry", ed. by W. A. Noyes Jr., G. S. Hammond and J. N. Pitts Jr., Vol. 4, 1966, p. 113, and ref. 14.

14. W. G. Dauben and W. Todd Wipke, *Pure and Applied Chem.*, *9*, 539 (1965).

15. R. J. DeKock, N. G. Minnaard and E. Havinga, *Rec. Trav. Chim.*, *79*, 922 (1960).

16. R. Srinivasan, J. Am. Chem. Soc., 83, 2806 (1961).

17. R. Srinivasan, J. Am. Chem. Soc., 82, 5063 (1960).

18. P. De Mayo and S. T. Reid, Quart. Rev. London, 15, 393 (1961).

19. G. J. Fonken, Tetrahedron Letters, 549 (1962).

20. R. Srinivasan, J. Am. Chem. Soc., 83, 4344 (1961).

21. J. Meinwald and P. H. Mazzocchi, J. Am. Chem. Soc., 88, 2850 (1960).

22. W. G. Dauben and R. L. Cargill, J. Org. Chem., 27, 1910 (1962).

23. K. J. Crowley, J. Chem. Soc., 12 (1964).

24. J. Meinwald, A. Eckell and K. L. Erickson, J. Am. Chem. Soc., 87, 3532 (1965).

25. J. Baldwin and J. P. Nelson, J. Org. Chem., 88, 336 (1966).

26. D. F. Evans, J. Chem. Soc., 1735 (1960).

27. R. E. Kellogg and W. T. Simpson, J. Am. Chem. Soc., 87, 4230 (1965).

28. K. Sandros and H. L. Bäckström, Acta Chem. Scand., 16, 958 (1962).

29. A. J. Fry, R. S. H. Liu and G. S. Hammond, J. Am. Chem. Soc., 88, 4781 (1966).

30. K. Sandros, Acta Chem. Scand., 18, 2355 (1964).

31. G. S. Hammond and J. Saltiel, J. Am. Chem. Soc., 85, 2516 (1963).

32. D. H. Valentine, Ph.D. Thesis, California Institute of Technology, 1966.

33. A. A. Lamola and G. S. Hammond, J. Chem. Phys., 43, 2129 (1965).

34. G. S. Hammond and P. A. Leermakers, J. Am. Chem. Soc., 84, 207 (1962).

35. S. Schonberg and A. Mustafa, Chem. Rev., 40, 181 (1947).

36. M. Kasha, Discussions Faraday Soc., 9, 14 (1950).

37. F. Wilkinson, unpublished results.

38. T. Medinger and F. Wilkinson, Trans. Faraday Soc., 61, 620 (1965).

39. A. R. Harrocks, T. Medinger and F. Wilkinson, Chem. Comm., 526, 452 (1965).

40. I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules", Academic Press, New York, 1965.

41. E. H. Gilmore, G. E. Gibson and D. S. McClure, J. Chem. Phys., 20, 829 (1952) ; ibid 23, 399 (1955).

42. C. A. Parker and C. G. Hatchard, Analyst, 87, 644 (1962).

43. L. M. Stephenson, Ph.D. Thesis, California Institute of Technology, 1968.

44. H. Labhart, *Helv. Chim. Acta*, *47*, 2279 (1964).

45. G. F. Vesley, S. M. Pokras and G. S. Hammond, unpublished results. These values were obtained by the method of Lamola (33).

46. D. S. McClure, *J. Chem. Phys.*, *17*, 905 (1949).

47. E. J. Bowen, "Advances in Photochemistry", Vol. 1, ed. by W. A. Noyes Jr., G. S. Hammond and J. N. Pitts Jr., John Wiley & Sons, New York, 1963, p. 23.

48. G. Weber and F. W. J. Teal, *Trans. Faraday Soc.*, *53*, 646 (1957).

49. Dr. Eigenman (CIBA Aktiengesellschaft, Basel). quoted in ref. 44.

50. J. B. Birks, D. J. Duson and T. A. King, *Pro. Roy. Soc.* (London), *A277*, 270 (1964).

51. A. A. Lamola, W. G. Herkstroeter, C. J. Dalton and G. S. Hammond, *J. Chem. Phys.*, *42*, 1715 (1965).

52. W. Ware, *J. Chem. Phys.*, *37*, 923 (1962).

53. W. J. Potts Jr., *J. Chem. Phys.*, *23*, 65 (1955).

54. C. C. Wamser and G. F. Vesley, unpublished results.

55. G. W. Robinson and R. Frosch, *J. Chem. Phys.*, *38*, 1187 (1963), *37*, 1962 (1962).

56. C. D. DeBoer, Ph.D. Thesis, California Institute of Technology, 1966.

57. E. Y. Lam, D. H. Valentine and G. S. Hammond, *J. Am. Chem. Soc.*, *89*, 3482 (1967).

58. A. Schonberg, A. Mustafa and M. Z. Barakat, *Nature*, *160*, 401 (1947).

59. A. Schonberg and A. Mustafa, *J. Chem. Soc.*, 2126 (1948).

60. G. F. Vesley and K. S. Kamm, unpublished results.

61. L. M. Stephenson, D. G. Whitten, G. F. Vesley and G. S. Hammond, *J. Am. Chem. Soc.*, *88*, 3665 (1966).

62. M. A. Slifkin, *Nature*, *200*, 766 (1963).

63. J. B. Birks, J. D. Dyson and J. H. Munro, *Proc. Roy. Soc.*, *A275*, 575 (1963).

64. G. S. Hammond, S. Murov, G. F. Vesley, R. S. Cooke and J. M. King, informal discussions.

65. L. A. Singer and G. A. Davis, *J. Am. Chem. Soc.*, *89*, 158 (1967).

66. G. O. Schenck and R. Steinmetz, *Bull. Soc. Chim. Bel.*, *71*, 781 (1962).

67. E. J. Banner and D. W. Tanner, *Trans. Faraday Soc.*, *51*, 475 (1955).

68. For examples of this see the spectrum of the benzfluorenes whose λ_{max} = 3400A. Ref. 69.

69. H. H. Jaffe and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy", John Wiley & Sons, New York, p. 314.

70. J. Lambert, *J. Am. Chem. Soc.*, *89*, 183 (1967).

71. This compound was obtained from L. Sharp.

72. This nmr spectrum was obtained by R. S. Cooke.

73. E. C. Taylor and R. O. Kan, *J. Am. Chem. Soc.*, *85*, 776 (1963). These authors present several derivatives with this basic structure.

74. R. B. Woodward and T. J. Katz, *Tetrahedron*, *5*, 70 (1959).

75. H. Vollmann, H. Becker, M. Corell and H. Streeck, *Ann.* *531*, 1 (1937).

76. C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, (London) A., *235*, 518 (1956).

77. W. G. Herkstroeter, Ph.D. Thesis, California Institute of Technology, 1966.

78. H. Linschitz and K. Sarkanen, *J. Am. Chem. Soc.*, *80*, 4826 (1958).

79. G. Porter and M. R. Wright, *Discussions Faraday Soc.*, *27*, 18 (1959).

80. G. Jackson, R. Livingston and A. Pugh, *Trans. Faraday Soc.*, *56*, 1635 (1960).

81. H. Linschitz and L. Pekkarinen, *J. Am. Chem. Soc.*, *82*, 2411 (1960).

82. E. A. Bailey and G. K. Rallefson, *J. Chem. Phys.*, *21*, 1315 (1953).

83. E. J. Bowen, *Chemistry in Britain*, *2*, 249 (1966).

84. This measurement was made by S. Murov.

85. W. G. Herkstroeter, A. A. Lamola and G. S. Hammond, *J. Am. Chem. Soc.*, *86*, 4537 (1964).

86. E. Clar and M. Zander, *Chem. Ber.*, *89*, 749 (1956).

87. D. S. McClure, *J. Chem. Phys.*, *17*, 905 (1949).

88. F. Dorr and H. Gropper, *Ber. Bunsenges. Physik. Chem.*, *67*, 193 (1963).

89. M. M. Moodie and C. Reid, *Brit. J. Cancer*, *8*, 380 (1954).

90. M. R. Padhye, S. P. Mc Glynn and M. Kasha, *J. Chem. Phys.*, *24*, 588 (1956).

91. B. Muel and M. Hubert-Habart, *J. Chim. Phys.*, *55*, 377 (1958).

92. B. Muel and M. Hubert-Habart, *Proc. Intern. Meeting Mol. Spectroscopy. 4th Bologna, 1959*, *2*, 647 (1962).

93. "Introduction to Probability and Statistics" D. W. Lindgren and G. W. Mc Elrath, The Macmillan Co., New York, 1959, p. 231.

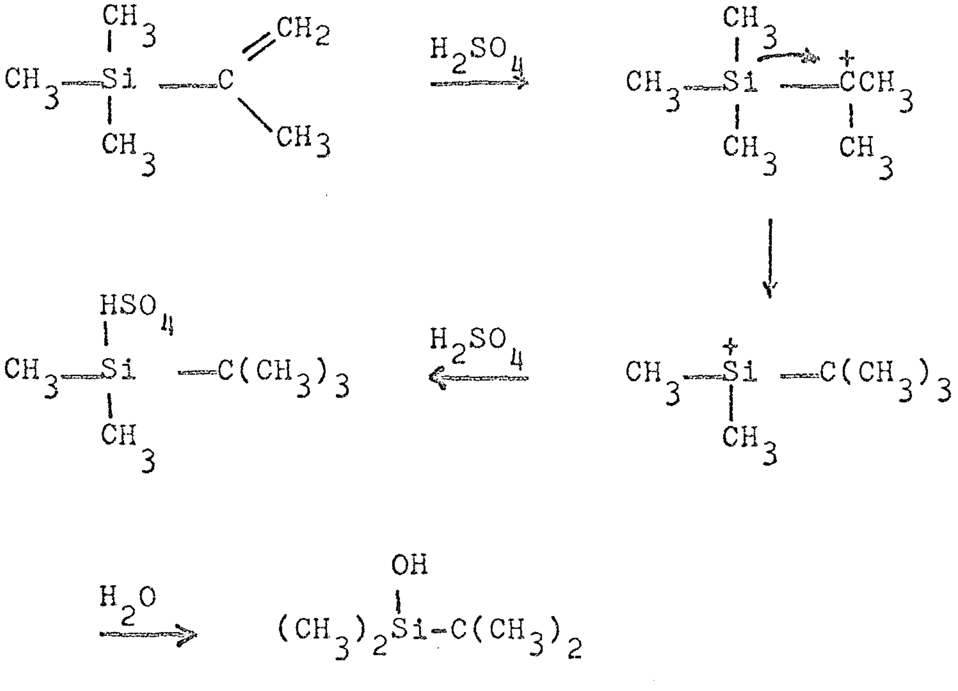
PROPOSITIONS

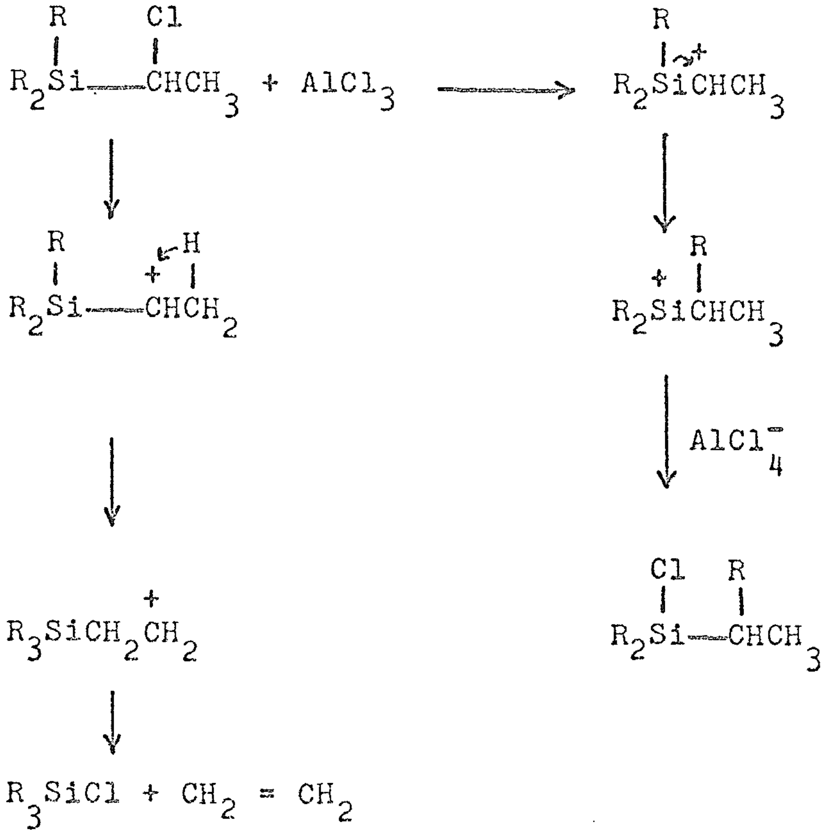
PROPOSITION I

It is proposed to synthesize 1,2-dimethyl-1,2-diethyl-1-phenyl-2-chlorodisilane in order to investigate Wagner - Meerwein type rearrangements of silicon.

In recent literature there has been increasing interest in the chemistry of silicon. Several Wagner-Meerwein type rearrangements of carbon from silicon to carbon (1,2,3) have been found, (equation 1,2,3).

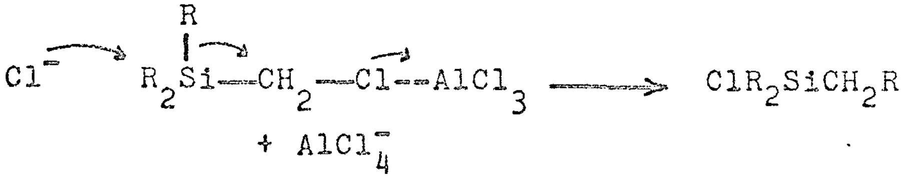
$$\begin{tikzcd}
(CH_3)_3SiCH_2Cl + AlCl_3 \arrow[r, shift left, harpoon] & (CH_3)_3Si\overset{+}{C}H_2 + AlCl_4 \arrow[l, shift left, harpoon] \arrow[d] \\
(CH_3)_2ClSiCH_2CH_3 & (CH_3)_2\overset{+}{Si}CH_2CH_3 \arrow[l, "AlCl_4^-"']
\end{tikzcd} \qquad (1)$$


(2)



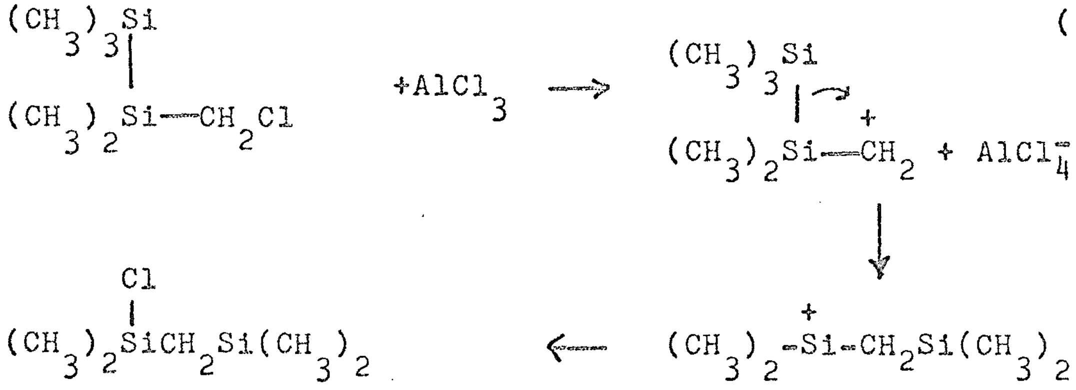
(3)

Although carbonium and siliconium ion intermediates seem attractive, they may not be free in solution; they may exist as ion pairs or not at all. Reaction 3 could also be written as follows:



(3')

There has also been a report of silicon migration from silicon to carbon (4), (see reaction 4).


(4)

These are typical rearrangements found in silicon chemistry. It is still unknown whether migrations from silicon to silicon exist. The 1,2-dimethyl-1,2-diethyl-1-phenyl-2-chlorodisilane system would be ideal to investigate a Wagner-Meerwein type migration.

Two reactions would be appropriate for this study, the aluminum chloride catalyzed rearrangement or the cyclohexylammonium chloride induced racemization of α-naphthylphenylmethylchlorosilane (5). There seems to be more evidence for siliconium ions or siliconium ion pairs in the latter reaction.

$$R_3Si^*Cl + CycloC_6H_{11}NH_3Cl^{36} \rightleftharpoons \qquad (5)$$

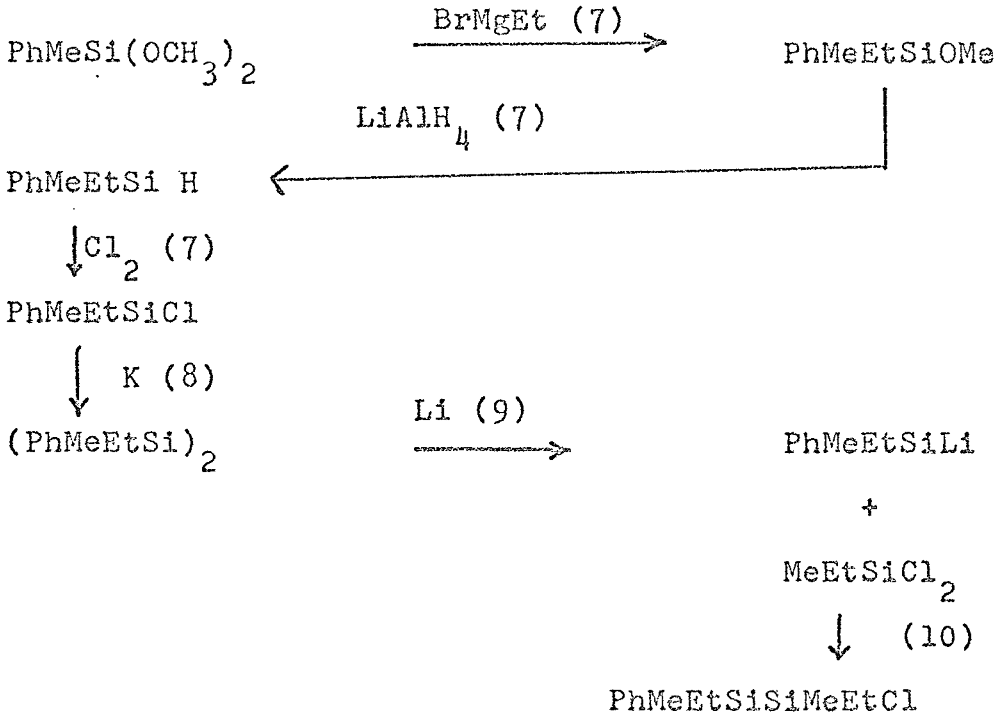
$$R_3Si^*Cl^{36} + CycloC_6H_{11}NH_3Cl$$

Sommer proposes a classical siliconium ion intermediate in which the chloride equilibrates with the medium before recombination of the siliconium ion with chloride; or an ion pair intermediate for this reaction. This ion pair undergoes fast retention and inversion exchanges at equal rates, and returns to reactants with retention of configuration.

$$(+)R_3Si^*Cl \rightleftharpoons (+)[R_3Si^*]^+[Cl]^- \rightleftharpoons \qquad (6)$$
$$(+)[R_3Si]^+[Cl^{36}]^- \rightleftharpoons R_3Si^*Cl^{36}$$

$$(+)R_3Si^*Cl \rightleftharpoons (+)[R_3Si]^+[Cl]^- \rightleftharpoons \qquad (7)$$
$$(-)[R_3Si]^+[Cl^{36}]^- \rightleftharpoons (-)R_3Si^*Cl^{36}$$

The synthesis of this new disilane should be straightforward. All of the reactions used have analogies in silicon chemistry. The 1,2-dimethyl-1,2-diethyl-1-phenyl-1-chlorosilane can be resolved by the method of Sommer (6).



Synthesis

A mixture of erythro and threo disilane will be obtained. These can be separated by adsorption chromatography. Only the erythro or the threo need be used.

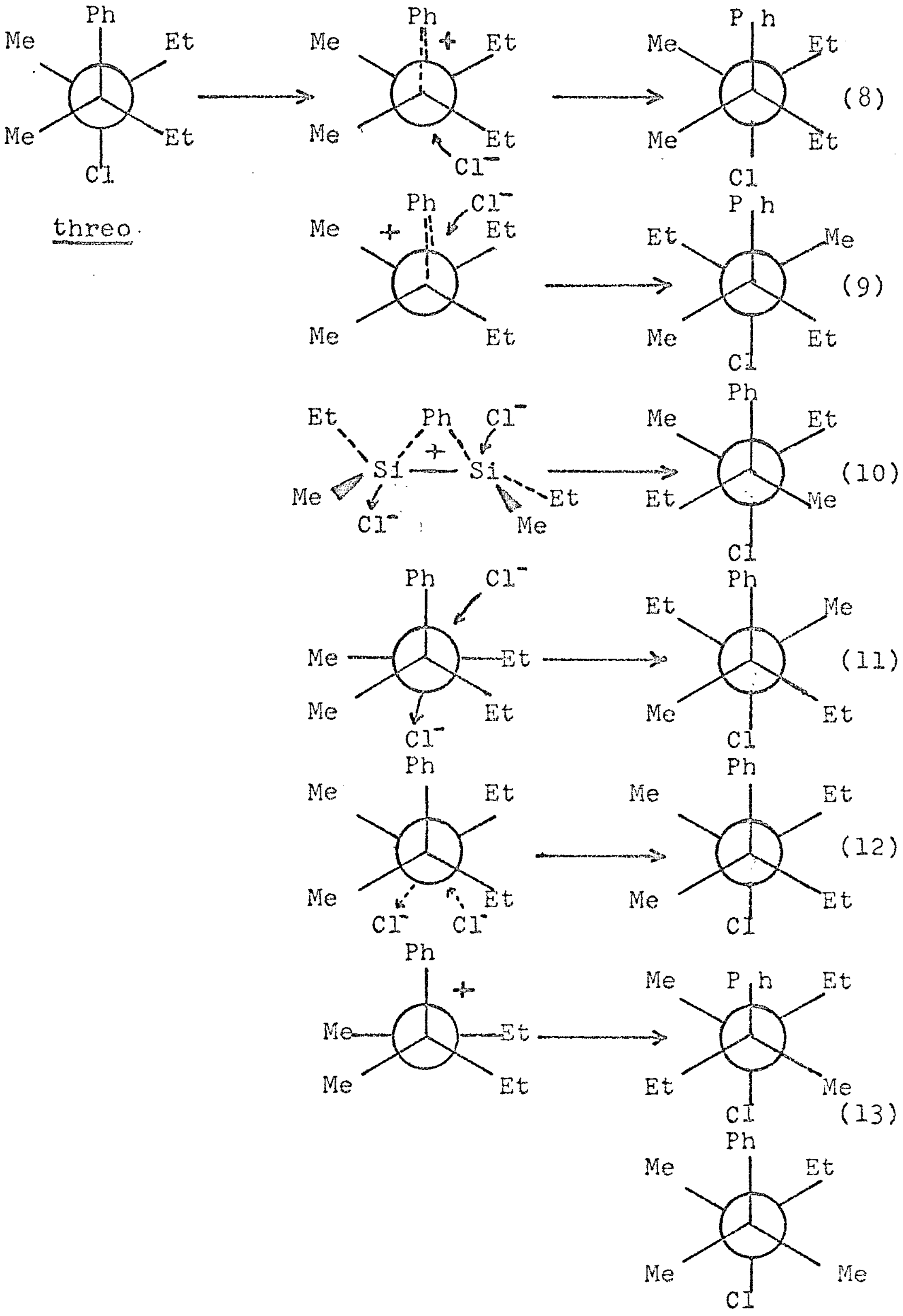
The reaction of cyclohexylammonium chloride with threo-1,2-dimethyl-1,2-diethyl-1-phenyl-1-chlorodisilane should produce interesting results. If the phenyl group migrates and forms a symmetrical intermediate, the threo compound would result, (equation 8). This assumes that chloride attacks from the rear. It is known that front side attack can occur in silicon chemistry, analogous to Sommer's Sn^i-Si mechanism (11). If this is the case, the *erythro* would be formed, (equation 9). The reaction could also take place by a mechanism analogous to 3'. This also would give the *erythro* compound, (equation 10). All three of these possibilities would show phenyl participation. Mechanisms in which phenyl participation does not occur can also be written. Sommer has suggested that a Sn^2-Si mechanism may compete with Sn^1-Si mechanism (6). If an Sn^2-Si mechanism operated, inversion would occur at one silicon center yielding the *erythro* compound, (equation 11).

If front side attack occurred at one silicon center which did not involve phenyl migration, the *threo* compound would be obtained, (equation 12). A siliconium ion or ion pair which did not involve phenyl migration would lead to a mixture of *threo* and *erythro*, (equation 13).

If a mixture of *threo* and *erythro* is obtained the conclusion is obvious. In two cases a *threo* compound would result. In these cases it would be necessary to show that a reaction took place, which can be done in several ways. The Cl^{36} salt, or the optically pure *threo* compound can be used. If the latter was done, *l-threo* would give *dl-threo*. There are two cases in which *threo* would be formed, (equations 8 and 12), and there are three cases in which erythro would be formed, (equations 9,10 and 13). The two *threo* and three *erythro* mechanisms can be distinguished from each other by labeling the ethyl group on the silicon with the phenyl. After the chloride-chloride exchange reaction, the product is hydrolyzed, (7) cleaved with lithium (9) and coupled with bromobenzene (12). Analysis of the products should distinguish between the possibilities presented. The expected products are listed in Table I.

TABLE I

Mechanisms	Product of Cl-Cl exchange	Products after cleavage	
8	*threo*	$MeEt^{*}PhSiOH$ $MeEt^{*}SiPh_2$	$MeEtSiPh_2$ $MeEtPhSiOH$
9	*erythro*	$Ph_2SiMeEt^{*}$ $MeEt^{*}SiPhOH$	$MeEtSiPhOH$ $MeEtSiPh_2$
10	*erythro*	$PhEt^{*}MeSiOH$	$Ph_2SiEtMe$
11	*erythro*	$Ph_2MeSiEt^{*}$	$PhEtMeSiOH$
12	*threo*	$MeEt^{*}SiPh_2$	$MeEtPhSiOH$


threo
Ph
Me
Et
Cl
Cl⁻
Si
+
(8)
(9)
(10)
(11)
(12)
(13)

REFERENCES

1. F. C. Whitmore, L. H. Sommer and J. R. Gould, J. Am. Chem. Soc., 69, 1976 (1947).
2. L. H. Sommer and F. J. Evans, J. Am. Chem. Soc., 76, 1186 (1954).
3. L. H. Sommer, D. L. Bailey, J. R. Gould and F. C. Whitmore, J. Am. Chem. Soc., 76, 801 (1954).
4. M. Kumada, J. Nakajima, M. Ishikawa and Y. Yamamoto, J. Org. Chem., 23, 292 (1958).
5. L. H. Sommer, F. O. Stark, K. W. Michael and G. A. Parker, J. Am. Chem. Soc., 86, 5683 (1964).
6. L. H. Sommer and K. T. Rosborugh, J. Am. Chem. Soc., 89, 1756 (1967).
7. L. H. Sommer, C. L. Frye, G. A. Parker and K. W. Michael, J. Am. Chem. Soc., 86, 3271 (1964).
8. H. Gilman and T. C. Wu, J. Org. Chem., 18, 753 (1953).
9. L. H. Sommer and R. Mason, J. Am. Chem. Soc., 87, 1619 (1965).
10. a. L. H. Sommer, P. G. Radewald and G. A. Parker, Tetrahedron Letters, 18, 821 (1962).
    b. A. G. Brook and S. Wolfe, J. Am. Chem. Soc., 79, 1431 (1957).
11. L. H. Sommer, C. L. Frye and G. A. Parker, J. Am. Chem. Soc., 86, 3276 (1964).
12. R. A. Benkeser and R. G. Severson, J. Am. Chem. Soc., 73, 1424 (1951).

PROPOSITION II

It is proposed to study the fluorescence quenching of optically active sensitizers with an optically active diene.

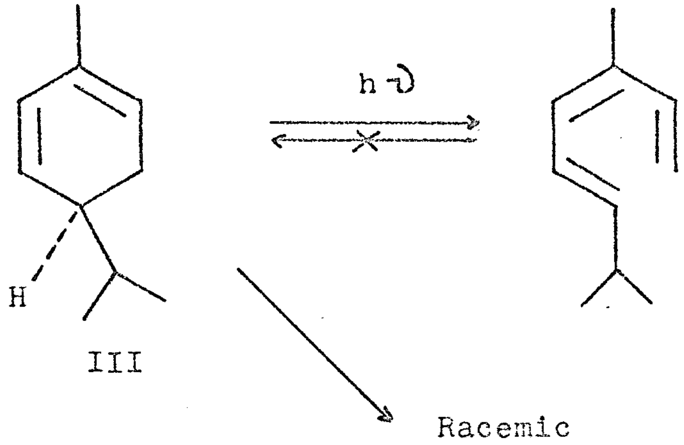
The quenching of the fluorescence of aromatic hydrocarbons by conjugated dienes has received considerable attention by the Hammond group in the past year (1). In this quenching process the diene apparently decays to the ground state without chemical reaction (no normal reactions of the singlet or triplet state of the diene) (2). There are however, several reports of dienes adding to aromatic hydrocarbons, naphthalene in the presence of piperylene is consumed on prolonged irradiation (2) and a photo adduct is formed between 1,3-cyclohexadiene and 1,2-benzanthracene (1). The exact mechanism of these photoadditions is not known but it is conceivable, in the case of 1,3-cyclohexadiene and 1,2-benzanthracene, that the adduct may be the result of this singlet quenching process (1).

Cole has shown that optical activity can be induced during energy transfer (3). Irradiation of (+)N-acetyl-1-(1-naphthyl)-ethylamine (I) in the presence of *cis*-1,2-diphenylcyclopropane (II), initially produces optically inactive *trans*-(II). Upon further irradiation, optical activity was induced in *trans*-(II). Irradiation of (+)(I) and (+)*trans*-(II) showed immediate induction of optical activity in the *trans*-(II). Although (+)*trans*-(II) did not measurably quench the fluorescence of (+)(I), it was shown that the excited singlet state of (I) and ground state of (II) were involved in this process. These experiments indicate the relative orientation of the donor and acceptor during energy transfer. Cooke (4) has found that naphthalene photoracemizes sulfoxides and is trying to correlate this racemization with singlet quenching.

It has been shown that the singlet quenching process may lead to photoadducts and there is an intimate relation between donor and acceptor. The use of an optically active diene to quench the fluorescence of optically active sensitizers should indicate the relation between the quencher and sensitizer.

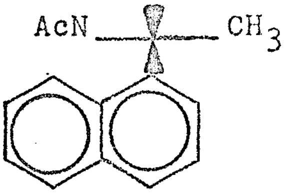
An excellent diene for this experiment is (-)α-phellandrene (III), an analog of 1,3-cyclohexadiene. This optically active diene is commercially available and should quench the fluorescence of optically active naphthalenes. The quenching rate would be expected to be less than that observed with 1,3-cyclohexadiene due to steric effects (2). This is consistant with the report that α-phellandrene containing naphthalene dimerizes (5). No quantum yields are reported for this dimerization, but the total yield of dimers was small.

The main reason for choosing α-phellandrene was a report that it is photoracemized (6). The mechanism of this photoracemization is not understood. One would think that 1,3-hexatriene would be an intermediate in this racemization, but the closure of 1,3-hexatrienes to cyclic dienes appears to be a reaction of a "hot" ground state, and it is not observed in solution (7). The mechanism for this racemization by direct irradiation should be further investigated.

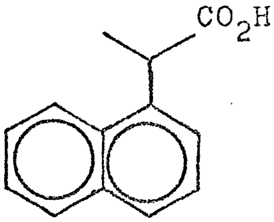


III

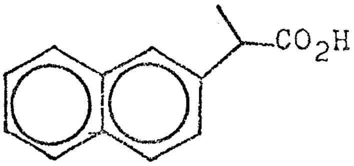
Cole (3) has synthesized several optically active sensitizers which can be used for this experiment. These sensitizers are shown below.



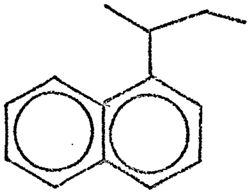
I



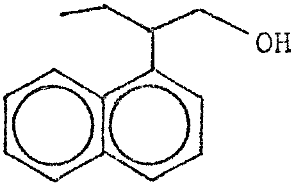
IV



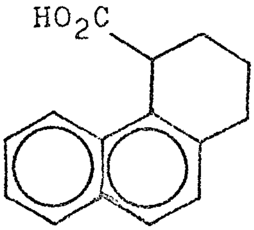
V



VI



VII



VIII

It is proposed to study the rates of quenching of both optically active isomers of these sensitizers with (-) α-phellandrene. This should give information concerning the mechanism of this quenching process.

It is also proposed to attempt to racemize (-) α-phellandrene with these optically active sensitizers, and to induce optical activity in a racemic mixture of α-phellandrene by a process which involves the excited state of the naphthalene and the ground state of the diene. A correlation may exist between the induced optical activity and the amount of fluorescence quenching observed.

The experimental procedures for these experiments have previously been reported (1,2).

REFERENCES

1. For a review of singlet quenching, see page 51 of this thesis.
2. L. M. Stephenson, Ph.D. Thesis, California Institute of Technology, 1968.
3. R. S. Cole, Ph.D. Thesis, California Institute of Technology, 1968.
4. R. S. Cooke, unpublished results.
5. J. Baldwin and J. P. Nelson, J. Org. Chem., 31, 336 (1966).
6. R. J. De Kock, N. G. Minnaard and E. Havinga, Rec. Trav. Chim., 79, 922 (1960).
7. G. J. Fonken, Tetrahedron Letters, 549 (1962).

PROPOSITION III

A favorable model for an
allenyl radical intermediate is proposed;
chlorination of a 1,4-diyne with *tert*-
butyl hypochlorite.

Compared to allylic free radicals, there have been relatively few studies concerning the propargylic free radicals. This radical can be represented as a hybrid of propargyl and allenyl structures I and II.

I II

The mercury-photosensitized decomposition of allene and 1,3-butadiene led to a C_3H_3 radical, which was concluded to have the structure I (I). The C_3H_3 radical has been generated photolytically in a rigid glass at 77°K (2). The esr spectrum of this radical under these conditions showed two different hyperfine spilling constants. The spin density on the CH_2 group was calculated to be 0.8, and on the CH group was 0.6.

Poutsma and Kartch (3) have found evidence, from the photo-induced chlorination of 1-butyne, for both radicals (I and II). They isolated 3-chlorobutyne and 1-chloro-1,2-butadiene from these reactions.

Walling and co-workers (4) have studied the reaction of t-butyl hypochlorite with acetylenes and found large yields of products derived from propargyl radicals, but no chloroallenes. Recently Caserio and

Pratt (5) have reported the reaction of t-butyl hypochlorite with allene and propyne. The main products observed in this reaction were propargyl chloride and t-butyl alcohol. No chloroallenes were obtained. Their results are interpreted in terms of the following mechanism, and indicate that the C_3H_3 radical is best described by the propargyl structure I.

$$\left.\begin{array}{l} CH_3C \equiv CH + \underline{t}\text{-}BuO\cdot \\ CH_2 = C = CH_2 + \underline{t}\text{-}BuO\cdot \end{array}\right\rangle \longrightarrow \cdot C_3H_3 + \underline{t}\text{-}BuOH$$

$$\cdot C_3H_3 + \underline{t}\text{-}BuOCl \longrightarrow ClCH_2C \equiv CH + \underline{t}\text{-}BuO\cdot$$

From these results it appears that C_3H_3 radicals, generated chemically, are best described by structure I. It is proposed to study the reaction of t-butyl hypochlorite with a 1,4-diyne. Proton abstraction would yield the RC_5H_2 radical, which can be described by the following structures.

$$R-C\equiv C-CH_2-C\equiv CH \quad + \quad \underline{t}\text{-}BuO\cdot$$

$$[R-C\equiv C-\dot{C}H-C\equiv CH \longleftrightarrow R-C\equiv C-CH=C=\dot{C}H$$

III IV

$$\longleftrightarrow R\dot{C}=C=CH-C\equiv CH]$$

V

The use of the 1,4-diyne should stabilize the allenylic radical due to the increased conjugation.

The 1,4-diyne can be prepared by a coupling reaction of $RC{\equiv}CCH_2MgBr$ and $BrCH_2C{\equiv}CH$ or coupling of $RC{\equiv}CNa$ and $BrCH_2C{\equiv}CH$ (6).

An analysis of the chlorides obtained will infer which radical structure is the greatest contributor to the hybrid.

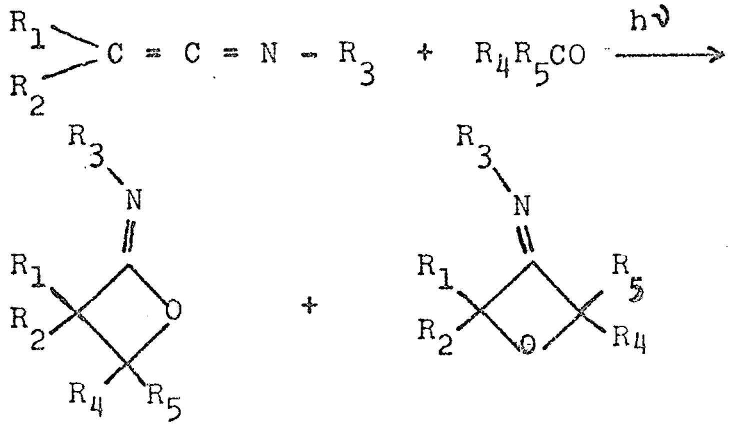
REFERENCES

1. J. Collin and F. P. Lossing, *Can. J. Chem.*, **35**, 778 (1957).
2. D. H. Volman, K. A. Maas and J. Wohstenholme, *J. Am. Chem. Soc.*, **87**, 3041 (1965).
3. M. L. Poutsma and J. L. Kartch, *Tetrahedron*, **22**, 2167 (1966).
4. C. Walling, L. Heaton and D. D. Tanner, *J. Am. Chem. Soc.*, **87**, 1715 (1965).
5. M. C. Caserio and R. E. Pratt, *Tetrahedron Letters*, **91**, (1967).
6. W. J. Gensler and J. Casella, *J. Am. Chem. Soc.*, **80**, 1376 (1958).

PROPOSITION IV

A reinterpretation of singlet quenching data in the fluorenone ketenimine photoaddition reaction is proposed in which a singlet complex intersystem crosses to the triplet.

Singer and Davis (1,2,3) have shown that the Paterno-Buchi (4) can be extended to ketenimine. Both possible adducts have been isolated.



The evidence presented for the addition of benzophenone to several ketenimines indicates that the triplet state of benzophenone complexes with the ground state ketenimine (1). This complex can decay or lead to the stable adducts.

Interesting results are obtained in the reaction of fluorenone with dimethyl-N-(cyclohexyl) ketenimine (3). A plot of the reciprocal quantum yield for adduct formation versus reciprocal ketenimine concentration possesses a minimum (see figure 1). The open circles are Singer's data (3). The following mechanism was proposed to account for this unusual behavior.

$$F \xrightarrow{h\nu} F^1 \qquad (1)$$

$$F^1 \xrightarrow{k_{ic}} F^3 \qquad (2)$$

$$F^3 \xrightarrow{k_d} F \qquad (3)$$

$$F^3 + K \xrightarrow{k_r} \text{Adduct} \qquad (4)$$

$$F^1 \xrightarrow{k_f} F + h\nu \qquad (5)$$

$$F^1 + K \xrightarrow{k_q} (F^1K) \longrightarrow F + K \qquad (6)$$

Extrapolation of the data to infinite K concentration gives an intersystem crossing yield for fluorenone of 0.93. This is in excellent agreement with that obtained by Lamola and Hammond (5). The sharp decrease in the quantum yield at high ketenimine concentration is attributed to deactivation of the fluorenone singlet state *via* complex formation with ground state ketenimine (equation 6). This is supported by the fact that this ketenimine quenches the fluorescence of fluorenone. At 0.2M. ketenimine the fluorescence is 89% and at 0.006M. ketenimine the emission is *ca.* 5% quenched.

Careful analysis of the data shows that singlet quenching can not be completely responsible for this decrease. From the presented mechanism (equations 1-5), the quantum yield for adduct formation is represented by the following:

$$\frac{1}{\phi} = \frac{1}{\phi_{ic}} \left(1 + \frac{k_d}{k_r[K]} \right) \qquad (7)$$

This represents the linear portion of figure 1. Assuming that k_q is the only energy wasting step, equation 7 becomes equation 8.

$$\frac{1}{\phi} = \frac{1}{\phi_{ic}} \frac{\phi_{fo}}{\phi_f} \left(1 + \frac{k_d}{k_r[K]} \right) \qquad (8)$$

The function ϕ_{fo}/ϕ_f is the ratio of fluorescence intensity in the absence of ketenimine to the fluorescence intensity in the presence of ketenimine. A plot of ϕ_{fo}/ϕ_f is related to [K] by equation 9, where $\tau_s k_q$

$$\frac{\phi_{fo}}{\phi_f} = 1 + \tau_s k_q[K] \qquad (9)$$

is the slope of a plot of ϕ_{fo}/ϕ_f versus [K] and τ_s is the singlet lifetime. From the quenching data reported (3), a slope of 40.5 is calculated. From the ratio of k_d/k_r (= 0.0057) and the singlet quenching data, the quantum yield can be adjusted for the quenching effect. This procedure has been applied to other systems with good success (6,7). The results of these calculations appear in Table 1. The x points in figure 1 represent the calculated points.

It can be seen that these calculations predict a smaller quantum yield than is obtained. For the observed data to correspond with that calculated in Table 1, the value of $\tau_s k_q$ must equal 15.8. This should be well outside the experimental error. Two possibilities exist for this difference. The adduct may be partially formed as a result of the singlet complex formed in equation 6, or this complex intersystem crosses to the triplet part of the time. Since the data obtained using benzophenone are best explained by a triplet complex, it would be expected that the fluorenone reaction also proceeds <u>via</u> a triplet complex. The simplest path to a triplet complex in this system is through the singlet complex. If the adduct results from the independent formation of a triplet complex ($F^3 + K \longrightarrow (FK)^3$), the adduct formation should be quenched by a triplet quencher such as azulene (8).

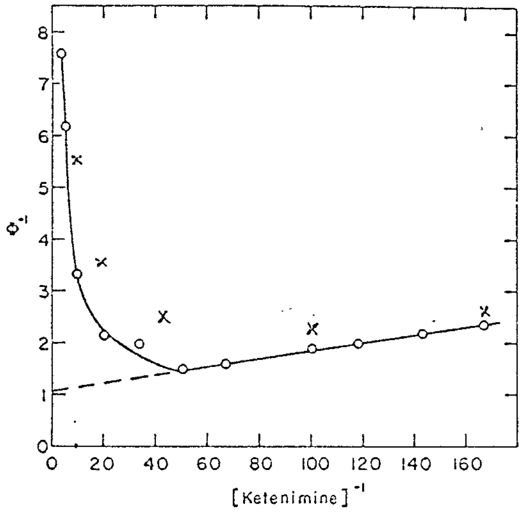


Figure 1

Table 1

[K]	$1/\phi_{ic}\left(1+\frac{k_d}{k_r[K]}\right)$	ϕ_{fo}/ϕ_f	$1/\phi$
0.100	1.15	5.05	5.80
0.050	1.20	3.025	3.60
0.025	1.34	1.97	2.64
0.010	1.67	1.41	2.36
0.00625	2.10	1.25	2.62

The feasibility of azulene quenching the fluorenone triplet can be determined by singlet-triplet absorption. The singlet complex, $(FK)^1$ due to its short lifetime, will not be quenched by azulene, but the triplet complex $(FK)^3$, may or may not be quenched depending on its lifetime. Similar information can be obtained using a triplet sensitizer.

This reaction should also be investigated by flash photolysis. A triplet complex should have a long enough lifetime to be detected by triplet-triplet absorption.

A combination of quenching and flash experiments should help elucidate this mechanism.

REFERENCES

1. L. A. Singer and G. A. Davis, J. Am. Chem. Soc., 89, 598 (1967).
2. L. A. Singer and G. A. Davis, J. Am. Chem. Soc., 89, 941 (1967).
3. L. A. Singer and G. A. Davis, J. Am. Chem. Soc., 89, 158 (1967).
4. E. Paterno and G. Chieffi, Gazz. Chim. Ital., 39, 341 (1909).

   G. Buchi, C. G. Inman and E. S. Lipinsky, J. Am. Chem. Soc., 78, 876 (1956).
5. A. A. Lamola and G. S. Hammond, J. Chem. Phys., 43, 2129 (1965).
6. L. M. Stephenson, D. G. Whitten, G. F. Vesley and G. S. Hammond, J. Am. Chem. Soc., 88, 3665 (1966).
7. L. M. Stephenson, Ph.D. Thesis, California Institute of Technology, 1968.
8. Reference 7 and 8 of this thesis.

PROPOSITION V

Experiments are proposed to show if saturated radical anions are stable, or if reported esr signals are due to impurities.

Recently there have been several reports concerning the detection of saturated radical anions. The radical anions of cyclopropane (1) and adamantane (2) have been generated in tetrahydrofuran-dimethoxyethane (2:1) solution containing sodium potassium alloy. The cyclopropyl radical anion (1) showed seven lines in the esr spectrum at -168°. This spectrum disappeared on warming to -110°, but reappears on cooling. This is due to a temperature effect on the following equilibrium:

$$\text{Na-K} + \text{RH} \rightleftharpoons \text{RH}^{\dot{-}} + \text{K}^{+}$$

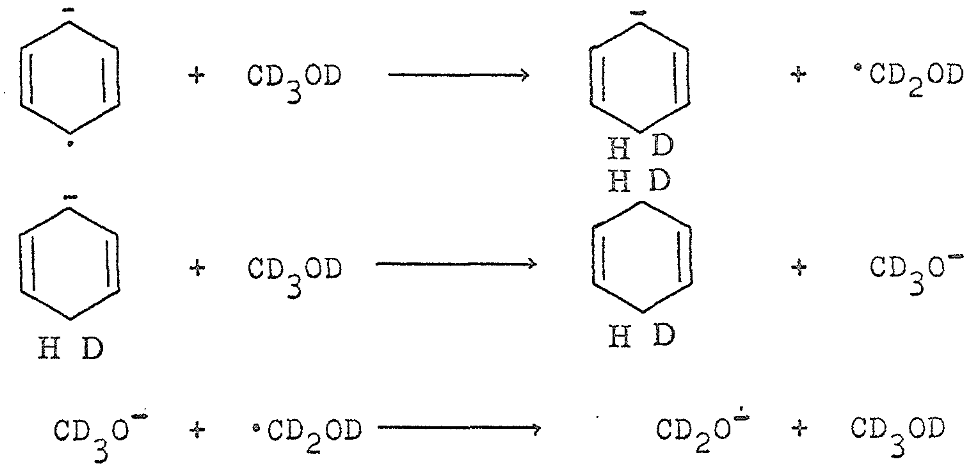
The radical anion will be stabilized at the lower temperature and the esr sensitivity is increased at lower temperatures. The esr spectrum of the adamantane radical anion, in the same solvent at -150° showed five lines. Since THF-dimethoxyethane freezes at -130°, the radical anion solution was probably prepared above this temperature. No temperature studies were reported by these authors.

A later report has shown that the esr spectrum of the adamantane radical anion showed seven lines at -110° (3). Upon cooling to -150° the lines are broadened and appear as five lines. This author has also studied the benzene radical anion under these conditions at various temperatures. The benzene radical anion and the adamantane radical anion had identical spectra (ie. a_H = 3.80±.01 oersteds, g = 2.00277 at -110°).

Therefore it is possible that the observed adamantane radical anion spectrum could be that of the benzene radical anion. The benzene could be an impurity or a product of the reaction of Na-K alloy with adamantane.

Since Na-K alloy is capable of reducing adamantane, electrochemical techniques should produce the same result. Adamantane and benzene should have different half-wave potentials, so a benzene impurity should be detected, (this assumes $E_{1/2}$ benzene $<$ $E_{1/2}$ adamantane). A benzene control should be run.

In order to determine if the benzene radical anion was responsible for the esr signal, the reaction could be quenched with CD_3OD.



By the above mechanism D could be incorporated into the benzene. (The 1,3-cyclohexadiene derivative could also be formed.) If products derived from benzene radical anions contained D, the existence of this radical anion would be confirmed. This does not rule out the existence of the adamantane radical anion, they both could be present. Deuterium could not be incorporated in the adamantane by a radical anion mechanism due to the reaction:

$$RH^{\dot{-}} + CD_3OD \longrightarrow RH + CD_3O^- + D\cdot \quad .$$

Preliminary experiments using various concentrations of benzene will show the products to be expected, and give a limit on the concentration of benzene which could be detected.

Since methanol freezes at -98°, there should be no problem with the solution freezing. The experiment should be done on a large volume of solution which is efficiently stirred, with rapid injection of the alcohol ($\sim 10\%$). This must be done in an inert atmosphere. The solution may be concentrated by distillation and the products separated by VPC. The benzene derivatives can be isolated by preparative VPC and analyzed by mass spectroscopy.

Helpful results may be obtained by measuring the esr spectra of adamantane with various concentrations of benzene. It is difficult to predict the results of this experiment.

Since there is doubt concerning the formation of the adamantane radical anion, the cyclopropane radical anion should also be reinvestigated. Quenching of this system should show if aromatic impurities are present.

REFERENCES

1. K. W. Bowers and F. D. Greene, *J. Am. Chem. Soc.*, **85**, 2331 (1963).
2. K. W. Bowers and F. D. Greene, *J. Am. Chem. Soc.*, **85**, 3707 (1963).
3. M. T. Jones, *J. Am. Chem. Soc.*, **88**, 174 (1966).