

QUANTUM YIELD STUDIES OF THE PHOTOLYSES
OF VARIOUS TETRAHYDRO-1,4-NAPHTHOQUINONES

BY

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August, 1975

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ABSTRACT.

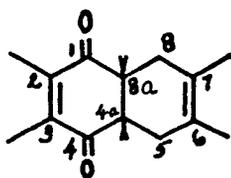
The 366 nm photolysis of 2,3,4a,6,7,8a-hexamethyl-4a β ,5,8,8a β -tetrahydro-1,4-naphthoquinone (27) in benzene yielded 28 with a quantum yield of 0.066 ± 0.003 and 29 with a quantum yield of 0.089 ± 0.003 . The formation of 28 was suggested to occur via a C₈ hydrogen abstraction by C₁ oxygen in a five membered transition state (β -hydrogen abstraction), and the formation of 29 was believed to occur via a C₈ hydrogen abstraction by C₃ carbon in a six membered transition state (γ -hydrogen abstraction). A Stern-Volmer analysis (effect of triplet quencher concentration on quantum yield) showed that 28 was formed from a singlet excited state, whereas 29 was formed from a triplet excited state.

The 366 nm photolysis of 6,7-dimethyl-4a β ,5,8,8a β -tetrahydro-1,4-naphthoquinone (10) in benzene yielded 12 with a quantum yield of 0.0080 ± 0.0008 and 13 with a quantum yield of 0.0164 ± 0.0012 . The 366 nm photolysis of 10 in tert-butanol yielded 11 with a quantum yield of 0.0081 ± 0.0008 . All three photoproducts of 10 were suggested to occur via β -hydrogen abstraction by oxygen. Stern-Volmer analyses showed that both photoproducts 12 and 13 arise via a triplet and a singlet excited state, whereas 11 only arises via a singlet state.

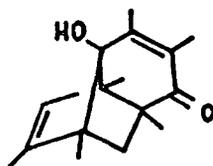
A mechanism is proposed explaining why products similar to 11 and

12 are not observed in the photolysis of 27. This mechanism is based on conformational control of the biradical intermediate by the bridgehead substituents.

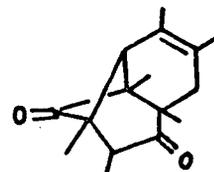
The effect of methyl substituents on the chromophore of 27 are implicated in shifting down the energy of the (π, π^*) triplet. It is argued that 29 arises via γ -hydrogen abstraction by this (π, π^*) triplet.



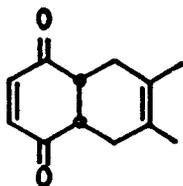
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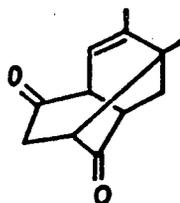
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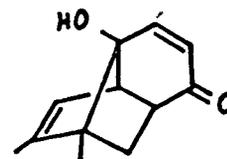
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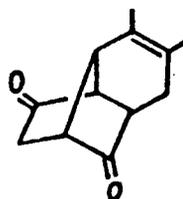


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John R. Scheffer



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To my Mother
for her love and wisdom
and to Charlene
for everything

INTRODUCTION

A. General

Until about twenty years ago, photochemistry was largely a branch of physical chemistry.¹ Organic chemists depended largely on the Bunsen burner or its equivalent and on the use of catalysts to make or break bonds. The development of the gas chromatograph and new spectroscopic tools allowed organic chemists to study photoreactions which often yielded small quantities of material.

Since then the interest in photochemistry has expanded enormously. Organic chemists have discovered reaction pathways which were previously unknown and which afforded in some cases, simple methods for making compounds which were hitherto difficult to prepare.

Conventional organic photochemistry relies on the use of light of wavelength in the range of 200 - 400 nm. Molecules that are able to absorb this light contain π bonds and are excited by 140 to 70 kcal/mole. Since only π electron systems are able to absorb in this wavelength range, the excitation occurs in specific areas of the molecule called chromophores. There are several types of chromophores, more notably: 1) carbon-carbon double bonds and conjugated polyenes which are able to promote upon excitation a π -electron to a π^* antibonding orbital (designated $\pi - \pi^*$); 2) carbonyl containing compounds which can have $\pi - \pi^*$

excitation, usually from absorption of 200 - 250 nm light, and have a high extinction coefficient ($\sim 10,000$); and 3) $n - \pi^*$ excitation (promotion of an electron from a nonbonding orbital on oxygen to the π^* orbital of the carbonyl group) in the range of 270 - 400 nm, depending on substitution and the degree of conjugation. The latter are forbidden transitions and have low extinction coefficients (~ 100).

The chromophores of the molecules studied in this work were conjugated ² carbonyl groups.

The ground state of nearly any molecule has all electron spins paired, has a multiplicity of one ³, and is thus called a singlet. Absorption of light excites a molecule to an excited singlet state S_1 or S_2 (spin must nearly always be conserved in an electronic transition). The molecule in an excited singlet state has several avenues open for deactivation. The more important of these are reaction to give products, deactivation to the ground state, and a process known as intersystem crossing.⁴ This involves spin inversion and results in an excited triplet state. It is clear that for every singlet excited state there will be a corresponding excited triplet state. According to Hund's first rule⁵ this will have a lower energy than the corresponding excited singlet state.

The excited triplet state has also the possibility of reacting to give products and of deactivating to the singlet ground state.

Figure 1 represents the different pathways available for deactivation of an electronically excited molecule.

It is of great importance to realize that for a triplet state to deactivate to the singlet ground state, a spin inversion must accompany the loss of energy. The selection rules ⁶ for electronic

transitions formally forbid this type of transition and it becomes possible only by the mixing of the states due to molecular perturbations.⁷

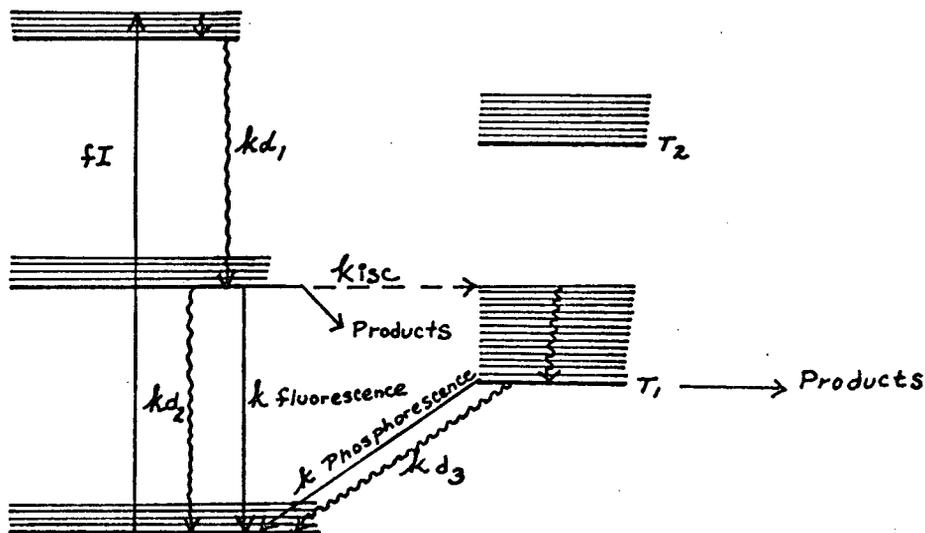


Figure 1. Jablonski Diagram.

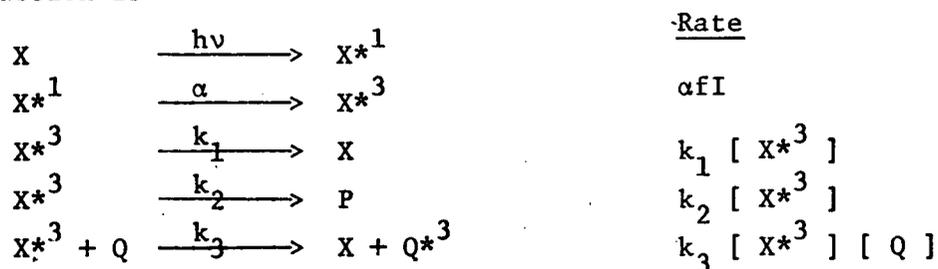
Horizontal lines represent vibrational levels. Solid arrows represent absorption or emission of light, wavy arrows represent nonradiative deactivation pathways, and the dotted line represents intersystem crossing.

This results in a much longer lived triplet state relative to the singlet state. The singlet has a lifetime of 10^{-6} to 10^{-12} sec whereas the triplet can have a lifetime of 10^{-3} to 10^{-9} sec and sometimes can be as long lived as a second or more.

One of the most useful and fundamental quantities in the study of photochemical reaction mechanisms is the quantum yield (Φ). Its value and the influence of the experimental variables upon it, give important information as to the nature of the reaction. The quantum yield for disappearance of reactant can be defined as the number of molecules

reacting per photon absorbed. One can have a quantum yield for formation of product, a quantum yield for fluorescence, phosphorescence, intersystem crossing and so on. In general, quantum yields vary between zero and unity. In some cases, however, the quantum yield for disappearance of reactant can exceed unity if a reactive intermediate consumes starting material. In the case of the photon acting only as a "catalyst" to promote the initiation step of chain reactions, the quantum yield can be extremely large (e.g. the photolysis of Br_2 in the formation of HBr from H_2 and Br_2).⁸

If one considers the photoreaction of a compound X, whose triplet state results in product formation, the simplest scheme for such a reaction is



α = efficiency of intersystem crossing; f = efficiency of light absorption; I = light intensity; Q = triplet quencher.

The rate of formation of triplet (X^{*3}) is given by

$$d[X^{*3}] / dt = \alpha f I - [X^{*3}] (k_1 + k_2 + k_3 [Q])$$

and the steady state approximation gives the expression

$$\alpha f I = [X^{*3}] (k_1 + k_2 + k_3 [Q])$$

The quantum yield of product (P) formation in the presence of quencher is

$$\phi_p = k_2 [X^{*3}] / f I = \alpha k_2 / (k_1 + k_2 + k_3 [Q])$$

in the absence of quencher it is

$$\phi_o = \alpha k_2 / (k_1 + k_2)$$

The ratio of these quantum yields is the Stern-Volmer expression

$$\phi_o / \phi_p = 1 + k_3 [Q] / (k_1 + k_2)$$

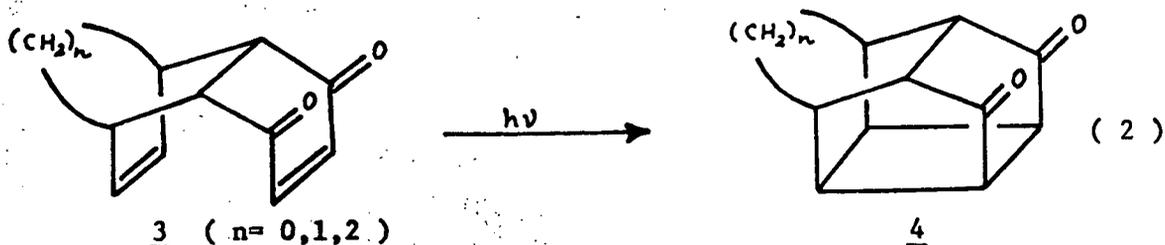
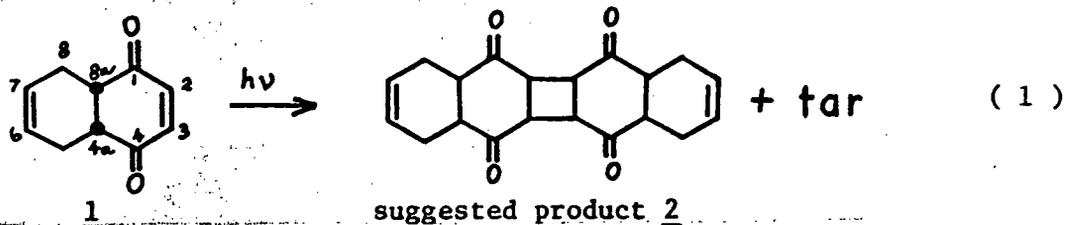
If one plots ϕ_o / ϕ_p vs. $[Q]$ one will obtain a straight line (if the mechanism is correct) with a slope $k_3 / (k_1 + k_2)$, i.e. the ratio of quenching rate constant to the sum of the rates of all triplet deactivation processes). If the quenching is diffusion controlled then an approximate value can be assigned to k_3 depending on the solvent used by applying the simplified Debye expression⁹

$$k \text{ (diffusion controlled)} = 8RT / 3000\eta \text{ (liter mole}^{-1}\text{sec}^{-1} \text{)}$$

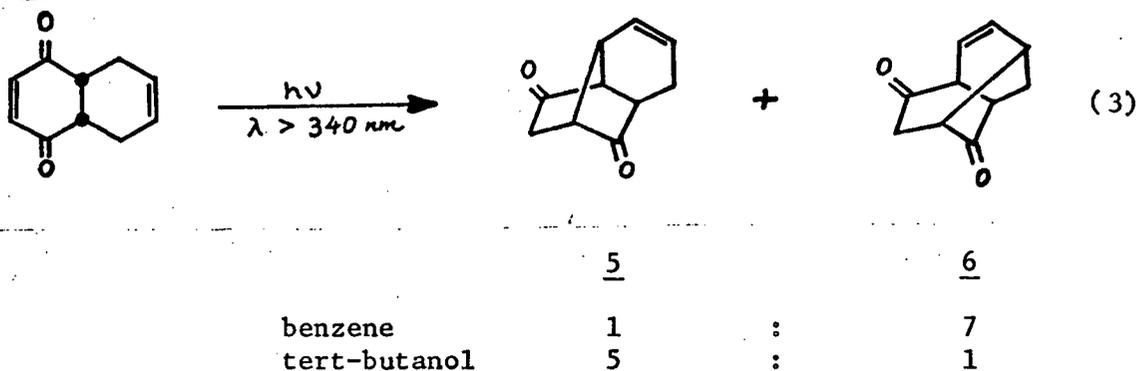
where η is the viscosity of the solvent in poise. One can then obtain a value for the triplet lifetime $\tau = 1 / (k_1 + k_2)$.

B. Photochemistry of Various Tetrahydro-1,4-naphthoquinones.

The study by Cookson et al¹⁰ on the photoreaction of compound 1 revealed a different behavior than expected from comparison to similar structures 3 which gave rise to only cage products 4



This unusual behavior by 1 intrigued our research group who set out to reinvestigate the reaction.¹¹ Photolysis of compound 1 using a filter transmitting light of $\lambda > 340$ nm led to the discovery of two new products 5 and 6.



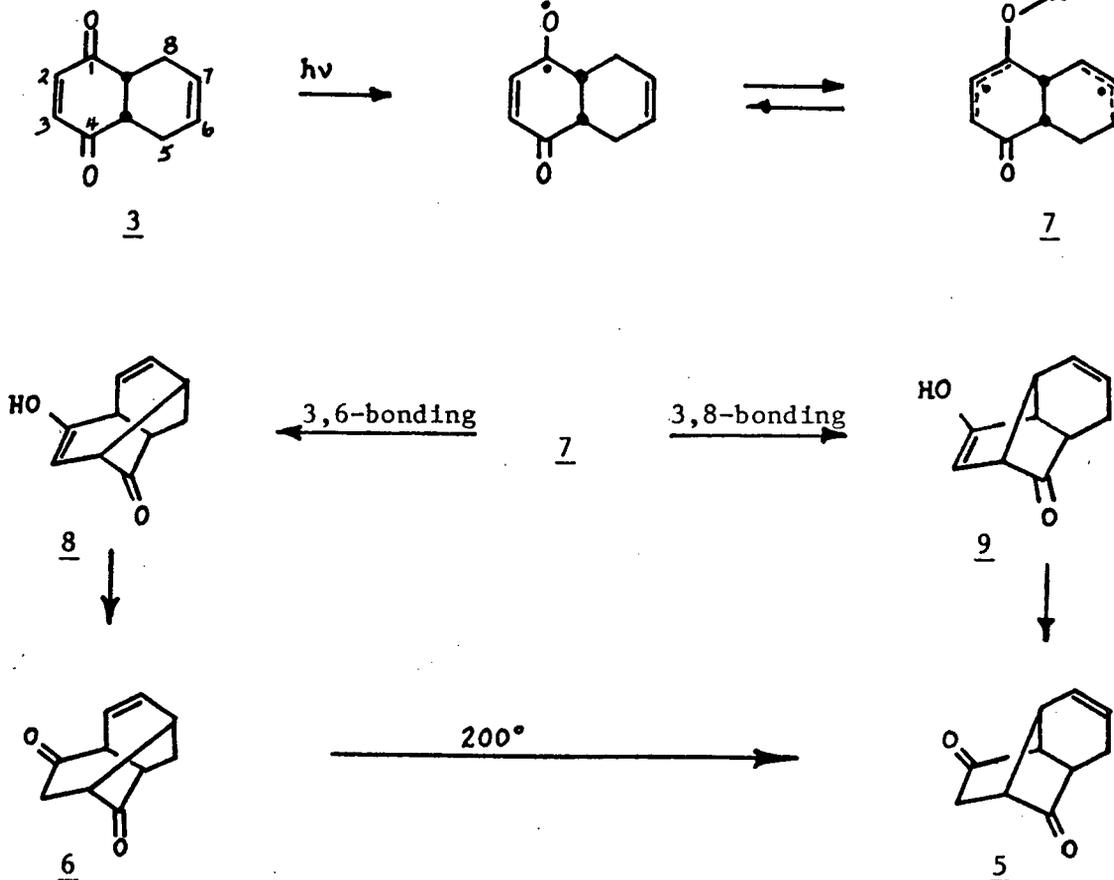
The proposed mechanism for the formation of these products is presented in Scheme 1. This involved the novel hydrogen abstraction by the carbonyl oxygen through a five-membered transition state to give a bis-allylic biradical 7. Bonding at different termini of the allylic radicals leads to the formation of enols 9 and 8, which upon ketonization yield the observed products 5 and 6.

The successful investigation of compound 1 led our research team to study the effect of substituents on the photochemistry of the tetrahydronaphthoquinone ring. In the case of the 6,7-dimethyl-4 α β ,5,8,8 α β -tetrahydro-1,4-naphthoquinone 10,¹² aside from the products analogous to 5 and 6, a new product 13 was observed (Scheme 2). This new product formed from the photolysis of 10 in benzene, can also be formed through a bis-allylic biradical intermediate as suggested for the unsubstituted case.

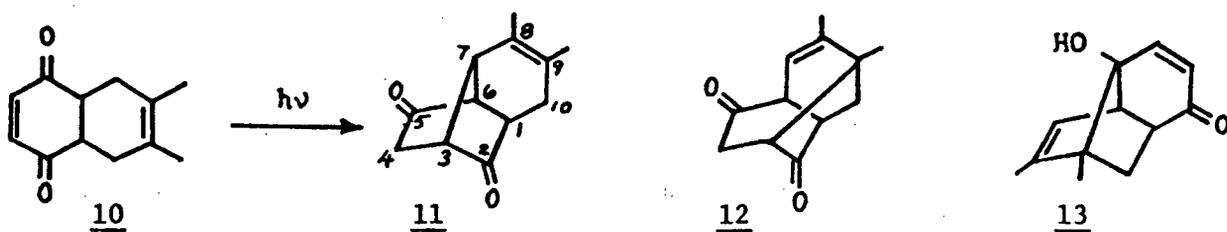
The photolysis of the enone-alcohol 13 in tert-butanol gave rise to ene-dione 11, and photolysis in benzene afforded ene-dione 12, showing the same solvent dependence as the photolysis of 10. This observation gave added strength to the argument of a common intermediate such as 14 in both photoreactions.

Scheme 1

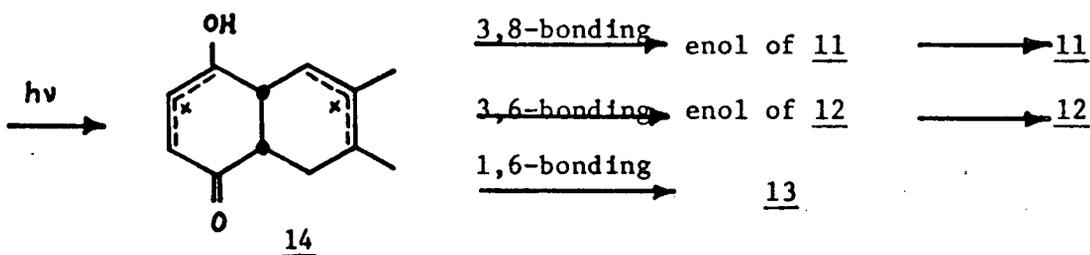
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Scheme 2



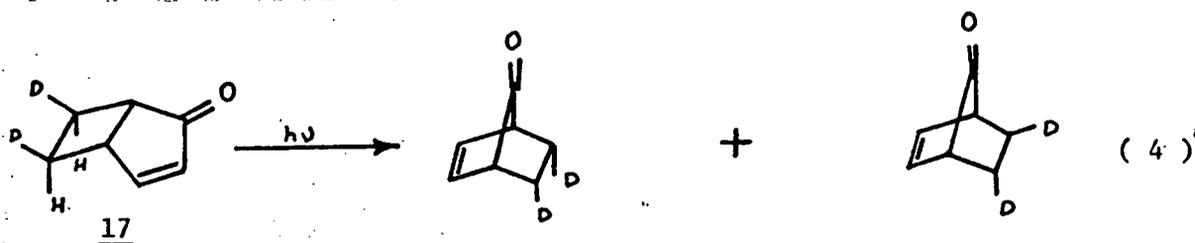
benzene	-	:	1	:	2
<u>tert</u> -butanol	1	:	-	:	-



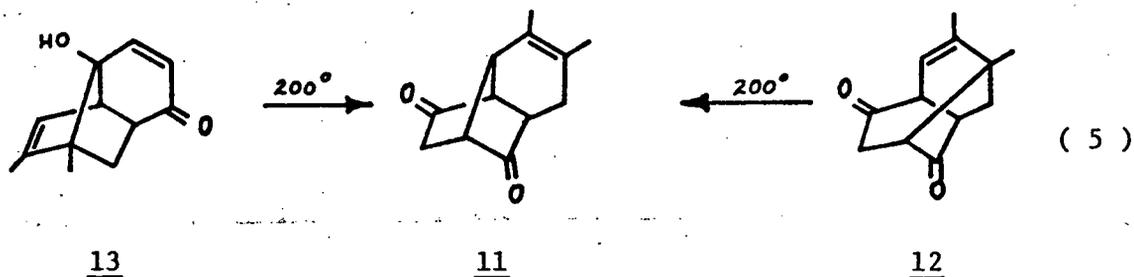
(x, x = •, • or +, -)

The formation of ene-dione 11 from the enone-alcohol 13 is formally a [3,3]-suprafacial sigmatropic rearrangement, however, this process is not allowed photochemically to be concerted.¹³

The formation of ene-dione 12 from the alcohol 13 on the other hand is formally a [1,3]-suprafacial sigmatropic rearrangement. This process is allowed by the Woodward Hoffmann rules.¹³ Nevertheless, the study by Cargill et al¹⁴ on compound 17 suggested that the 1,3 shift of the γ -carbon in the α,β -unsaturated ketone could occur in a nonconcerted mode.



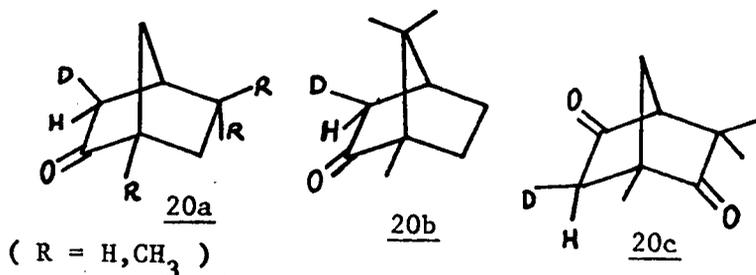
Both the thermolysis of the alcohol 13 and of the ene-dione 12 led to the exclusive formation of ene-dione 11. It is probably the presence of a more substituted double bond which makes dione 11 thermodynamically more stable.



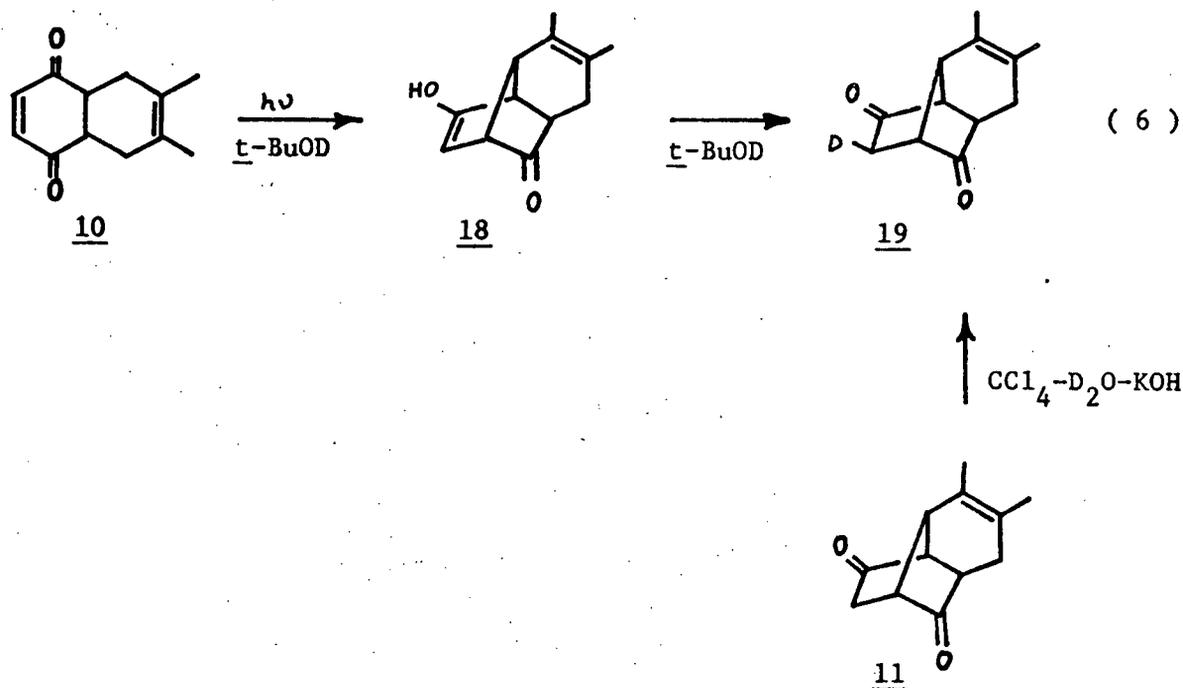
The alcohol 13 can give rise to product 11 in an allowed [3,3]-suprafacial sigmatropic rearrangement. However, the thermal reaction

of dione 12 to give 11 may not occur in a concerted manner because this would involve a forbidden [1,3]-suprafacial rearrangement.¹³

Experiments using *tert*-butanol-*O*-d as a solvent for the photolysis of compound 10 gave rise to the *exo*-deuterated ene-dione 19. The same product was obtained by the base-catalyzed deuterium exchange of ene-dione 11. Studies by Thomas¹⁵, and Werstiuk¹⁶ on base catalyzed deuteration of several methyl substituted bicyclo[2.2.1]heptanones also resulted in the preferential deuteration of the *exo* position on the carbon

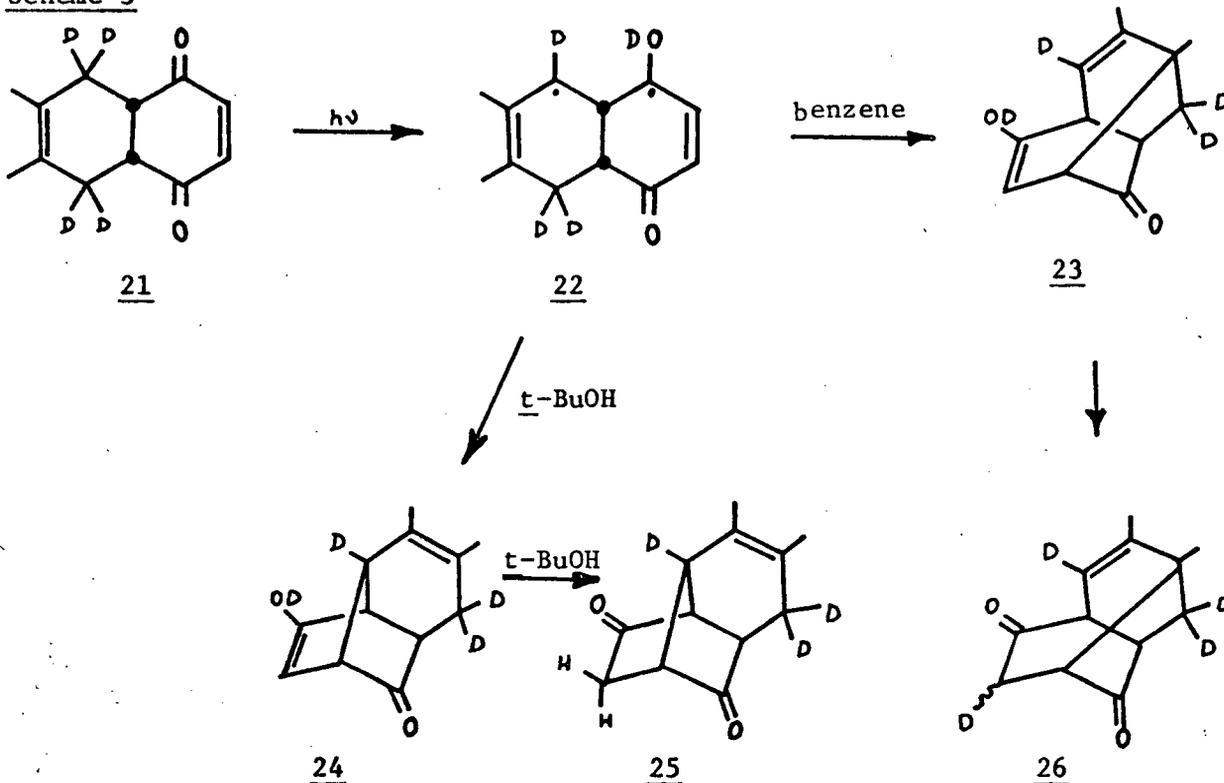


adjacent to the carbonyl cf. 20. These experiments proved the intermediacy of the enol 18 in the photochemical reaction.



Finally a tetradeuterated form 21 of quinone 10 was photolyzed both in benzene and in tert-butanol.

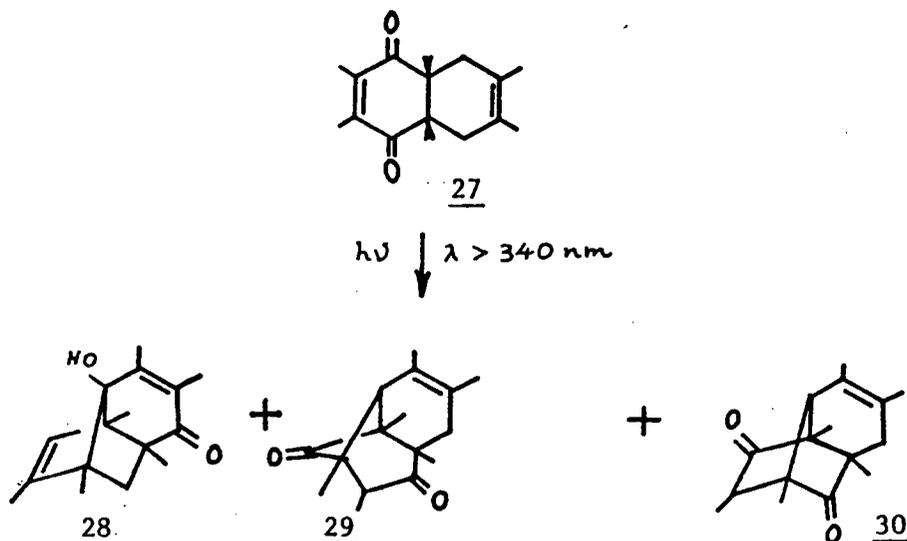
Scheme 3



The experiment was designed to test the hypothesis of β -hydrogen abstraction by oxygen and enol formation. Note that in tert-butanol, the enol deuterium can exchange with the solvent, resulting in a compound with only 3.0 D. This was in fact observed. In benzene, 60% D was found at C₄, cf., 26. This was explained on the basis that the remainder had exchanged for hydrogen due to some moisture present in the benzene.

The investigation of the effect of substituents on the photolysis of tetrahydro-1,4-naphthoquinones led to the study of the hexamethyl substituted compound 27.¹⁷ It was anticipated that this compound might react in a manner different from its less substituted analogues.¹⁸ The $\lambda > 340$ nm photolysis of 27 led to three products (Scheme 4).

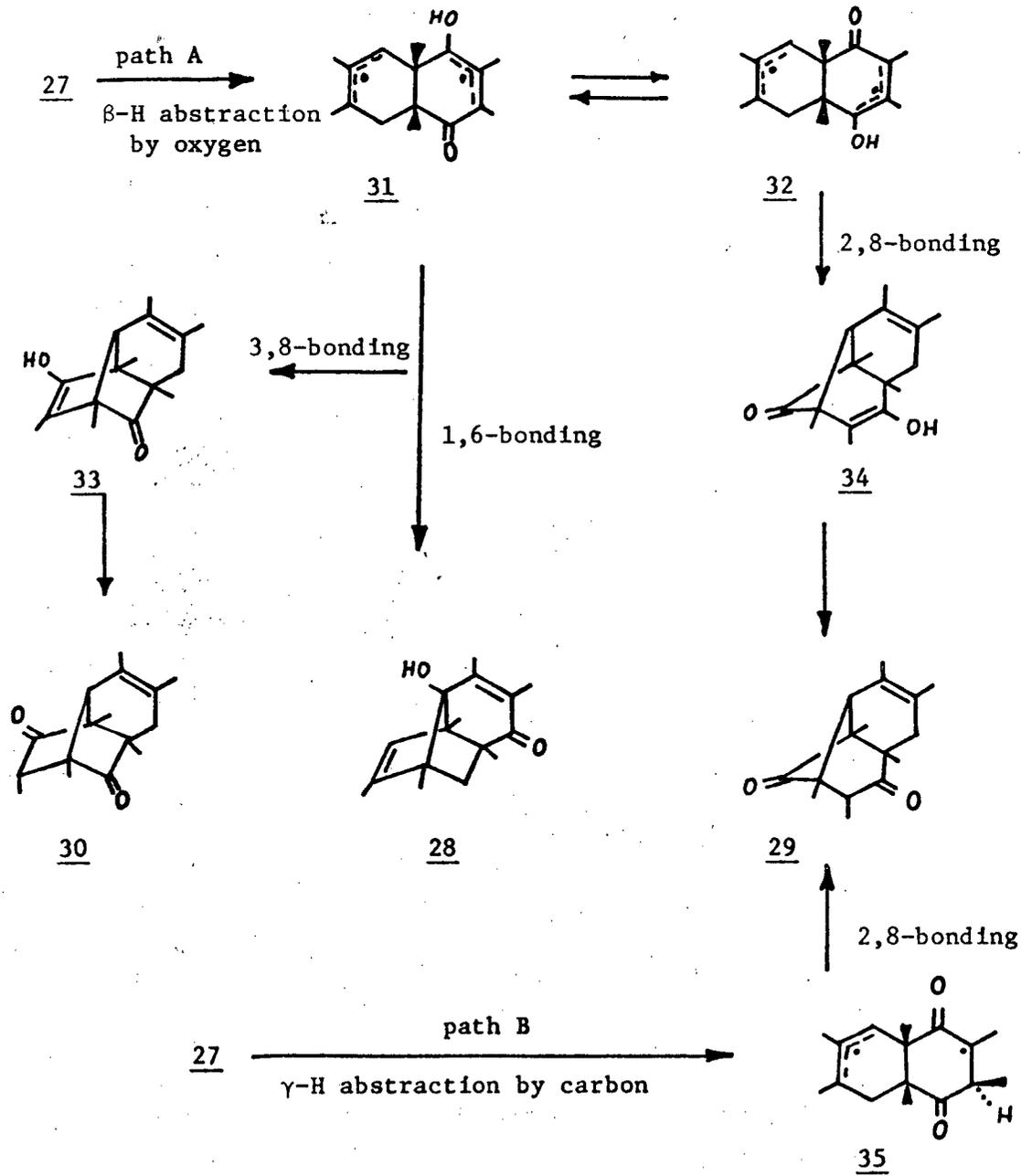
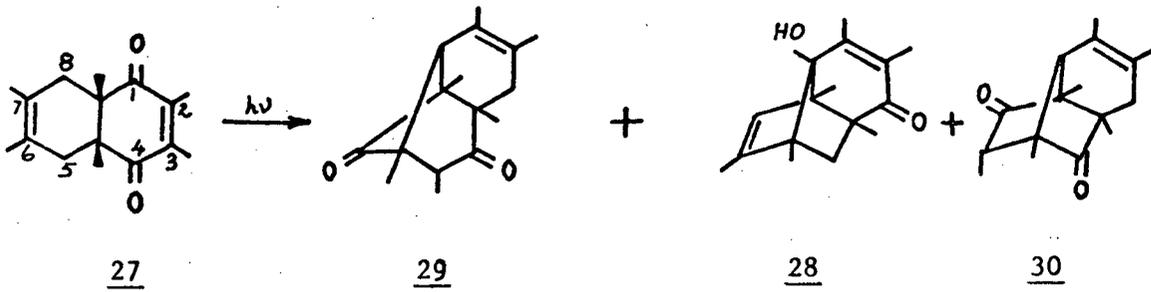
Scheme 4



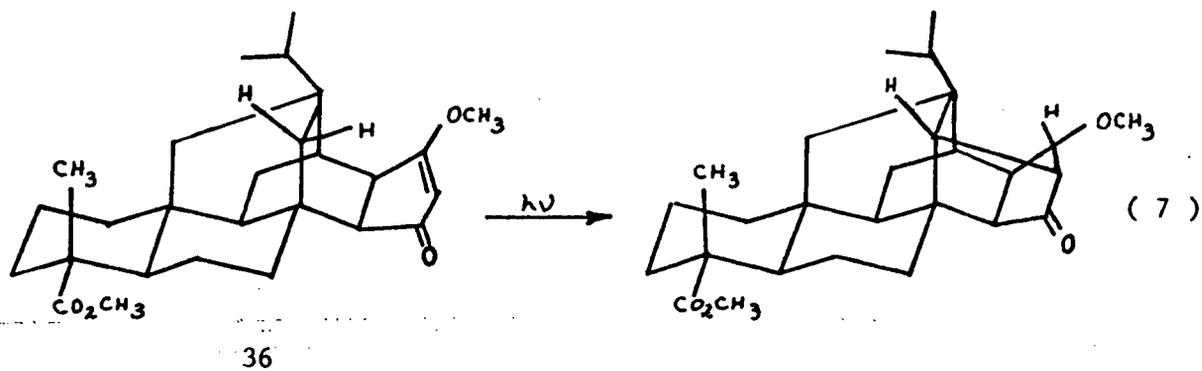
Relative Ratios

benzene	0.5	1.0	-
<u>t</u> -BuOH	1.1	1.0	-
CH ₃ CN	4.0	1.0	-
MeOH	13	1	2
dioxane-H ₂ O	30	1	6

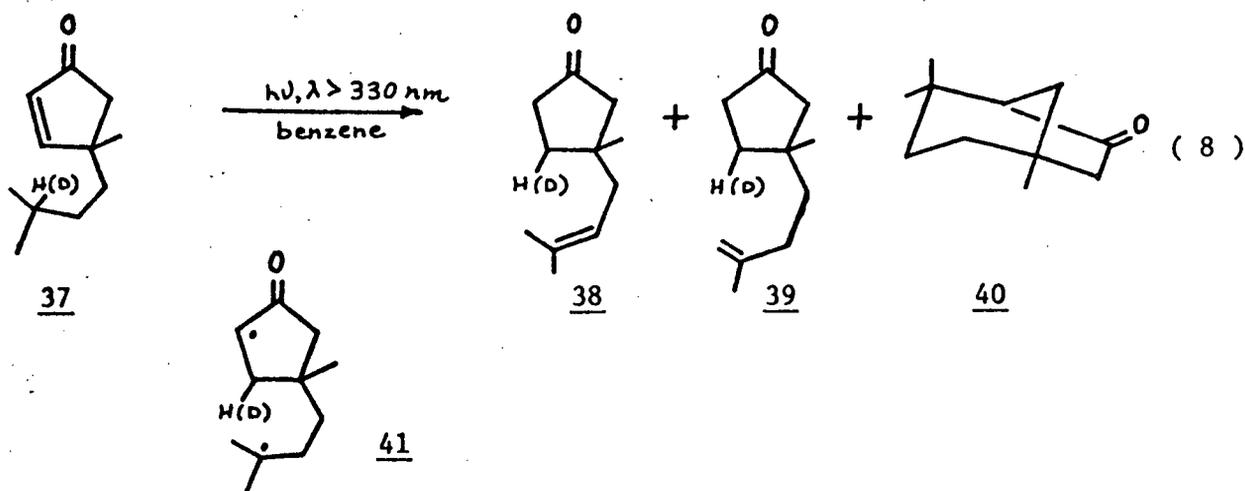
Scheme 5



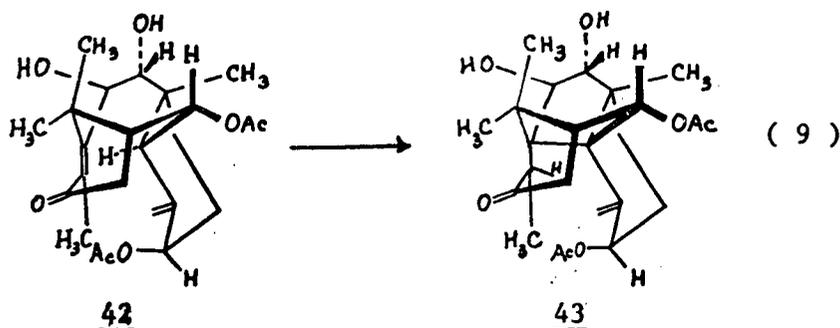
The structure of the enone-alcohol 28 was identified by X-ray analysis. The formation of both products 28 and 30 can be rationalized by invoking the intermediacy of a bis-allylic biradical species 31 (scheme 5) formed via β -hydrogen abstraction by oxygen. Similarly, the formation of the ene-dione 29 can be thought of as arising from intermediate 32.



This intermediate can be formed from biradical 31 by a shift of the hydroxyl hydrogen. The intermediate thus formed can close, giving the enol 34 which upon ketonization, gives product 29.¹⁹ However, a second mechanism (B) can be visualized. This involves a γ -hydrogen abstraction by a β carbon atom on the quinone ring to give intermediate 35. Collapse of the biradical yields the ene-dione 29 directly, without involving an enol. Hydrogen abstraction by a β enone carbon atom has been observed by Herz and Nair²⁰ in the photolysis of 36, and by Agosta et al²¹ in the photolysis of various cyclopentenones.

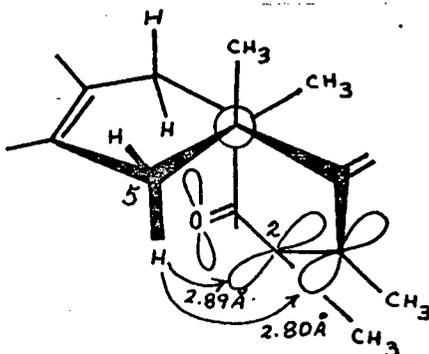


In the case of cyclopentenone 37, this was suggested to occur through a six-membered transition state resulting in the formation of biradical 41. Closure affords the bicyclic structure 40. Structures 38 and 39 arise from 41 by a second hydrogen abstraction, but this time by the carbon α to the carbonyl. The reaction was believed to arise via a triplet state based on the evidence of the effect of quenchers and sensitizers. Similarly, Nakanishi, et. al.²² found that taxinines such as 42 underwent photoinduced H-abstraction by an α -enone carbon atom to yield structures like 43. Once again, sensitization studies suggested that the reaction proceeded via a triplet state.



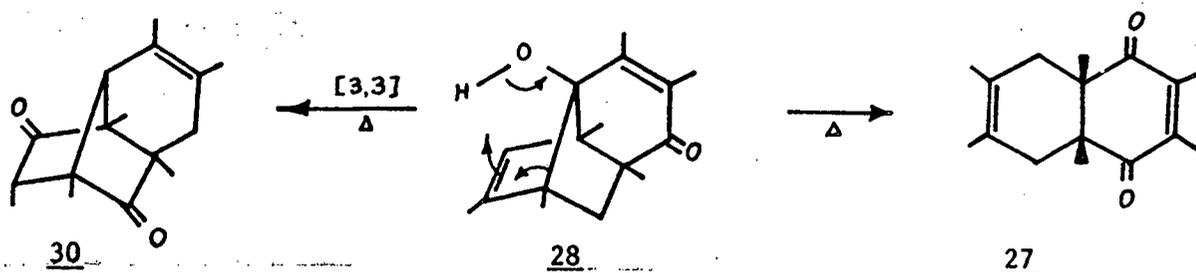
The photolysis of the tetrahydronaphthoquinone 27 in tert-butanol- O - d and in 1:1 dioxane/deuterium oxide showed no incorporation of deuterium in the ene-dione 29. In the latter more polar solvent, ene-dione 30 was formed containing exactly one deuterium per molecule in the 4 exo position as expected. This evidence thus gave support to the mechanism for ene-dione 29 formation not involving an enol intermediate. Thus, it is likely that the ene-dione 29 arises by a mechanism involving γ -hydrogen abstraction by the enone carbon (path B), whereas enone-alcohol 28 and ene-dione 30 arise through initial β -hydrogen abstraction by oxygen.

The γ -hydrogen abstraction by carbon (i.e., transfer of hydrogen from C_5 to C_2) may be facilitated in the photolysis of compound 27 by the effect of the bridgehead methyl groups. An X-ray study of 27²³ revealed that these methyls, to remain staggered, hold rings A and B in close proximity. This arrangement places the abstracted "down" hydrogen at C_5 close to the abstracting p-orbital at carbon 2.



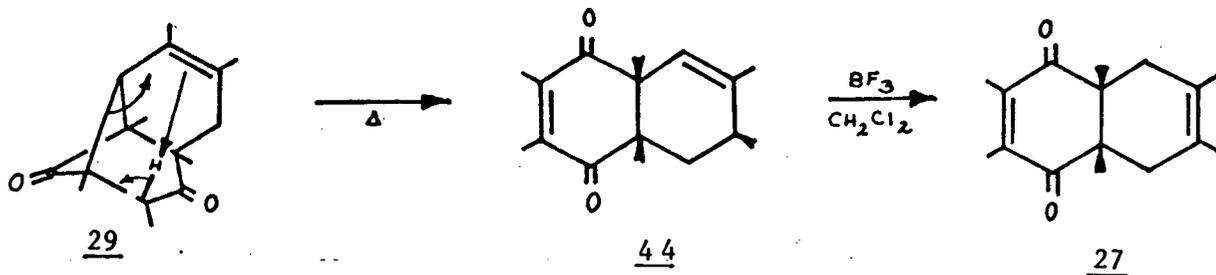
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Thermolysis of the alcohol 28 resulted in the conversion to ene-dione 30 and to quinone 27. The former reaction can formally be considered as an allowed [3,3] - suprafacial sigmatropic rearrangement. The latter has been suggested¹⁷ to occur through an oxy-retro-ene reaction²⁴ (see arrows in equation (10)).



(10)

Thermolysis of the ene-dione 29 resulted in the formation of the naphthoquinone 44. Its mechanism was postulated to be a retro-ene reaction²⁴ (see arrows in equation 11).



(11)

The driving force for the reaction is probably in part due to relief of strain of the cyclobutanone ring and the formation of a highly conjugated chromophore.

C. Objectives of the Present Research

The main objective of this work was to try to elucidate the electronic states involved in the photolysis of the tetrahydronaphthoquinones 10 and 27. It was hoped that this knowledge might shed further light on the exact nature of the mechanism for the formation of all the observed photoproducts of 10 and 27.

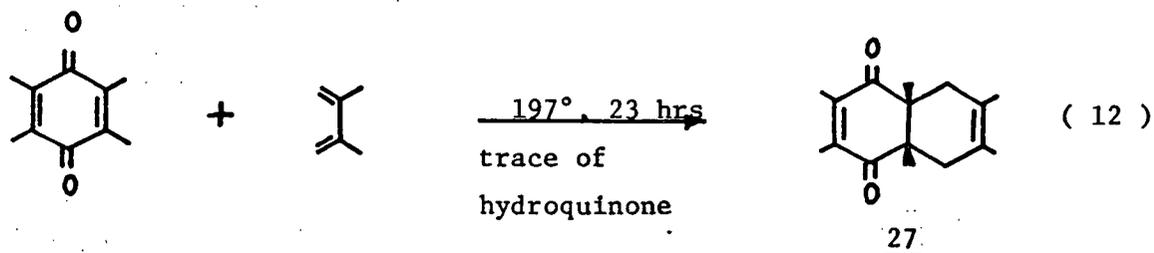
In the case of the photolysis of compounds 10 and 27, literature analogy suggested that a singlet state might form the enone alcohols 13 and 28 and the ene-diones 11, 12, and 30 while a triplet state might lead to the ene-dione 29. Thus Agosta has recently found that β -hydrogen abstraction by oxygen typically occurs from a singlet state²⁵ whereas γ -hydrogen abstraction by a carbon β to a carbonyl is commonly a triplet process.²¹ In the case of triplet reactions it was hoped that diffusion controlled quenching might be achieved in order to obtain values for the rates of reaction.

RESULTS & DISCUSSION

A. Quantum Yield Studies of 2,3,4a β ,6,7,8a β -Hexamethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone(27) in Benzene.

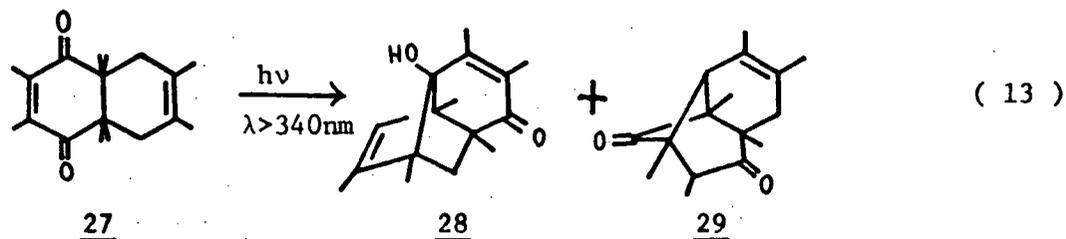
1. Synthesis and Photolysis.

The method of Ansell et al²⁶ was followed for the preparation of 27. This material was photolyzed on a large scale (2.5 gm/400ml of benzene) using a filter transparent to $\lambda > 340$ nm.



The two products formed were isolated by column chromatography to yield 54% of the ene-dione 29 and 27% of the enone-alcohol 28.¹⁹

Gipc response curves were obtained for the response of the flame ionization detector to each of the two photoproducts compared to biphenyl used as internal standard.



2. Unquenched Quantum Yield Measurements.

A series of 366 nm photolyses of 0.015 M degassed solutions of 27 in benzene were carried out. A 15 ml portion of the photolysate was combined with a 2 ml of a stock solution of biphenyl (internal standard) in benzene. Glpc analysis determined the amount of each of the photoproducts formed. The measurement of the amount of ferrous ion produced in the actinometer reference cells yielded information on the amount of light absorbed by the test solution. The unquenched yield (ϕ_0) was determined for each photoproduct and listed in Table 1.

TABLE 1

<u>% Conversion of 27</u>	Quantum Yield of Formation of ene-dione <u>29</u>	Quantum Yield of Formation of alcohol <u>28</u>
1.4	0.086	0.069
1.2	0.084	0.066
1.2	0.088	0.066
3.6	0.088	0.064
6.9	0.094	0.070
13.3	0.093	0.066
13.3	0.093	0.066
14.3	0.089	0.060

The mean quantum yield for the formation of ene-dione 29 was calculated to be 0.089 ± 0.003 , and for the formation of enone-alcohol 28 the mean quantum yield was 0.066 ± 0.003 .

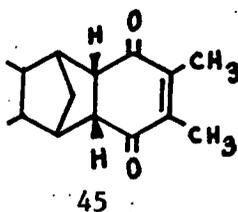
The percent conversion of 27 to photoproducts was kept low since both photoproducts are able to absorb 366 nm light. At high conversion percentages, one would thus expect the quantum yield for formation of

photoproducts to decrease. In addition it is conceivable (although unlikely) that photoproduct 28 could undergo secondary photolysis to afford ene-dione 29. In this case the quantum yield of formation of 29 should increase with time.

To test whether the observed quantum yields were due to primary processes, the length of irradiation was varied (Table 1). A ten-fold variation failed to have significant effect on the quantum yield of formation of 28 and 29. This indicated that complications due to photoproduct absorption and/or secondary photoreactions were insignificant under the conditions employed.

3. Photolysis of 27 using Piperylene as Quencher.

To study the effect of triplet energy quenchers on the photoreaction of 27 it was necessary to locate first of all, the position of the triplet energy of 27. Bartrop and co-workers²⁷ were able to observe the phosphorescence spectrum of 45 and calculated from the position of the 0-0 band, $E_T = 57.8 \pm 1.2$ kcal/mole.



Piperylene (a 1:1.89²⁸ mixture of cis- and trans-1,3-pentadiene) was used to help locate the triplet energy of 27. Piperylene has an average triplet energy of 58.1 kcal/mole ($E_T = 56.9$ kcal/mole, $E_{T\text{trans}} = 58.8$ kcal/mole),²⁹ but can quench systems as low as 56.9 kcal/mole.

A 0.0154 M solution of 27 with piperylene (0.597 M) in benzene

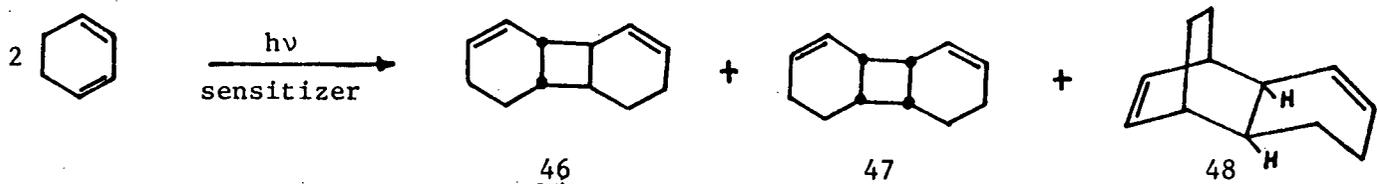
was photolyzed at 366 nm. This resulted in some quenching of the formation of ene-dione 29 $\phi = 0.025$ ($\phi_0 = 0.089 \pm 0.003$) and no appreciable effect on the formation of the alcohol 28, $\phi = 0.064$ ($\phi_0 = 0.066 \pm 0.003$). This indeed suggested that the triplet energy of 27 should lie above 57 kcal/mole.

4. Photolysis of 27 Using 1,3-Cyclohexadiene as Quencher.

To undertake meaningful studies of the effect of quenchers on photoreactions it is desirable to know whether quenching will occur at a diffusion controlled rate. If this rate is not approached, then the quenching efficiency may be very low and little information may be obtained as to the nature of the photoreaction. If one considers the case of a fast triplet reaction, then the lower the quenching efficiency of the triplet quencher becomes, the closer the reaction will appear to proceed through a singlet state.

Porter and Wilkinson³⁰ have suggested that bimolecular triplet energy transfer, exothermic by more than 3 kcal/mole, is diffusion controlled.

For this reason, 1,3-cyclohexadiene ($E_T = 53.0$ kcal/mole)²⁹ was chosen as a triplet quencher for the photoreaction of 27. A series of 366 nm photolyses were conducted on 0.015 M degassed solutions of 27 in benzene with varying amounts of 1,3-cyclohexadiene. The formation of dimers 46 and 47 of 1,3-cyclohexadiene was observed by glpc. Dimer formation is normally associated with triplet energy transfer to the quencher. Hammond, et al,³¹ reported the formation of three major product dimers 46, 47, and 48 for the triplet sensitized reaction of 1,3-cyclohexadiene.



(14)

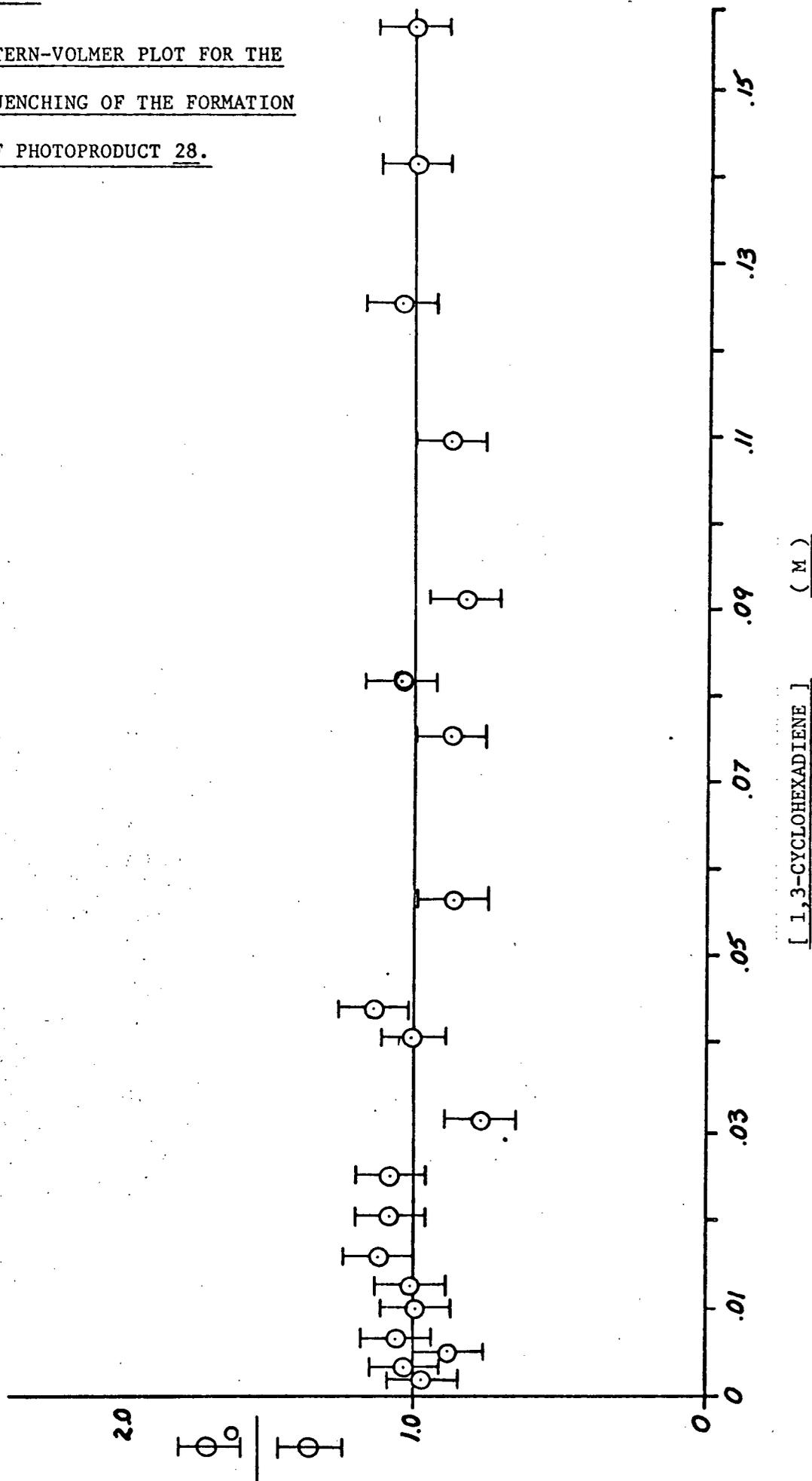
The quenching results (graphs 1 and 2) indicate that the formation of the ene-dione 29 proceeds through a triplet excited state whereas the formation of the enone-alcohol either via a singlet excited state or via a very short-lived triplet.

It is important to note the non-linear effect of changing quencher concentration at concentration levels > 0.1 M on the quantum yield for formation of ene-dione 29. This type of positive curvature was observed as well by Wagner³² in the quenching of γ -methylvalerophone by 2,4-hexadiene-1-ol. Wagner suggested that such an effect indicates quenching is occurring at a rate greater than diffusion controlled. His argument was that at quencher concentrations higher than ~ 0.1 M a significant number of excited state molecules will have, the instant they are formed, a quencher molecule as nearest neighbour. If exothermic energy transfer to the quencher is 100% efficient, that portion of the excited molecules "born" with quencher molecules as nearest neighbours will be quenched immediately. These molecules will thus never enter into normal competition between photoreaction and diffusion controlled quenching. The equation suggested for such a situation was:

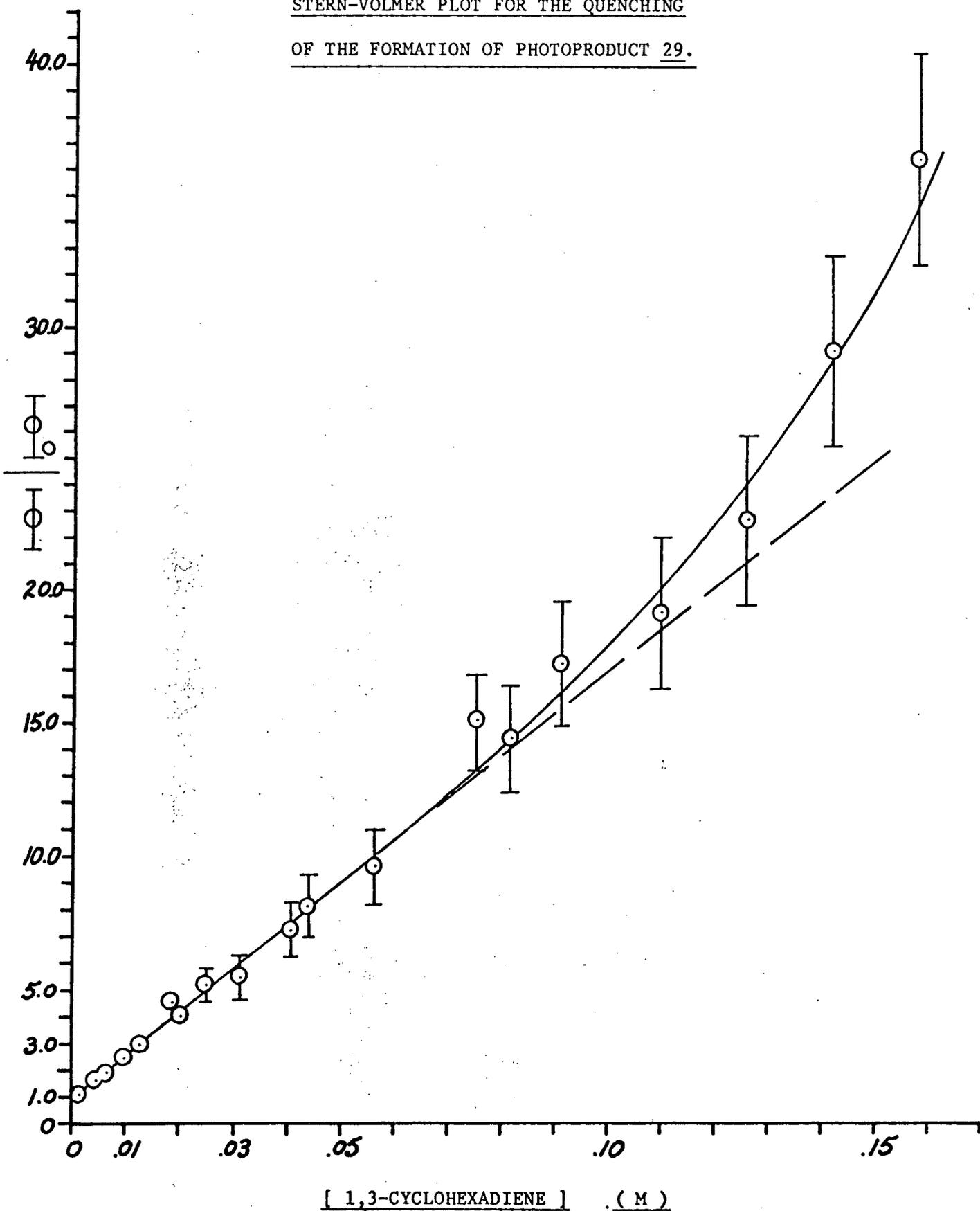
$$\frac{\phi_o}{\phi} = \frac{1 + k_q \tau [Q]}{1 - \alpha \mu}$$

where α = the probability that energy will be transferred to the quencher during an encounter and μ = the fraction of donor molecules which have at least one quencher

STERN-VOLMER PLOT FOR THE
QUENCHING OF THE FORMATION
OF PHOTOPRODUCT 28.



STERN-VOLMER PLOT FOR THE QUENCHING
OF THE FORMATION OF PHOTOPRODUCT 29.



molecule as nearest neighbour. When triplet energy transfer is truly diffusion controlled then $\alpha = 1$.

The least squares slope³³ for the quenching curve of ene-dione 29 formation at quencher concentration below 0.08 M was $158 \pm 70 \text{ M}^{-1}$ (99.9 % confidence limit), and for the quenching of the alcohol 28 the slope was $-0.03 \pm 10 \text{ M}^{-1}$.

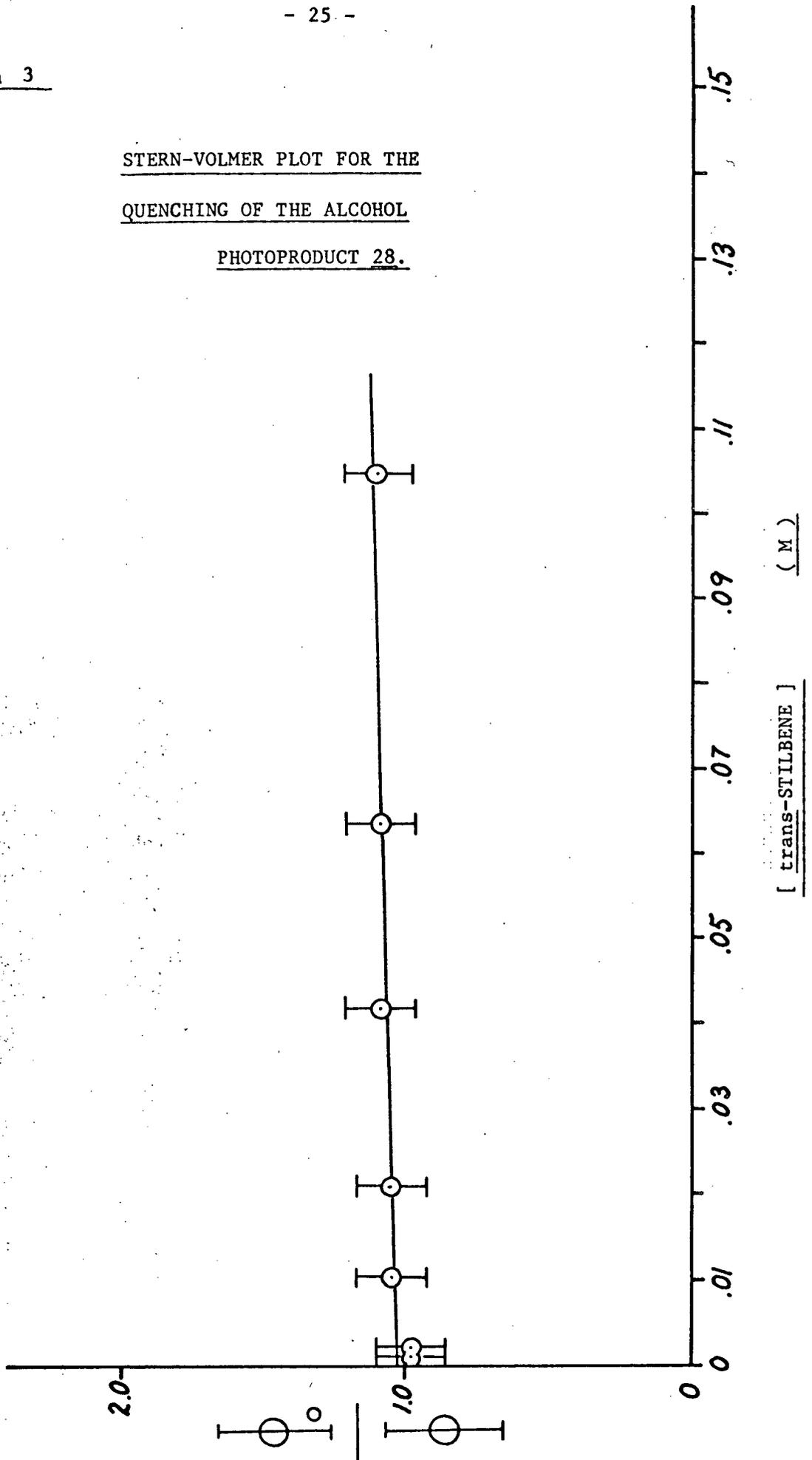
5. Photolysis of 27 Using trans-Stilbene as Quencher.

trans-Stilbene ($E_T = 49 \text{ kcal/mole}$) was also used as a triplet quencher for the photoreaction of 27. The purpose of these experiments was to test the hypothesis that 1,3-cyclohexadiene quenching was diffusion controlled, a conclusion that may be drawn if the quenching curves are the same for both quenchers. For example, Zimmerman³⁴ found that the rate of quenching of triplet excited 4,4-diphenylcyclohexenone ($E_T = 69 \text{ kcal/mole}$) by naphthalene ($E_T = 61 \text{ kcal/mole}$) did not seem to be diffusion controlled. Only when 2,5-dimethyl-2,4-hexadiene ($E_T = 58 \text{ kcal/mole}$) was used did the rate of quenching appear to be diffusion controlled. This conclusion was strengthened by the observation that the quenching rate was not increased when 1,3-cyclohexadiene ($E_T = 53 \text{ kcal/mole}$) was used as a quencher.

trans-Stilbene isomerizes to cis-stilbene upon triplet excitation.³⁵ The two isomers are easily detected and well separated in the glpc columns used in this work (10' x 1/8" and 3' x 1/8" columns packed with 20 % DEGS on 60/80 Chromosorb W). trans-Stilbene does absorb some light at the 366 nm excitation wavelength used for photolysis ($\epsilon 0.2$) and so does cis-stilbene ($\epsilon 0.6$). However, photolyses were performed on solutions containing only trans-stilbene in benzene.

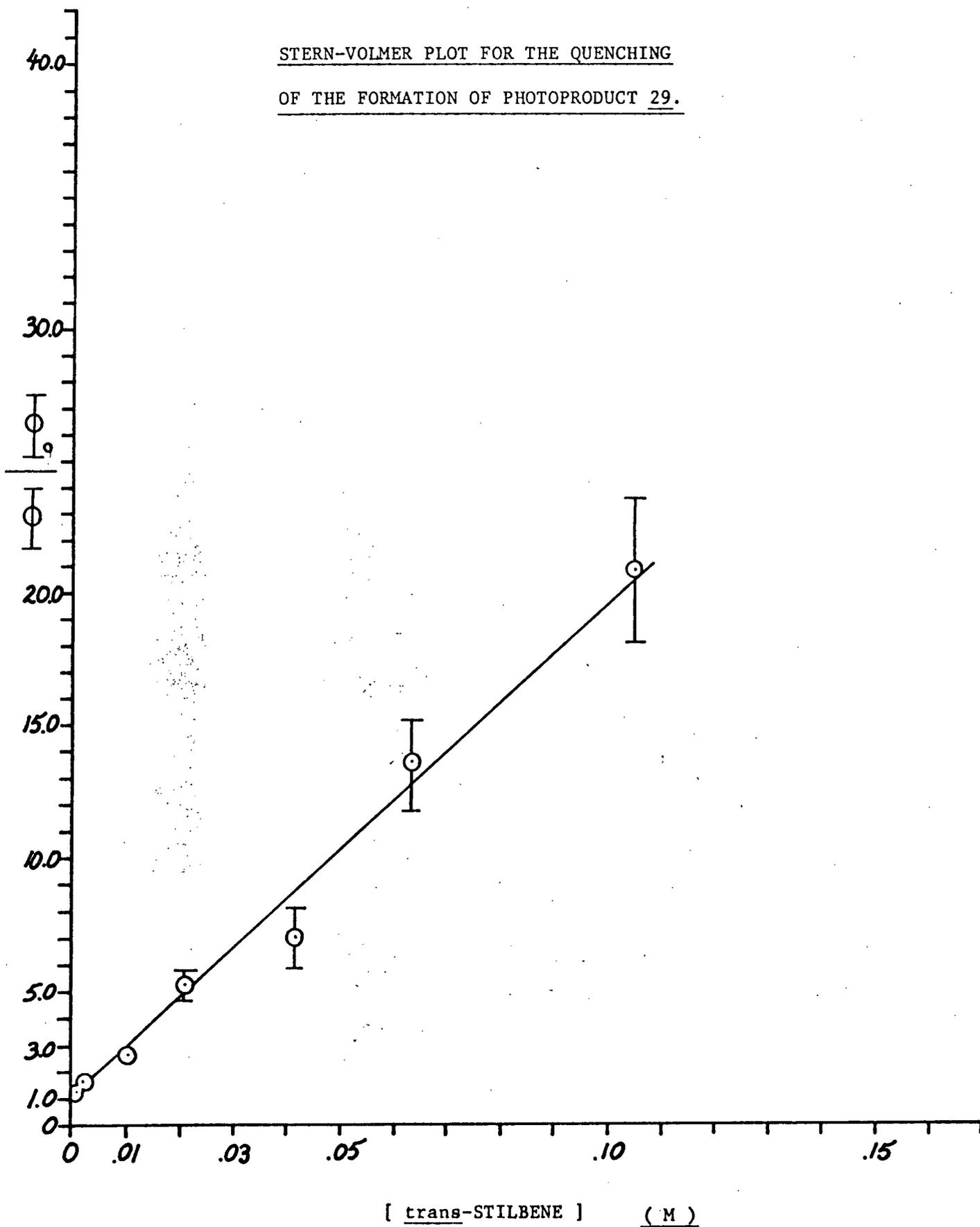
Graph 3

STERN-VOLMER PLOT FOR THE
QUENCHING OF THE ALCOHOL
PHOTOPRODUCT 28.



Graph 4

STERN-VOLMER PLOT FOR THE QUENCHING
OF THE FORMATION OF PHOTOPRODUCT 29.



The results indicated that the conversion of trans-stilbene to cis-stilbene by direct absorption of light represented about one fifth of the total of conversion of trans-stilbene to cis-stilbene in the sensitized experiments.

Once again the data obtained for the quenching of 27 by trans-stilbene was plotted in graphs 3 and 4 as the ratio ϕ_0 / ϕ versus trans-stilbene concentration. These Stern-Volmer plots show a slight increase in quenching rates by trans-stilbene as compared to 1,3-cyclohexadiene.

The slope for the least squares plot (graph 4) of quenching of ene-dione 29 was calculated to be $186 \pm 86 \text{ M}^{-1}$ (99.5 % confidence limit). The slope for the alcohol quenching plot (graph 3) was calculated by least squares to be $0.92 \pm 5.1 \text{ M}^{-1}$ (99.9 % confidence limits).

The variation in slopes between the plots for quenching by 1,3-cyclohexadiene and trans-stilbene of the quantum yield of formation of 28 and 29 may reflect the effect of absorption of light by trans-stilbene. This conclusion was reached by considering that the formation of enone-alcohol 28 was totally unquenched by 1,3-cyclohexadiene quencher (graph) when triplet energy transfer from 27 to the quencher was indicated by quencher dimer formation and when the formation of ene-dione 29 was 97 % quenched. Thus if 28 is unquenchable by using 1,3-cyclohexadiene as quencher it should also be unquenchable when using trans-stilbene.

Even so, the slopes of quenching of ene-dione 29 by both trans-stilbene ($186 \pm 86 \text{ M}^{-1}$) and 1,3-cyclohexadiene ($158 \pm 70 \text{ M}^{-1}$) are within experimental errors. Since the triplet energy separation for the two quenchers is 4 kcal, the comparable slopes suggest that quenching by 1,3-cyclohexadiene is controlled by diffusion.

and stilbene.

Barltrop²⁸ in his studies of the photoreaction of 1,4-quinones (including 45) with olefins, used trans-stilbene as one of the olefins. The experiment showed that the 1,4-quinone was deactivated by energy transfer, but no photoreaction between the 1,4-quinone and trans-stilbene was observed.

trans-Stilbene would thus not be expected to react chemically with 27. The fact that the quenching results of 27 are the same for both trans-stilbene and 1,3-cyclohexadiene rules out chemical quenching for either.

The Stern-Volmer equation for the plot ϕ_o / ϕ versus [Q] is:

$$\frac{\phi_o}{\phi} = 1 + k_q \tau [Q]$$

and the slope is $k_q \tau$ (τ = triplet state lifetime). The bimolecular diffusion controlled rate constant for benzene is $1.0 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$,⁹ and assuming this value for the quenching rate constant (k_q) then the triplet lifetime can be calculated from the slope quenching by 1,3-cyclohexadiene, $\tau = 1.58 \times 10^{-8} \text{ sec}$.

6. Photolysis of 27 Using Oxygen as Quencher.

Oxygen was used as a quencher in diagnostic tests for the participation of triplet states in the photolysis of 27. Oxygen is a very efficient quencher of triplet states. The purpose of its use was to determine if the formation of the alcohol photoproduct 28 could be quenched at all. Two experiments were performed on 0.015 M solutions of 27 in benzene which were degassed and then repressurized to one atmosphere with oxygen. The concentration of oxygen was calculated to be ca. 0.01 M.³⁶

The formation of ene-dione 29 was quenched as expected, $\phi = 0.0014$

($\phi_0 = 0.089$). However, it is important to note that the amount of quenching was greater than expected by the diffusion controlled rate (by comparison to 1,3-cyclohexadiene and to trans-stilbene). It is known that oxygen can successfully quench the formation of compounds that arise from free-radical intermediates by chemical reaction.³⁷ It is possible that this may be the reason for the exaggerated quenching effect by oxygen on the formation of ene-dione 29.

The formation of the enone-alcohol 28 was also quenched but to a small extent, $\phi = 0.043$ ($\phi_0 = 0.066$). Again, it is entirely possible that this quenching does not reflect only quenching of a triplet intermediate but also reaction with a biradical intermediate which is removed by oxygen.

The results for oxygen quenching are not conclusive. They reaffirm nevertheless, the observation that the ene-dione 29 arises from a triplet state.

7. Photolysis of 27 : Effect of Changing the Concentration of 27.

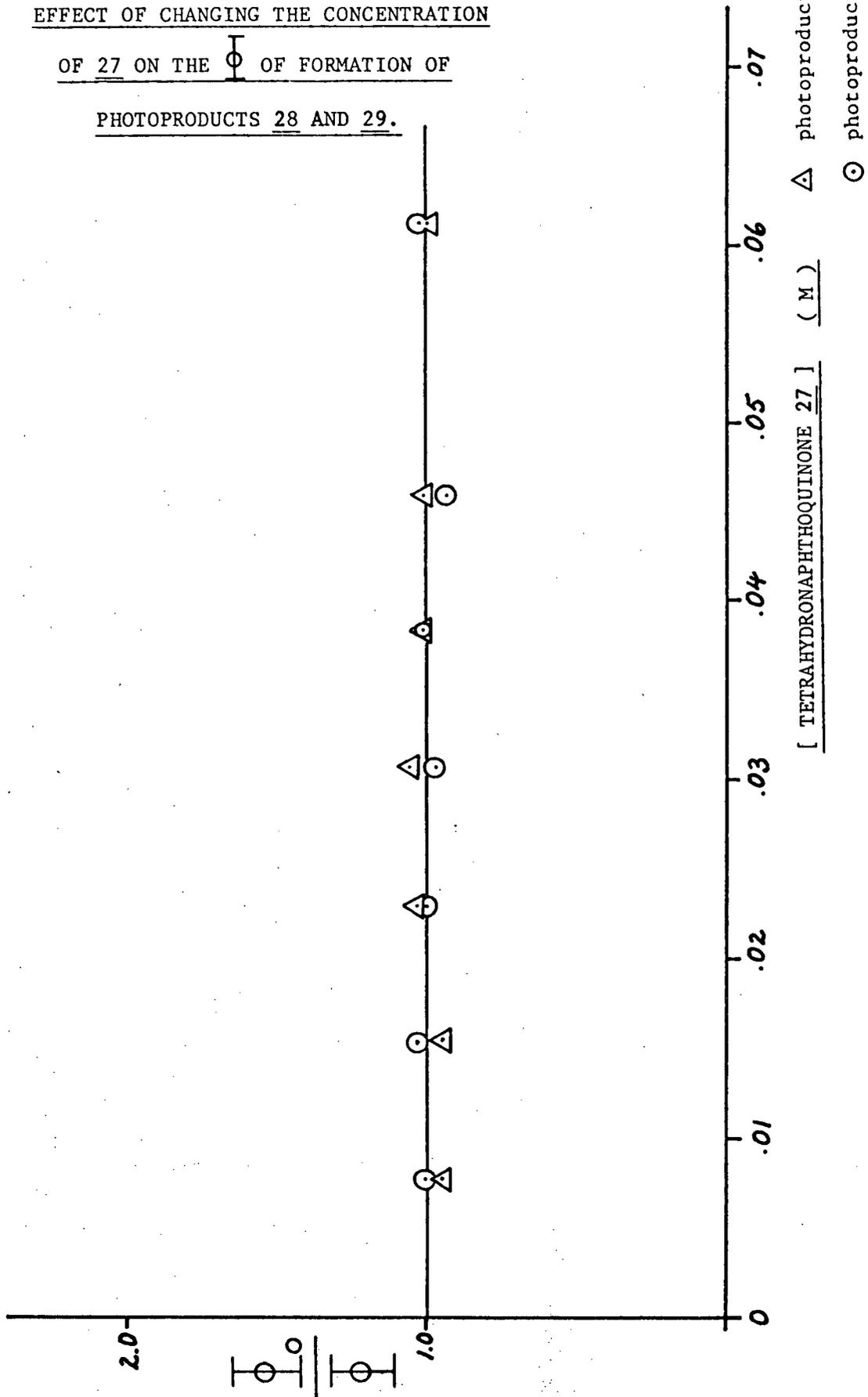
These experiments were designed to determine to what extent if any, the formation of "excimers" (excited dimers)³⁸ were responsible for the low quantum yields of formation of the photoproducts of 27.

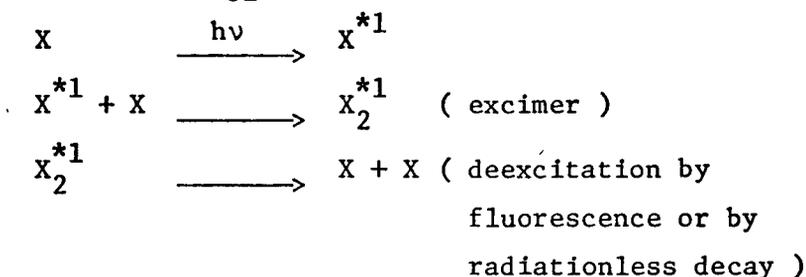
The term "excimer" is used to describe the excited complex formed as a consequence of the interaction of an excited and ground-state molecule. This complex is stable only in the excited state. After deexcitation the two partners repel each other as ground state monomers.

The phenomenon of self-quenching via excimer formation has recently been demonstrated in several systems,³⁹ and the mechanism associated with it is shown below:

Graph 5

EFFECT OF CHANGING THE CONCENTRATION
OF 27 ON THE Φ OF FORMATION OF
PHOTOPRODUCTS 28 AND 29.



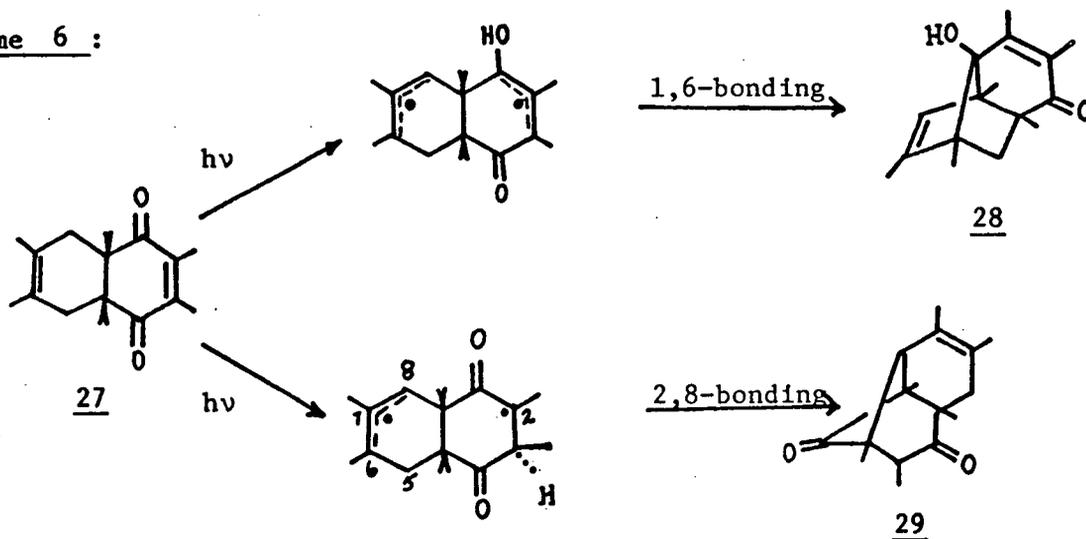


If self-quenching occurs, then a change in the concentration of the photoreactant would result in an inversely proportional change in quantum yield. The results of such experiments are plotted in graph 5 as Φ_0 / Φ versus concentration of photoreactant 27. Clearly no significant change in the quantum yields of formation of either photoproduct is observed, thus self-quenching is insignificant in this system under the conditions employed.

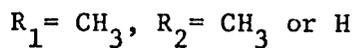
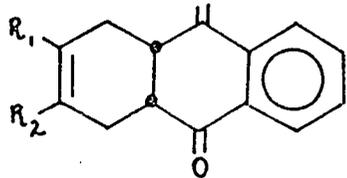
B. Interpretation of the Results of Quenching on the Photolysis of 27.

The photolysis of 27 yields both an enone-alcohol 28 and an ene-dione 29. The mechanism suggested by Gayler¹⁹ was: (a) β -Hydrogen abstraction of a C₈ hydrogen by the adjacent carbonyl oxygen. The biradical thus formed can bond C₁ to C₆ to yield 28. (b) γ -Hydrogen abstraction of a C₈ hydrogen by C₃. Bonding C₂ to C₈ of the biradical yields 29.

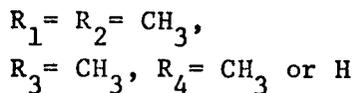
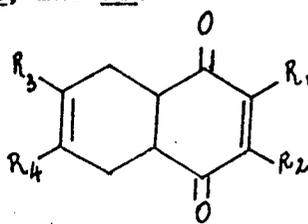
Scheme 6 :



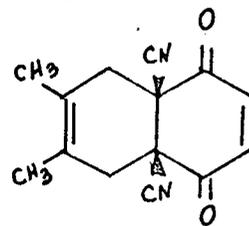
The formation of structure types of 28 was also observed in the photolysis of 49¹⁹, 50, 51, 52, and 53.⁴⁰



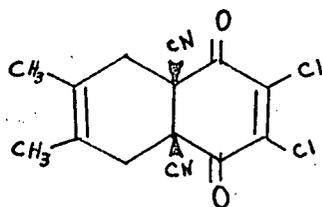
49



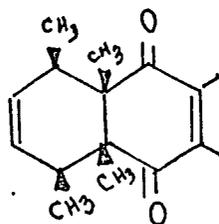
50



51



52

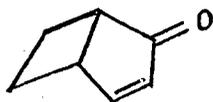


53

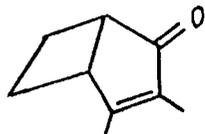
On the other hand, the formation of photoproduct type 29 is unusual in that it is only observed in the photolysis of tetrahydronaphthoquinones bearing methyl groups at the bridgehead and at carbon atoms 2 and 3, i.e. 27 and 53.

It is possible that the formation of the alcohol 28 occurs by excitation of 27 to an excited singlet by an $n - \pi^*$ transition. These $n - \pi^*$ excited systems have been shown to have reactivity similar to alkoxy free radicals and thus hydrogen abstraction by oxygen is a favourable process for these states.

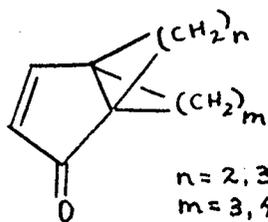
Studies by Cargill and coworkers⁴¹ on cyclopentenones showed that the lowest triplet state of 54 and 56 is an $(n, \pi^*)^3$ state whereas the lowest triplet state of 55 and 57, which have methyl



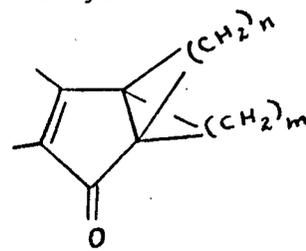
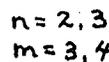
54



55



56



57

groups on the enone chromophore, is a $(\pi, \pi^*)^3$ state. It is thus possible to consider that the lowest triplet level of 27 is also a $(\pi, \pi^*)^3$ due to the effect of methyl substituents on the chromophore. Barltrop²⁷ suggested that 2+2 cycloaddition of 45, which has a similar chromophore to 27, originated from $(\pi, \pi^*)^3$. This was indicated by its lack of hydrogen abstraction from propan-2-ol and by solvent shifts in the uv absorption spectra, (π, π^* triplets of carbonyl groups do not abstract hydrogens).⁴²

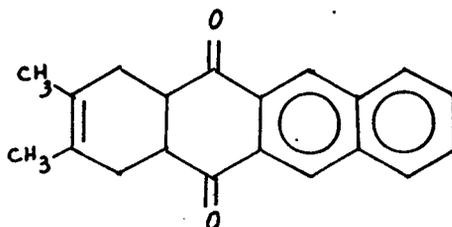
One can thus consider the hydrogen abstraction by carbon process in 27 which leads to the formation of 29 to occur via a $(\pi, \pi^*)^3$ excited state after $n \rightarrow \pi^*$ absorption by 27. The $(n, \pi^*)^3$ state is probably less likely to be populated than the lower energy $(\pi, \pi^*)^3$ state of 27. This may be a reason why no triplet products arising from hydrogen abstraction by oxygen are observed.

Notably the results are in agreement with the results of earlier investigations. The γ -hydrogen abstraction by a β -enone carbon atom was found to be a triplet process.^{21,22}

Furthermore, Schaffner has shown that hydrogen abstraction by the β -carbon of an α, β -unsaturated ketone is typical of (π, π^*) triplets.⁴³

X-ray studies of various tetrahydronaphthoquinones with and without bridgehead methyl groups indicated that the two rings are tucked close together.²³ Thus from a proximity standpoint it is possible for all such compounds to undergo γ -hydrogen abstraction by carbon, since the C_8 hydrogen is close to the π -orbital of the C_2 and C_3 carbon atoms. The fact that this is not observed in all cases suggests that a $(\pi, \pi^*)^3$ state may indeed be the factor necessary for such a hydrogen abstraction.

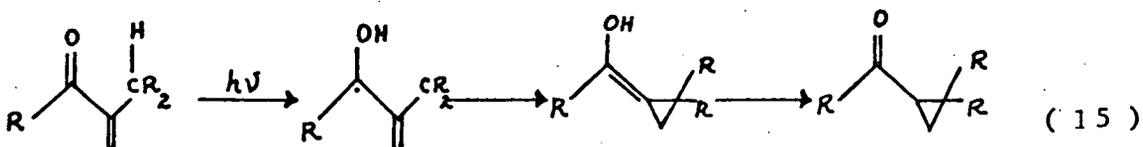
Photolysis of 49 and ⁴⁴58 does not lead to the formation of the analogue of dione 29.



58

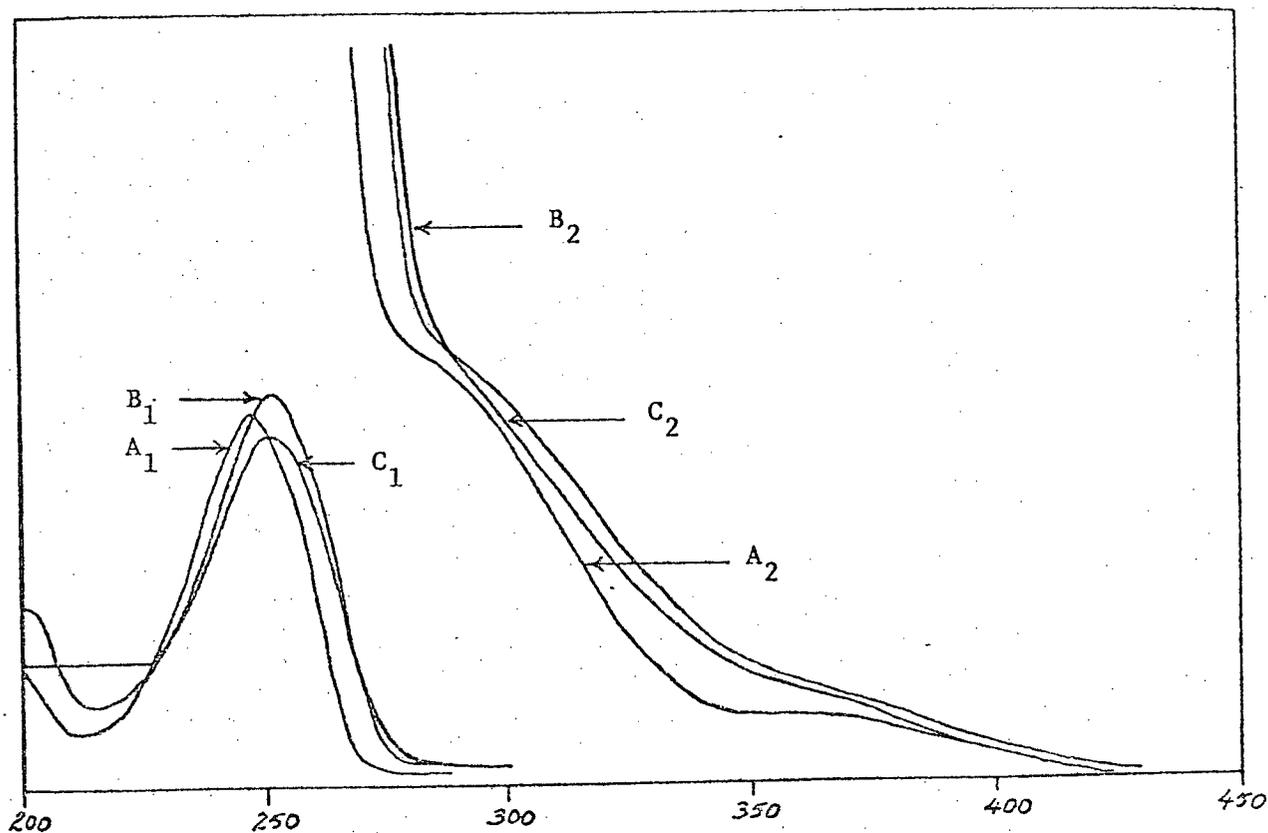
Studies on the position of the triplet energy levels of 1,4-naphthoquinone and 1,4-anthraquinone⁴⁵ revealed that the former has an $(n, \pi^*)^3$ as lowest triplet level while that for the latter is a $(\pi, \pi^*)^3$. From this standpoint one might argue that 58 should be able to abstract hydrogen by a carbon atom to give the analogue to 29. The fact that this does not occur may reflect the need to break the aromaticity of the system which is an unfavourable process.

Considering the formation of alcohol photoproduct 28, Agosta et al²⁵ has shown that β -hydrogen abstraction by oxygen in α -methylene ketones occurs via a singlet state (equation 15).



This is in accord with the present work. Photoproduct 28 has been shown¹⁷ to arise via a β -hydrogen abstraction by oxygen and is unquenchable when triplet energy quenching is demonstrated.

The 366 nm irradiation of 27 seems most probably to excite the ($n \rightarrow \pi^*$) absorption band of this compound.



UV absorption spectra of 27 in solvents of varying polarity:

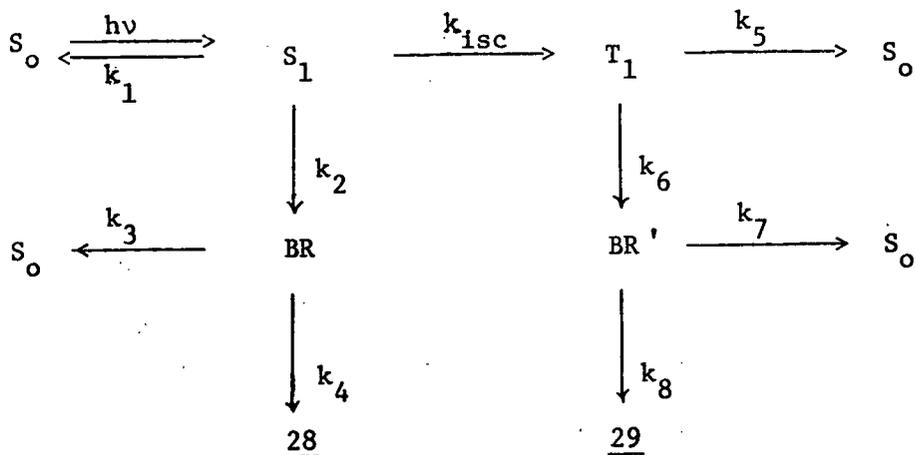
- A₁: n-hexane, B₁: dichloro methane (same concentration as A₁),
- C₁: methanol (same concentration as A₁),
- A₂: n-hexane, B₂: dichloro methane (same concentration as A₂),
- C₂: methanol (same concentration as A₂).

The slight blue shift of the uv absorption band of 27 centered at 363 nm (hexane) upon changing solvents to those of greater polarity,

and the very low extinction coefficient ($\epsilon_{366 \text{ nm}} 65$) suggests that this band represents an $n \rightarrow \pi^*$ absorption. The band at 285 nm (hexane) could be a $\pi - \pi^*$ absorption suffering a red-shift in methanol ca. 291 nm, however, the extinction coefficient is very low, $\epsilon_{285 \text{ nm}} 430$ (hexane).

The simplest scheme that accounts for all the experimental evidence for the photolysis of 27 is presented in scheme 7:

Scheme 7:



S_0 = singlet ground state of 27.

S_1 = singlet excited state of 27.

T_1 = triplet excited state of 27.

BR = biradical intermediate (BR \neq BR')

The quantum yield for the formation of enone-alcohol 28 is

$$\Phi_{\text{formation } \underline{28}}^0 = [k_2 / (k_{isc} + k_1 + k_2)] [k_4 / (k_3 + k_4)]$$

where the first term represents the probability that the excited singlet state gives rise to the biradical intermediate, and the second term the probability that this intermediate gives rise to photoproduct.

There are thus several pathways open for the system to deactivate without giving rise to the enone-alcohol photoproduct 28. Clearly in this system k_{isc} (the rate constant for intersystem crossing) is of the same order of magnitude as k_2 since the second photoproduct 29 arises from the triplet state with a quantum yield similar to that of 28. However it is not necessary that k_1 should be large to account for the low quantum yields. It is more likely that the low quantum yields are due to the expected facile collapse of the biradical to ground state photoreactant 27.⁴⁶ Thus the following conditions may hold:

$$k_3 > k_4 \gg k_1 \text{ and } k_2 \approx k_{isc}$$

The formation of the ene-dione 29 can also be accounted for in this manner. The quantum yield formation of 29 is:

$$\phi_{\text{formation } \underline{29}}^0 = [\alpha k_6 / (k_5 + k_6)] [k_8 / (k_7 + k_8)]$$

where α = the intersystem crossing efficiency, and $(\alpha k_6) / (k_5 + k_6)$ represents the quantum yield for formation of the triplet biradical, and $k_8 / (k_7 + k_8)$ the probability that this biradical collapses to product 29. In the presence of quencher the quantum yield becomes:

$$\phi_{\underline{29}} = [\alpha k_6 / (k_5 + k_6 + k_q [Q])] [k_8 / (k_7 + k_8)]$$

and the Stern-Volmer equation that results is:

$$\phi_{\underline{29}}^0 / \phi_{\underline{29}} = 1 + k_q [Q] / (k_5 + k_6)$$

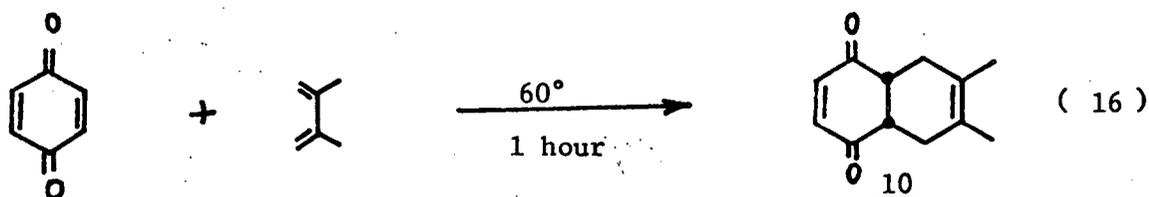
The slope of the Stern-Volmer plot for the quenching of the formation of ene-dione 29 by 1,3-cyclohexadiene was $158 \pm 70 \text{ M}^{-1}$ and the triplet lifetime was calculated to be $(1.6 \pm 0.7) 10^{-8}$ sec., cf. section A 3. This lifetime is dependent on two independent rate constants k_5

(rate constant for all triplet decay to the ground state) and k_6 (rate constant for biradical formation). As before it is likely that the low quantum yield of formation of the ene-dione is due to an efficient collapse process of the triplet biradical to the ground state. An attempt was made to obtain an independent measurement of the triplet lifetime of 27 by phosphorescence,⁴⁷ however, the compound did not phosphoresce, and no further information could be obtained. Considering the distinct possibility that $k_6 \gg k_5$ then the rate constant k_6 can be approximated from the lifetime of the triplet state $\tau = 1 / (k_5 + k_6)$ to be $k_6 \approx 6 \times 10^7 \text{ sec}^{-1}$.

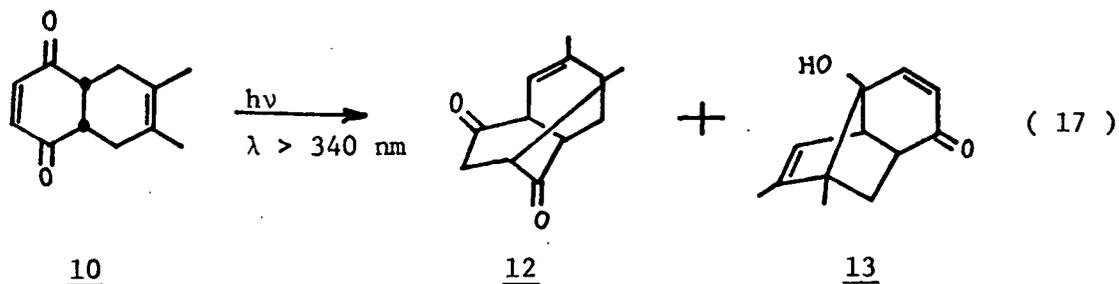
C. Quantum Yield Studies of the Photolysis of 6,7-Dimethyl-4a β ,5,8,8a β -tetrahydronaphthoquinone 10 in Benzene.

1. Synthesis and Photolysis.

The procedure of Mandelbaum and Cais⁴⁸ was followed for the synthesis of 10 (eq. 16).



A solution was prepared containing 1.5 g of this material in 400 ml of benzene, and photolyzed for 21 hrs using light of wavelength longer than 340 nm. The two products formed 12 and 13 were isolated by column chromatography to yield 30 % of dione 12 and 25 % of alcohol 13.



Glp response curves were obtained for each product using 1,4-naphthoquinone as an internal standard.

2. Unquenched Quantum Yield Measurements.

These experiments were designed to obtain the quantum yield of formation of the dione 12 and the alcohol 13. A series of 0.02 M degassed solutions of 10 in benzene were photolyzed at 366 nm for a period of less than 5 hours. The percent conversion was kept low to avoid secondary photoreactions. To test this, the length of photolysis was varied. There was no change within experimental error in the quantum yield of formation of each photoproduct.

TABLE 2

% Conversion of <u>10</u>	Quantum yield of formation of <u>13</u>	Quantum yield of formation of <u>12</u>
0.18	0.0149	0.0073
0.51	0.0169	0.0091
2.7	0.0180	0.0085
2.3	0.0158	0.0070

The mean quantum yield of formation for the dione 12 was calculated to be 0.0080 ± 0.0008 and for the alcohol 13 it was 0.0164 ± 0.0012 .

3. Photolysis of 10 Using Piperylene as Quencher.

These tests were performed solely to ascertain that the triplet energy of the chromophore of 10 was ≥ 57 kcal/mole.

Since the triplet energy of 27 was credited to be ≥ 57 kcal/mole it was unlikely to expect that the chromophore bearing no methyl groups⁴¹ should have a lower triplet energy than that bearing two methyl groups. A 0.02 M solution of 10 in benzene and containing piperylene at a concentration of 1.27 M was degassed and photolyzed at 366 nm for 4.5 hrs. Glpc analysis of the solution showed that both photoproducts were quenched, $\phi_{\text{formation } 12} = 0.0040$, $\phi_{\text{formation } 13} = 0.0104$.

4. Photolysis of 10 Using 1,3-Cyclohexadiene as Quencher.

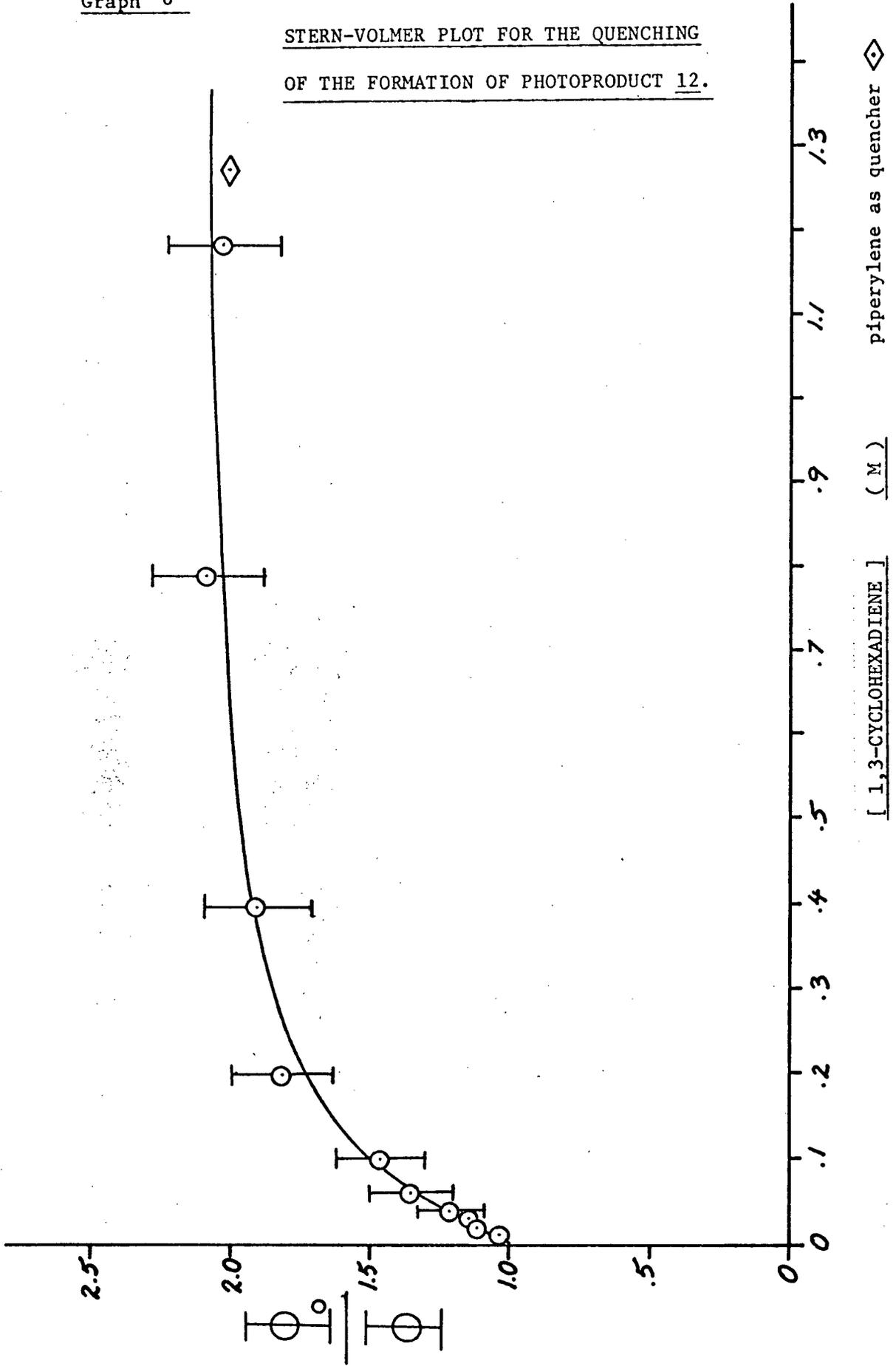
1,3-Cyclohexadiene ($E_T = 53$ kcal/mole)²⁹ was used as a quencher, first because piperylene quenching showed that the triplet energy of 10 was above 57 kcal/mole, and second because quenching of 27 by 1,3-cyclohexadiene appeared to occur at a diffusion controlled rate.

The quenching studies were performed on 0.02 M solutions of 10 in benzene, degassed and photolyzed at 366 nm. As was the case for the 1,3-cyclohexadiene quenched photolysis of 27, formation of quencher dimers 46 and 47 was detected.

The results are plotted in graphs 6 and 7. It is directly apparent that more than one excited state is responsible for the formation of 12 and 13. The modified Stern-Volmer equation that can be used to describe such a process is:⁴⁹

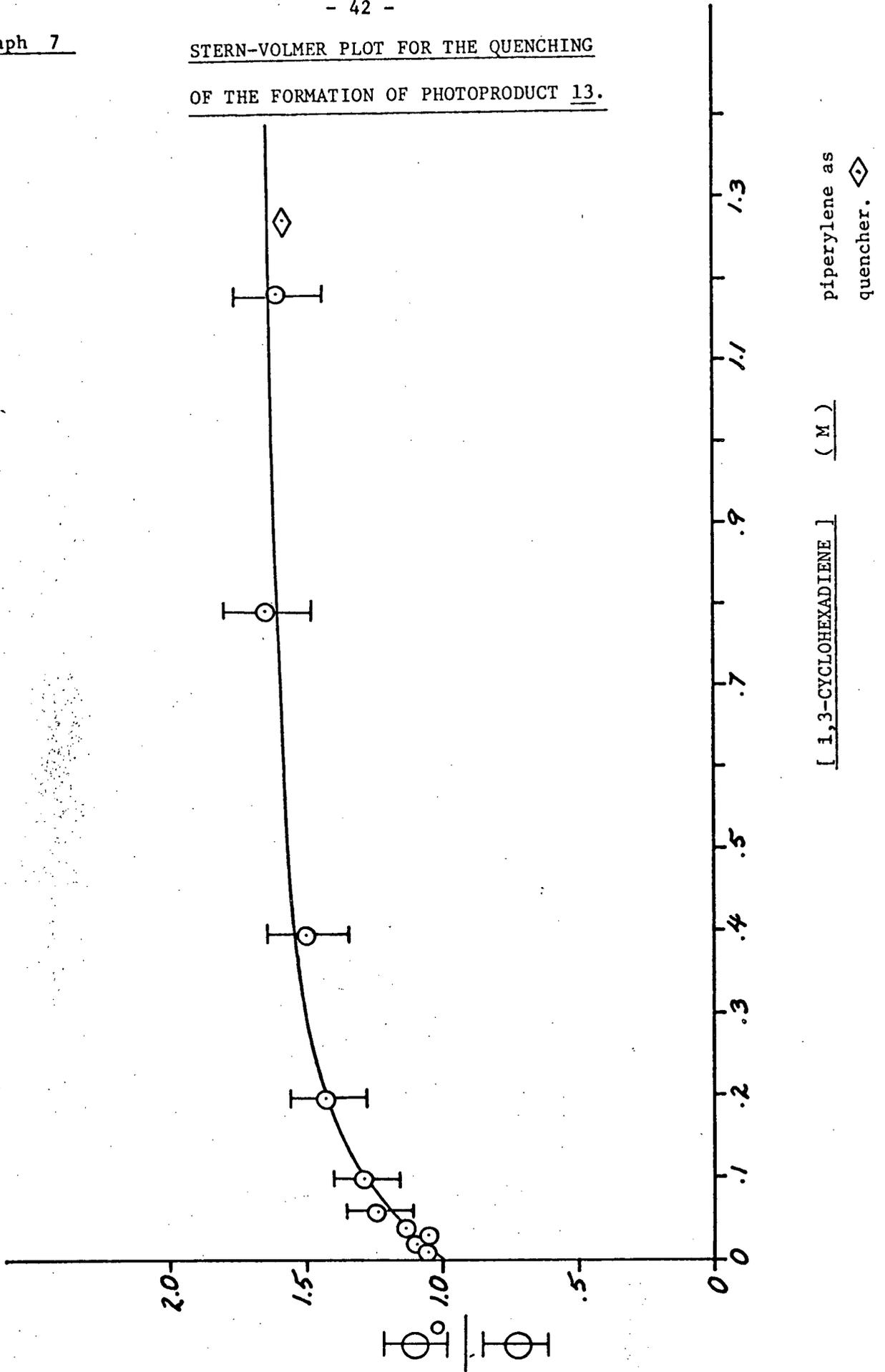
Graph 6

STERN-VOLMER PLOT FOR THE QUENCHING
OF THE FORMATION OF PHOTOPRODUCT 12.



Graph 7

STERN-VOLMER PLOT FOR THE QUENCHING
OF THE FORMATION OF PHOTOPRODUCT 13.



$$\frac{\phi_0}{\phi} = \left(1 + \frac{k_q [Q]}{k_r + kd} \right) / \left(1 + \frac{k_q [Q]}{kr + kd} \cdot \frac{\phi_\infty}{\phi_0} \right) \quad (18)$$

where ϕ_∞ = quantum yield at infinite quencher concentration.

It is possible to obtain from this Stern-Volmer plot an approximate upper limit value for the lifetime of the triplet state of 10. If one considers equation 18 then it is easy to see that the divisor approaches one if the quencher concentration approaches zero. Thus at this limit one gets the familiar Stern-Volmer equation:

$$\frac{\phi_0}{\phi} = 1 + (k_q [Q]) / (k_r + k_d)$$

where $\frac{1}{k_r + k_d} = \tau$ (lifetime of the triplet state).

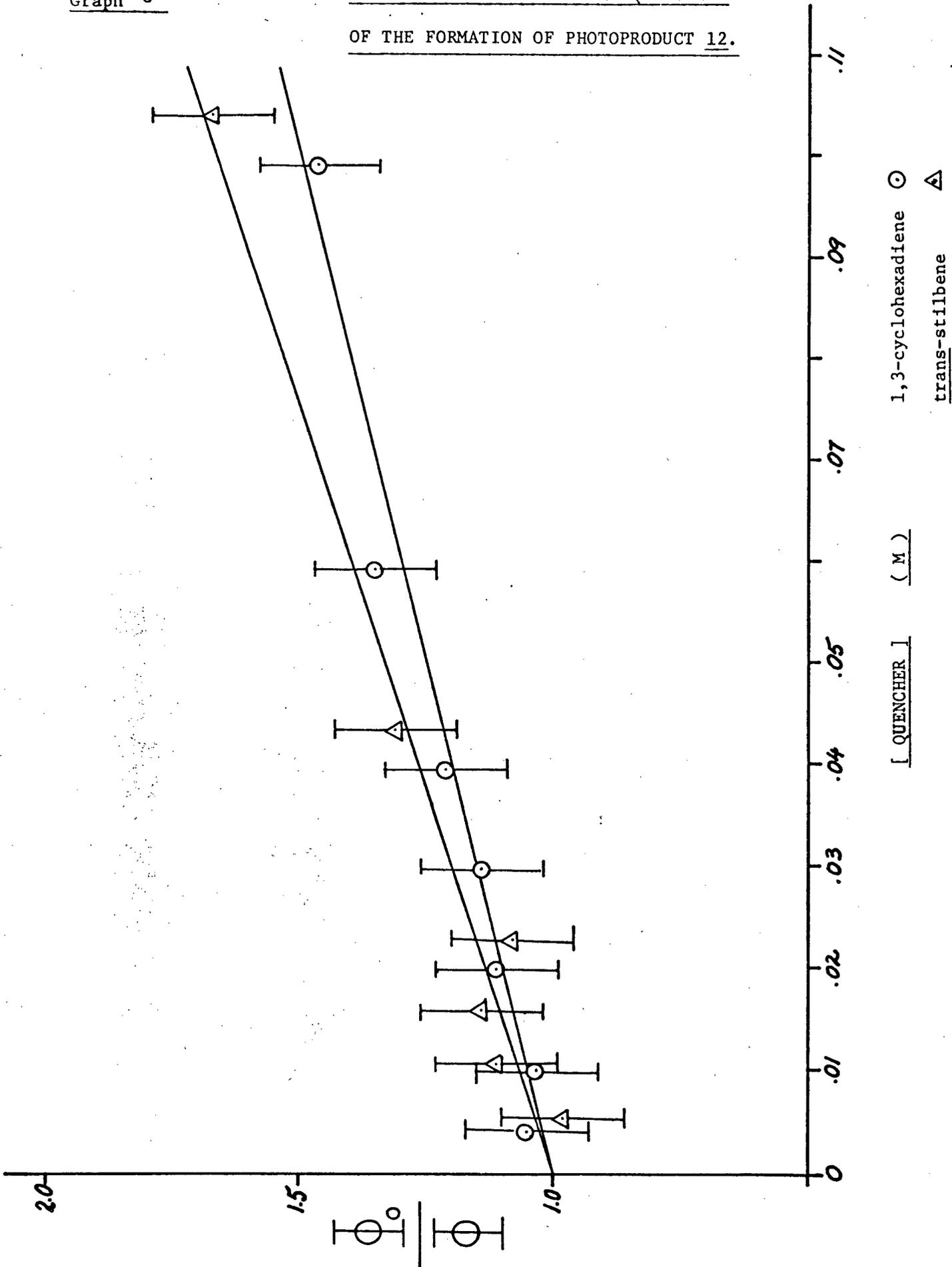
The data for quencher concentrations below 0.11 M are presented in graphs 8 and 9. The least squares slope for the plot of the dione 12 was calculated to be $4.8 \pm 6.2 \text{ M}^{-1}$ (99.9 % confidence limits). For the alcohol 13 the least squares slope was calculated to be $3.0 \pm 6.2 \text{ M}^{-1}$ (99.9 % confidence limits). These two slopes are very similar in value as they should be, considering that the quenching is occurring for the same triplet state intermediate. Taking the average value of 4 M^{-1} for the slope, and assuming a diffusion controlled quenching rate (cf. section A5) of $1.0 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ in benzene, then $\tau \leq 4 \times 10^{-10} \text{ sec}$. Thus the triplet state is very short lived.

Stern-Volmer plots give at the limiting value $[Q] \rightarrow \infty$ the ratio ϕ_0 / ϕ_s (ϕ_s = quantum yield of product formation from the singlet state). Furthermore $\phi_0 = \phi_T + \phi_s$ and thus ϕ_T (quantum yield of product formation from the triplet state) can be determined.

In the case of quenching of the formation of dione 12 $\phi_0 / \phi_s \rightarrow$

Graph 8

STERN-VOLMER PLOT FOR THE QUENCHING
OF THE FORMATION OF PHOTOPRODUCT 12.

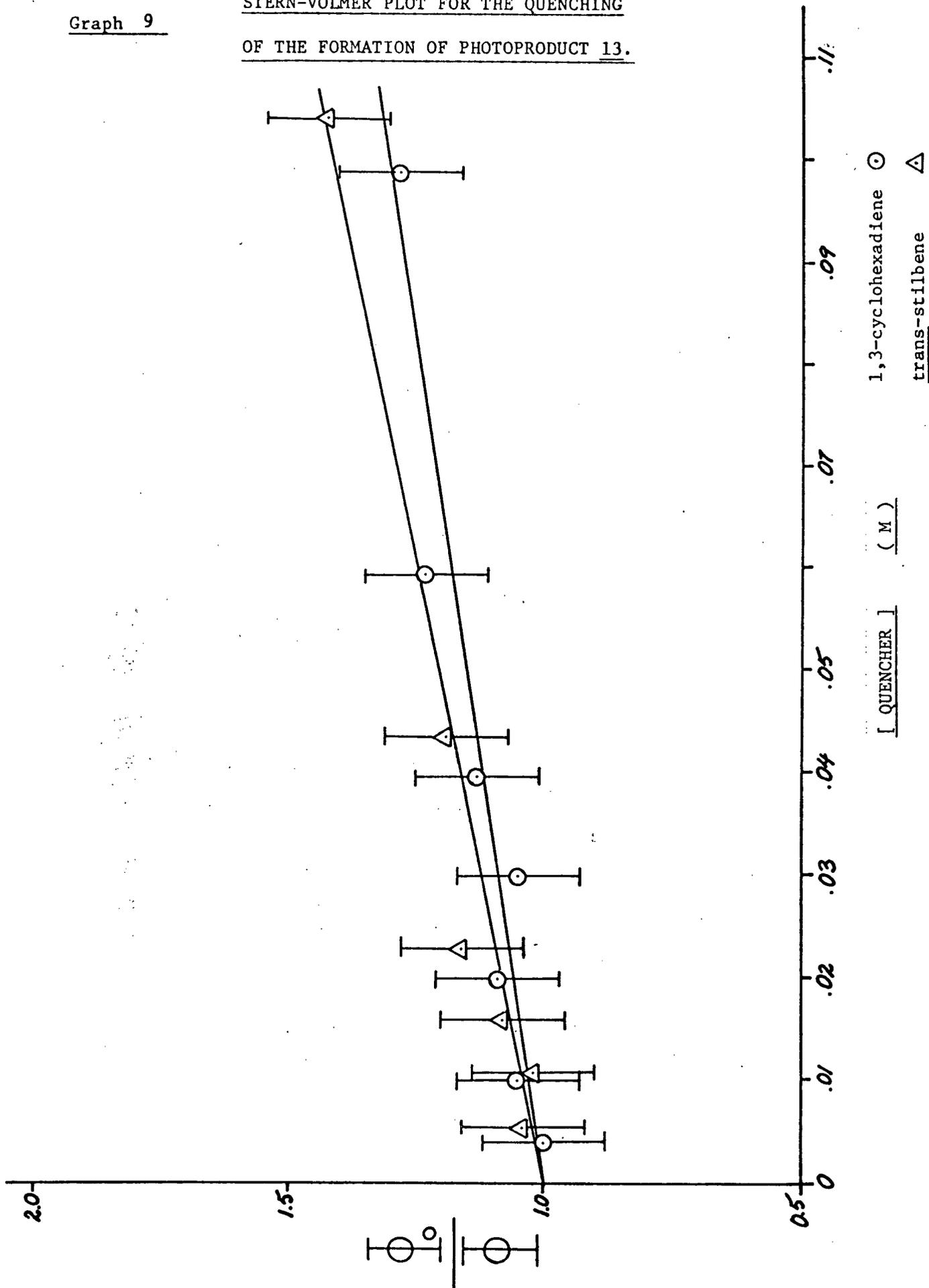


1,3-cyclohexadiene \odot
trans-stilbene \triangle

[QUENCHER] (M)

STERN-VOLMER PLOT FOR THE QUENCHING
OF THE FORMATION OF PHOTOPRODUCT 13.

Graph 9



2.08 at $[Q] = 1.4 \text{ M}$, $\phi_s = 0.0038$ and thus 48% of 12 is obtained via a singlet intermediate. In the quenching plot of formation of alcohol 13 $\phi_o / \phi_s \longrightarrow 1.65$ at $[Q] = 1.4 \text{ M}$, $\phi_s = 0.0099$ and thus 60% of 13 arises via the singlet state.

5. Photolysis of 10 Using trans-Stilbene as Quencher.

trans-Stilbene was used again as a diagnostic test for the assumption that 1,3-cyclohexadiene quenching of 10 was diffusion controlled and to show that chemical quenching was not occurring. The highest concentration level of trans-stilbene used was less than 0.17 M because of the absorption capacity of the quencher for 366 nm light ($\epsilon = 0.2$).

The results are plotted with the data of 1,3-cyclohexadiene quenching at low concentrations in graphs 8 and 9. The least squares slopes for the points were: (a) for the quenching of the formation of dione 12, $6.6 \pm 11.2 \text{ M}^{-1}$, and (b) for the alcohol 13, $3.9 \pm \text{M}^{-1}$. Here again it seems reasonable to assume that 1,3-cyclohexadiene quenching is likely to be diffusion controlled.

6. Photolysis of 10: Effect of Changing the Concentration of 10 on Quantum Yields.

The investigation of the effect of changing the concentration of 10 on the quantum yields of formation of photoproducts 12 and 13 showed (graph 10) that an eight-fold increase in concentration of 10 had no marked effect. Thus as argued earlier, (cf. section A) this was considered to be sufficient evidence to rule out self-quenching as a source for deactivation of excited states.

D. Quantum Yield Studies of the Photolysis of 10 in tert-Butanol.

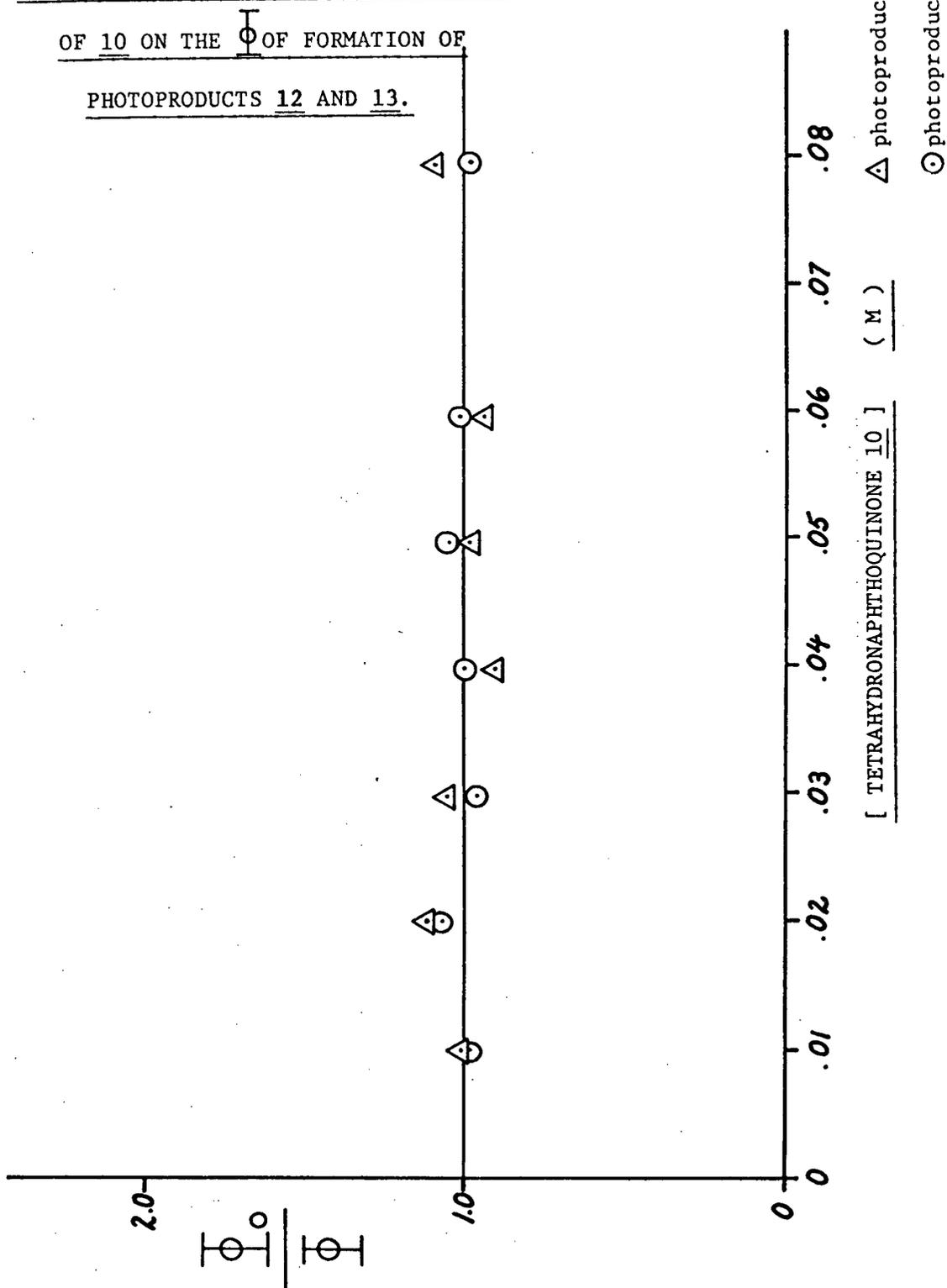
1. Photolysis.

A solution containing 1.00 g of 10 in 400 ml of 80:20 mixture of tert- butanol and benzene was degassed and photolyzed using light of

Graph 10

EFFECT OF CHANGING THE CONCENTRATION

OF 10 ON THE ϕ OF FORMATION OF
PHOTOPRODUCTS 12 AND 13.



$\lambda > 340$ nm for 20 hrs. One product 11 was obtained in 79 % yield.

A glpc calibration curve was obtained for the response of the flame ionization detector to 11 compared to 1,4-naphthoquinone (internal standard).

2. Unquenched Quantum Yield Measurements.

The quantum yield of formation of 11 in the absence of quencher was determined. The solutions were 0.02 M in 10 in 95:5 tert-butanol-benzene. These were compared to runs made in neat tert-butanol. No appreciable effect was observed by the introduction of 5 % benzene. This benzene allowed for easier handling of the solvent since tert-butanol freezes at 25.5°. Once again, changing the percent conversion of 10 to 11 had no effect on the quantum yield of formation of 11.

TABLE 3

Solvent used	% Conversion	Quantum Yield of formation of <u>11</u>
<u>tert</u> -Butanol-Benzene (95:5)	0.11	0.0084
<u>tert</u> -Butanol-Benzene "	0.22	0.0091
<u>tert</u> -Butanol	1.2	0.0095
<u>tert</u> -Butanol	0.77	0.0069
<u>tert</u> -Butanol-Benzene (95:5)	0.68	0.0075
<u>tert</u> -Butanol-Benzene "	0.74	0.0076
<u>tert</u> -Butanol-Benzene "	0.85	0.0079

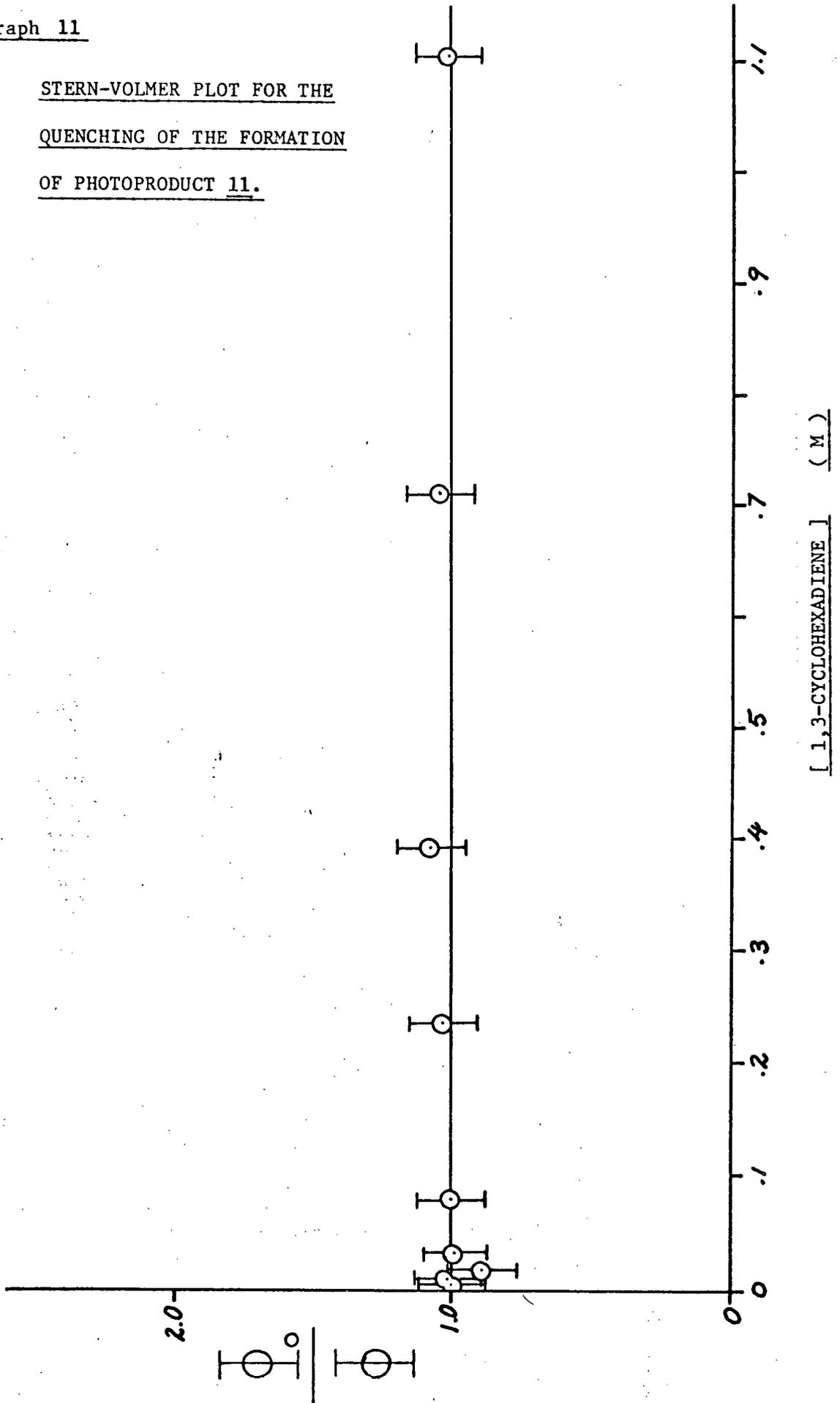
The mean value was calculated to be $\phi_0 = 0.0081 \pm 0.0008$

3. Photolysis of 10 using 1,3-Cyclohexadiene as Quencher in tert-Butanol.

The results for the quenching of 0.02 M solutions of 10 by 1,3-cyclohexadiene are presented graphically (graph 11). There appears to be no measurable quenching of the formation of 11. It is

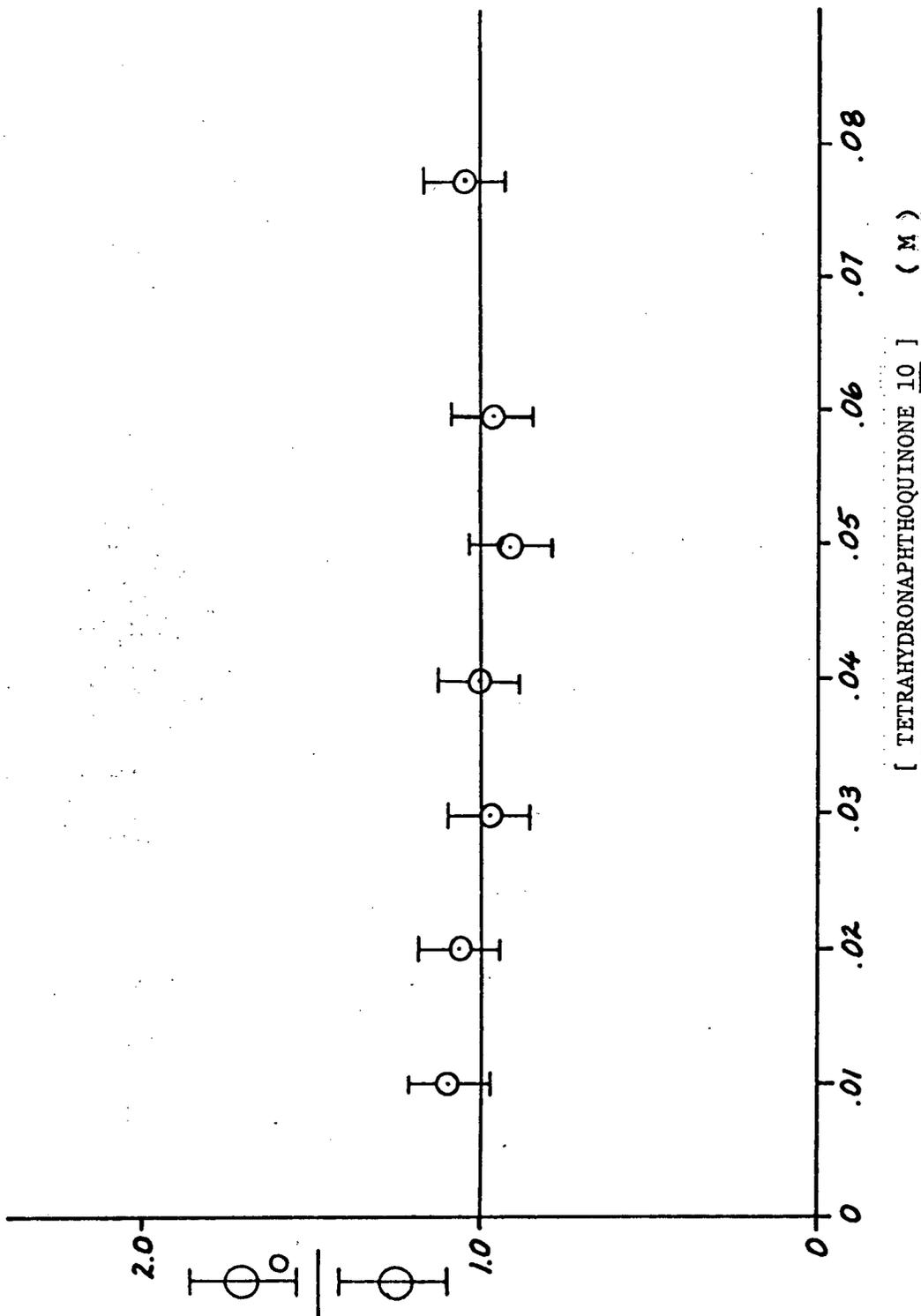
Graph 11

STERN-VOLMER PLOT FOR THE
QUENCHING OF THE FORMATION
OF PHOTOPRODUCT 11.



Graph 12

EFFECT OF CHANGING THE CONCENTRATION
OF 10 ON THE Φ OF FORMATION OF
ENE-DIONE 11 .



expected, however, that this is not a reflection of the inefficiency of 1,3-cyclohexadiene as a quencher since the triplet energy of 10 will, if it shifts in energy, become larger when using the more polar solvent tert-butanol considering that the lowest triplet energy of 10 is ($n - \pi^*$) in character.

Unfortunately trans-stilbene is not very soluble in tert-butanol and could not be used as a quencher in this system.

Oxygen was used as a quencher. The results showed some quenching but were rendered difficult to interpret by the appearance of a new unidentified product, probably from reaction of oxygen with one of the excited states and/or biradical intermediates involved.

4. Photolysis of 10 in tert-Butanol : Effect of Changing the Concentration of 10 on the Quantum Yield of Formation of 11.

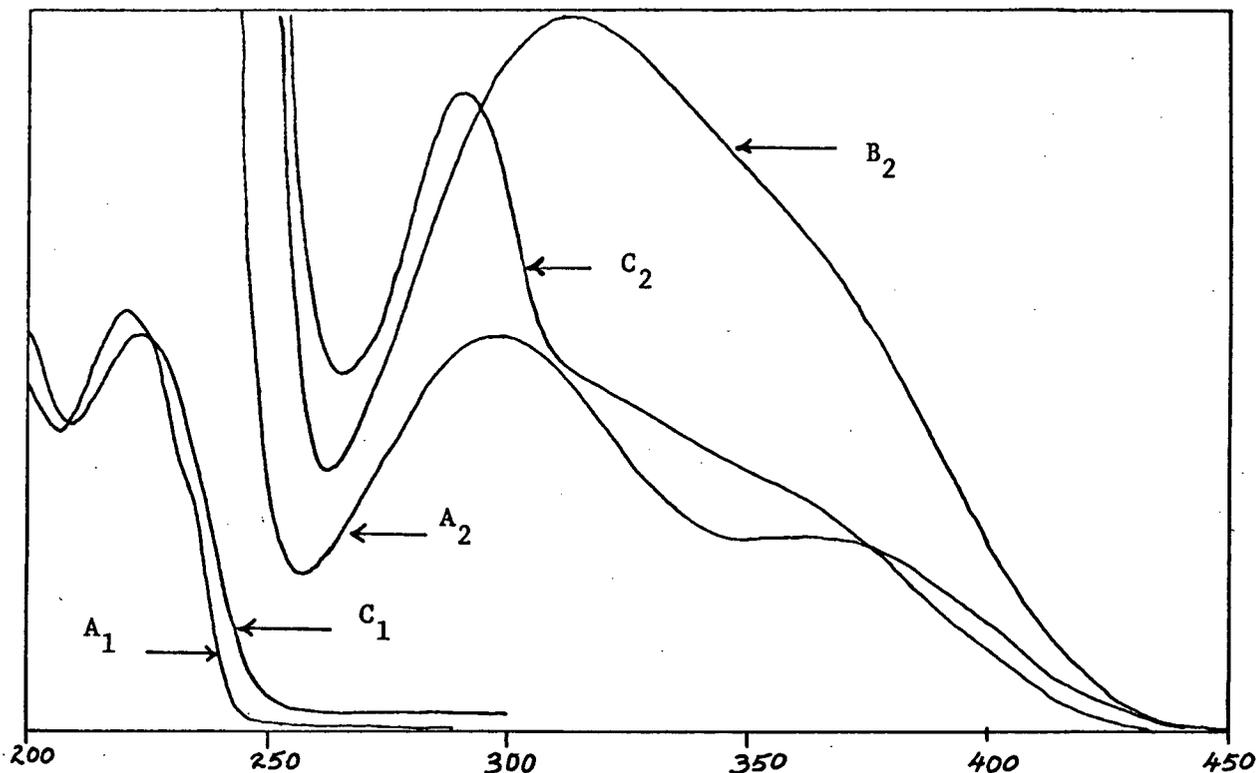
Within experimental error there was no significant effect on the quantum yield of formation of 11 when the concentration of 10 was varied eight-fold, (cf. graph 12). Thus again, no self-quenching was indicated.

E. Interpretation of the Results of Quenching the Photolysis of 10.

The mechanism for the photolysis of 10 in both benzene and tert-butanol has been suggested to occur via β -hydrogen abstraction by oxygen to give the bis-allylic biradical 14. This process as mentioned earlier, (cf. section B), has been documented to occur via a singlet state.²⁵ The work here presented throws light on the possibility that β -hydrogen abstraction by oxygen may also proceed via a triplet state.

The long wavelength uv absorption spectrum of 10 in solvents of different polarity shows quite clearly a blue-shift when going from nonpolar to polar solvents of the band centered at 365 nm (hexane),

355 nm (methanol). This band is thus probably an n- π^* transition.⁵⁰



Uv absorption spectra of 10 in solvents of varying polarity:

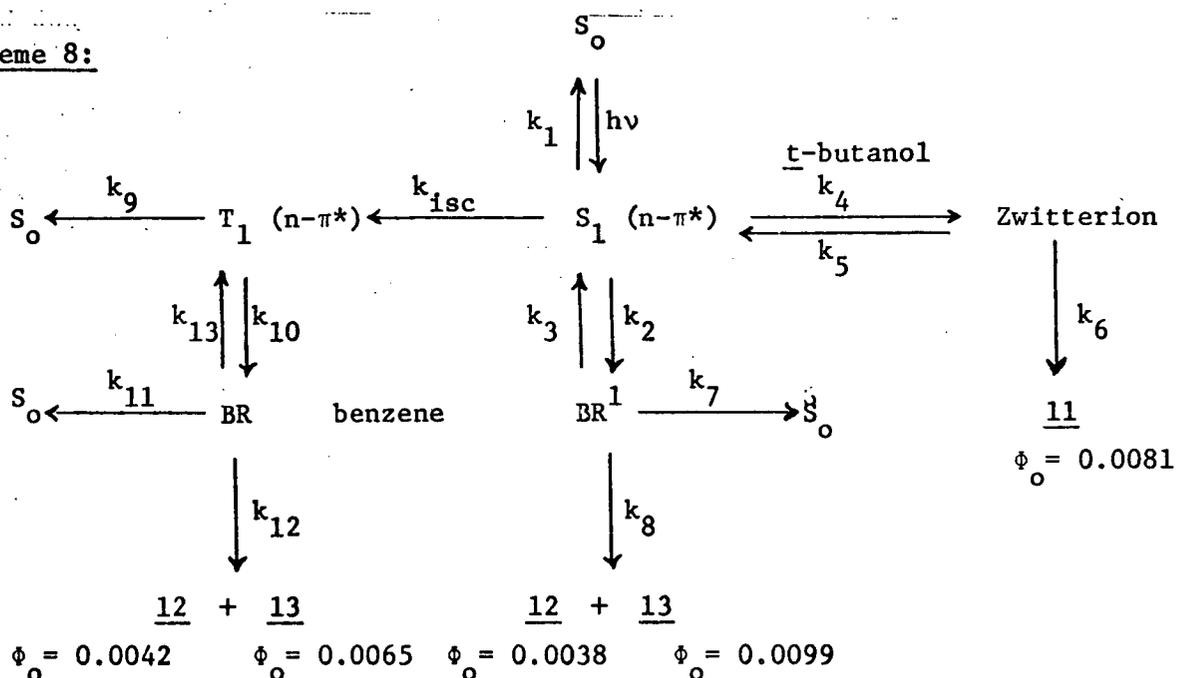
A₁: n-hexane, C₁: methanol (same concentration as A₁),

A₂: n-hexane, B₂: dichloro methane (twice the concentration of A₂)

C₂: methanol (same concentration as A₂).

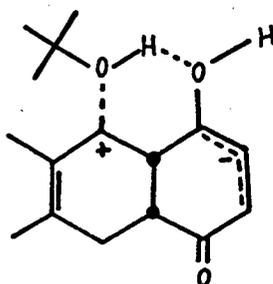
A scheme for the observed photoreactions of 10 could be:

Scheme 8:

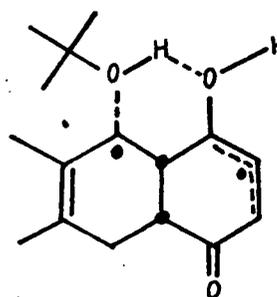


Again, as in the case of 27, the biradical collapsing to ground state reactant could account for the low quantum yields observed, $k_7 \gg k_1$ and $k_{11} \gg k_9$. No phosphorescence measurements were attempted on 10, and thus no independent measurement of the triplet lifetime was obtained.

The solvent effect is of course very important here. In both benzene and tert-butanol, all three products are observed (cf. appendix). However, the product ratios are enormously affected by the solvents. In benzene, 11 is only formed as a trace material. In tert-butanol on the other hand, both 12 and 13 are very minor products. An explanation⁵¹ for such an effect is that the solvent tert-butanol somehow is able to stabilize and localize the unpaired electron at C₈ resulting from β -hydrogen abstraction by oxygen. This localizing effect could then result in preferential collapse of the diradical to yield 11 through C₃ - C₈ bonding. This argument would also apply in the case of a Zwitterion intermediate.⁵¹ The structures proposed for such a solvation by a polar solvent like tert-butanol of the diradical intermediate or of a zwitterion intermediate are shown below (structures 60 and 61).

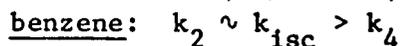


60



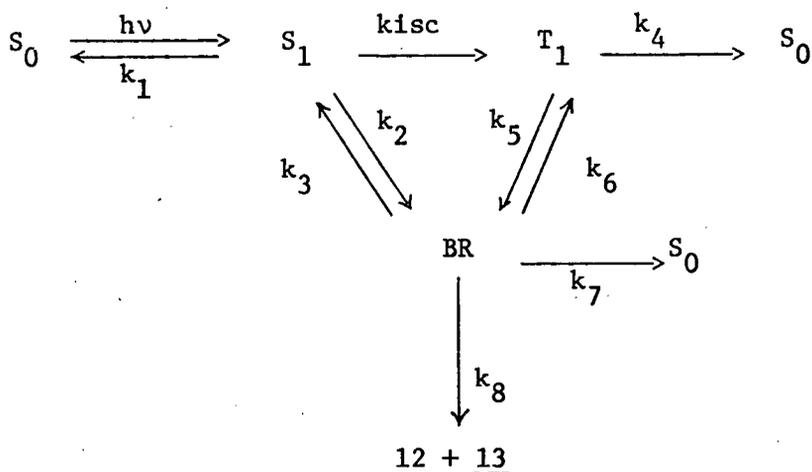
61

The expected kinetics are thus summarized:



The intermediacy of two different biradicals in the formation of 12 and 13 is suggested rather than a common species (eg. a singlet biradical) by the shapes of the Stern-Volmer plots for 12 and 13 then both plots ($\frac{\phi_0}{\phi}$ vs [Q]) would be identical.

Scheme 9 :

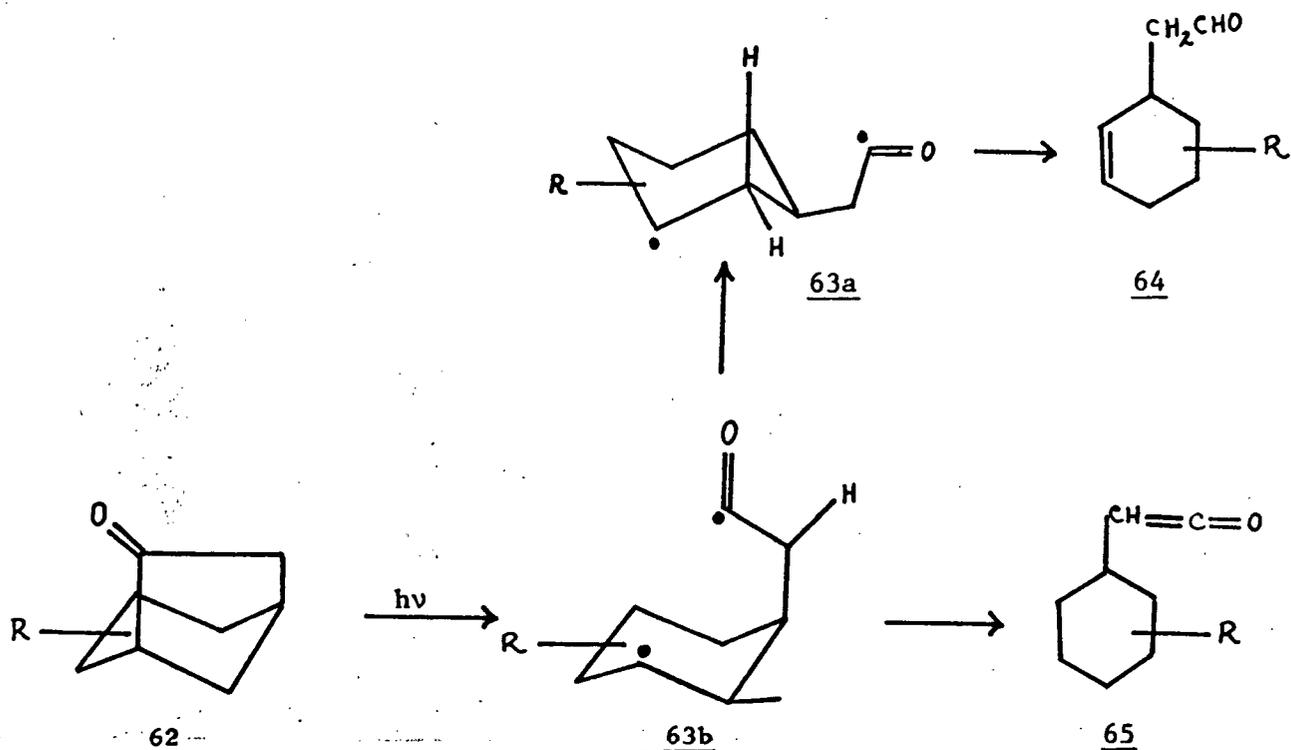


The Stern-Volmer plots for the formation of 12 and 13 reflects the efficiency of collapse of the singlet and triplet excited state of the photoreactant to biradical. Since the two photoproducts arise from the same biradical intermediate the Stern-Volmer plots for both 12 and 13 should be superimposable. In actuality the Stern-Volmer plots for 12 and 13 (graphs 6 and 7 respectively) do not overlap at higher quencher concentrations where triplet quenching is almost complete.

As was discussed earlier, the suggested reason why the triplet state of 27 leads to γ -hydrogen abstraction by carbon to yield 29 was because the lowest triplet for 27 was believed to be (π, π^*) in character. Whereas in 10 the lowest triplet state is most likely (n, π^*) in character and favours β -hydrogen abstraction by oxygen to yield the observed products.

It is entirely possible that the bridgehead substituents are also responsible for directing the fate of the photoreactions of 10 and 27, i.e. conformational control of the reaction pathway. This type of control on the mechanism of certain photoreactions was investigated by Alexander ⁵² in the photolysis of cyclobutaryl ketones and by Agosta ⁵³ in the photolysis of 62.

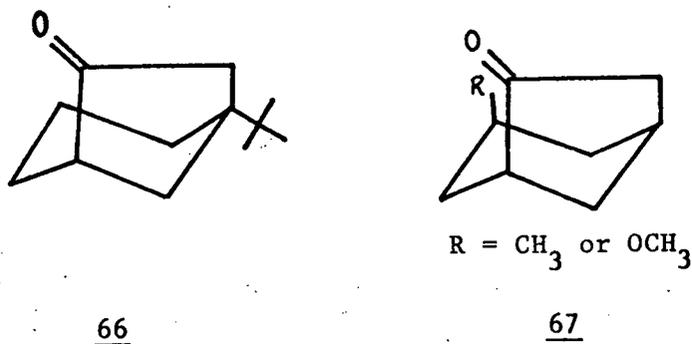
Scheme 10:



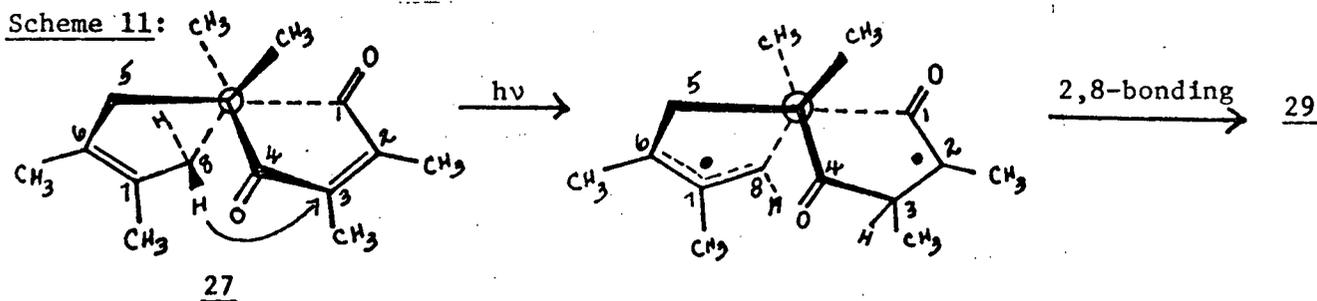
Agosta was able to direct the fate of the biradical 63 by placing substituents at key positions around the ring, thus obtaining either an aldehyde 64 or a ketene 65. He suggested that for conformational control argument to apply, the lifetime of the biradical had to be large enough to allow conformational relaxation of the biradical to compete successfully with the hydrogen transfer which leads to products (scheme 10).

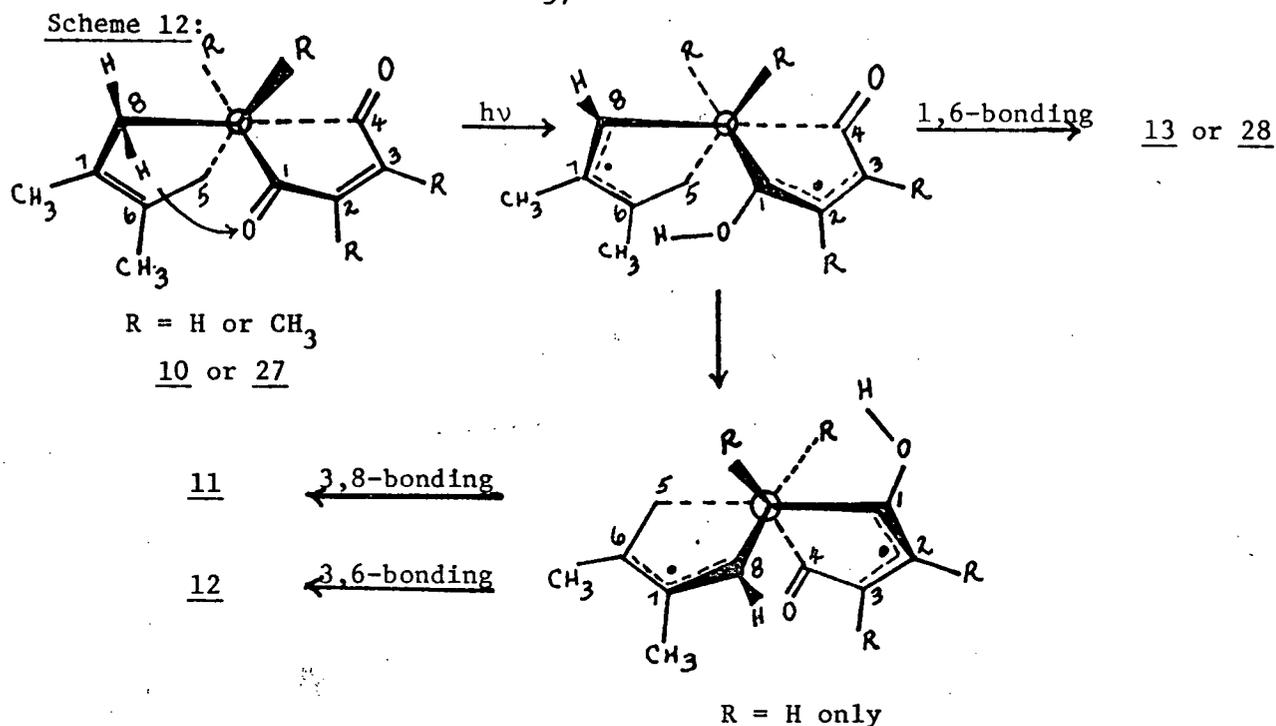
The presence of a tert-butyl group at the bridgehead, compound 66,

led to the exclusive formation of a ketene due to the steric effect of the bulky tert-butyl group preventing the conformer type 63a from forming. On the other hand, location of methyl or methoxy groups at other positions around the ring, compound 67, or of no substituents at all led to the exclusive formation of aldehyde. In this case, again the more stable biradical conformer seems to be favoured.



Similarly 27 may follow a reaction pathway which reflects conformational control due to the effect of methyl substituents at the bridgehead positions. The energy barrier for free rotation of eclipsing methyl groups in n-butane is 4.4 - 6.1 kcal / mole compared to 3 kcal / mole for ethane.⁵⁴ This is a 1.4 - 3.1 kcal / mole energy difference for this system. One can see that free rotation about the bridgehead bond of 27, which is not directly comparable to free rotation of n-butane, is going to be hindered nevertheless to a larger extent than free rotation about the bridgehead bond of 10, which has no bridgehead substituents.





The conformational requirement for the formation of both dione 11 and 12 from 10 is a "ring-flip" of the biradical formed after β -hydrogen abstraction by oxygen (cf. scheme 12).

This "ring-flip" involves the rotation of the bridgehead bond with concomitant eclipsing of the bridgehead groups. In the case of 27 the methyl substituents at the bridgehead may well suffice to sterically hinder such bond rotation. If this occurs, then the formation of structure types 11 and 12 are not possible for compound 27, and indeed these are not observed. On the other hand the formation of the enone alcohol 13 can be achieved without the "ring-flip" of the biradical (cf. scheme 12). In the same manner, the biradical formed after β -hydrogen abstraction by oxygen in 27 can collapse directly without "ring-flip" to yield the observed enone-alcohol photoproduct 28.

Finally, the formation of dione 29 can be understood without invoking the bridgehead bond rotation (cf. scheme 11). The C_3 carbon atom abstracts the C_8 hydrogen closest to it and the biradical

thus formed can readily collapse by bonding the C₂ and C₈ carbon atoms to yield the observed photoproduct 29.

F. Conclusions.

The main observation of this work was that the photolysis of compound 27 led to the formation of products 28 and 29 via totally different states. Photoproduct 28 arose from a singlet excited state and product 29 from a triplet excited state.

This discovery added weight to the suggested mechanisms for the formation of each product. Product 28 was thought to proceed via β -hydrogen abstraction by oxygen to yield a biradical which upon collapse formed 28. Literature²⁵ research revealed that this type of hydrogen abstraction had been attributed to singlet states. On the other hand, product 29 was thought to be produced via γ -hydrogen abstraction by carbon. Again, earlier researchers^{21,22} have observed that this process occurs via a triplet excited state.

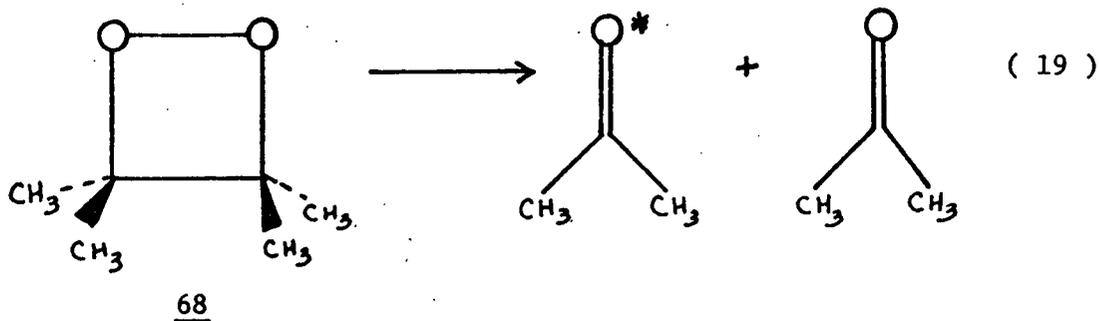
It is interesting to note that the photolysis of 10 in benzene to yield 12 and 13 proceeds apparently via both a singlet and a triplet excited state. The mechanism suggested for the formation of 12 and 13 was through a β -hydrogen abstraction by oxygen process, known to occur from only a singlet excited state. Furthermore, the photolysis of 10 in tert-butanol yields 11 only via a singlet excited state. The mechanism here again is a β -hydrogen abstraction by oxygen. No reason could be given why the solvent used should have such an effect on the rate of intersystem crossing of the excited state of 10, although changing solvents from benzene to tert-butanol for the photolysis of 27 is known to decrease the rate of intersystem crossing (Ratio of

$\frac{28}{29}$ in benzene is $\frac{0.5}{1.0}$, in tert-butanol it is $\frac{1.1}{1.0}$).

Finally and not least, an explanation was presented for the observation that 27 did not form upon photolysis, structures of the type of 11 and 12. The explanation involved the conformational control due to bridgehead substituents, of the biradical intermediate produced from β -hydrogen abstraction by oxygen. The argument presented was that to obtain products similar to 11 and 12 bridgehead bond rotation would have to occur. This process was sterically impeded by the bridgehead substituents. The only products observed for 27 are those not requiring such a bond rotation.

Triplet sensitization studies would certainly help to disprove any triplet intermediacy in the formation of alcohol 28 from 27. Likewise in the photolysis of 10 in tert-butanol, triplet sensitization would show whether the product 11 observed is truly obtained from only a singlet state.

The main problem of using sensitizers is that all the common triplet sensitizers, having a triplet energy high enough to sensitize either 10 or 27, absorb light in the same region as 10 and 27. There is however, a solution to this problem. Sensitization can also be performed by thermolyzing tetramethyldioxetane 68 (equation 19).



The thermal (68°) decomposition of 68 yields in 50 % a triplet excited and a ground state acetone molecule⁵⁵ leaving 0.5 % of the cases for a decomposition to a singlet excited and a ground state molecule.

Another interesting experiment would be to influence the rate of intersystem crossing in the photolysis of 10 and 27 in benzene. It is known that the presence of heavy atoms in the solvent or in the molecule itself can increase the rate of spin inversion of the excited state of that molecule via spin-orbit coupling of the heavy atom nucleus with the electronic system.⁵⁶ By increasing the rate of intersystem crossing from the excited singlet state to the excited triplet state of 27 there should be an increase in the rate of product formation 29/28. In the photolysis of 10 the yield of product 12 and 13 arising from the triplet excited state will increase in the presence of heavy atoms. The effect can be measured from the Stern-Volmer plot ($\frac{\phi_0}{\phi}$ vs [Q]). The limiting quantum yield ϕ_∞ at high quencher concentration will reveal that fraction of excited 10 molecules still converting to 12 and 13 through the singlet state.

APPARATUS

A. The Quantum Yield Apparatus: The U.B.C. Blue Box

The system used to determine all the quantum yields reported in this thesis stems from a similar unit used by Zimmerman,⁵⁷ "The Wisconsin Black Box". Our System is designed for small scale photolysis (27 ml cells were used) whereas the unit used by Zimmerman allowed the photolysis of 100 ml or more of solution.

The light source used was a Bausch and Lomb SP-200 housing fitted with an Osram HBO 200 (200 watts) super high pressure mercury lamp. A Bausch and Lomb 200-700 nm monochromator with 1200 grooves/mm grating was used to select out the desired wavelength, the band of light allowed through the monochromator being no larger than 5 nm.

The monochromator was fitted with a variable focal length quartz-fluoride condenser lens having a leaf type diaphragm.

The photolysis cells used were a matched pair of 10cm x 2cm quartz cylinders and one 5cm x 2cm quartz cylinder (all three from Hellma). The outer surfaces of the cells, except the end windows, were carefully silvered⁵⁸, and then coated with black epoxy paint⁵⁹. The cells were arranged such that one 10 cm test solution cell and the 5 cm reference cell were in line with the light source and monochromator,

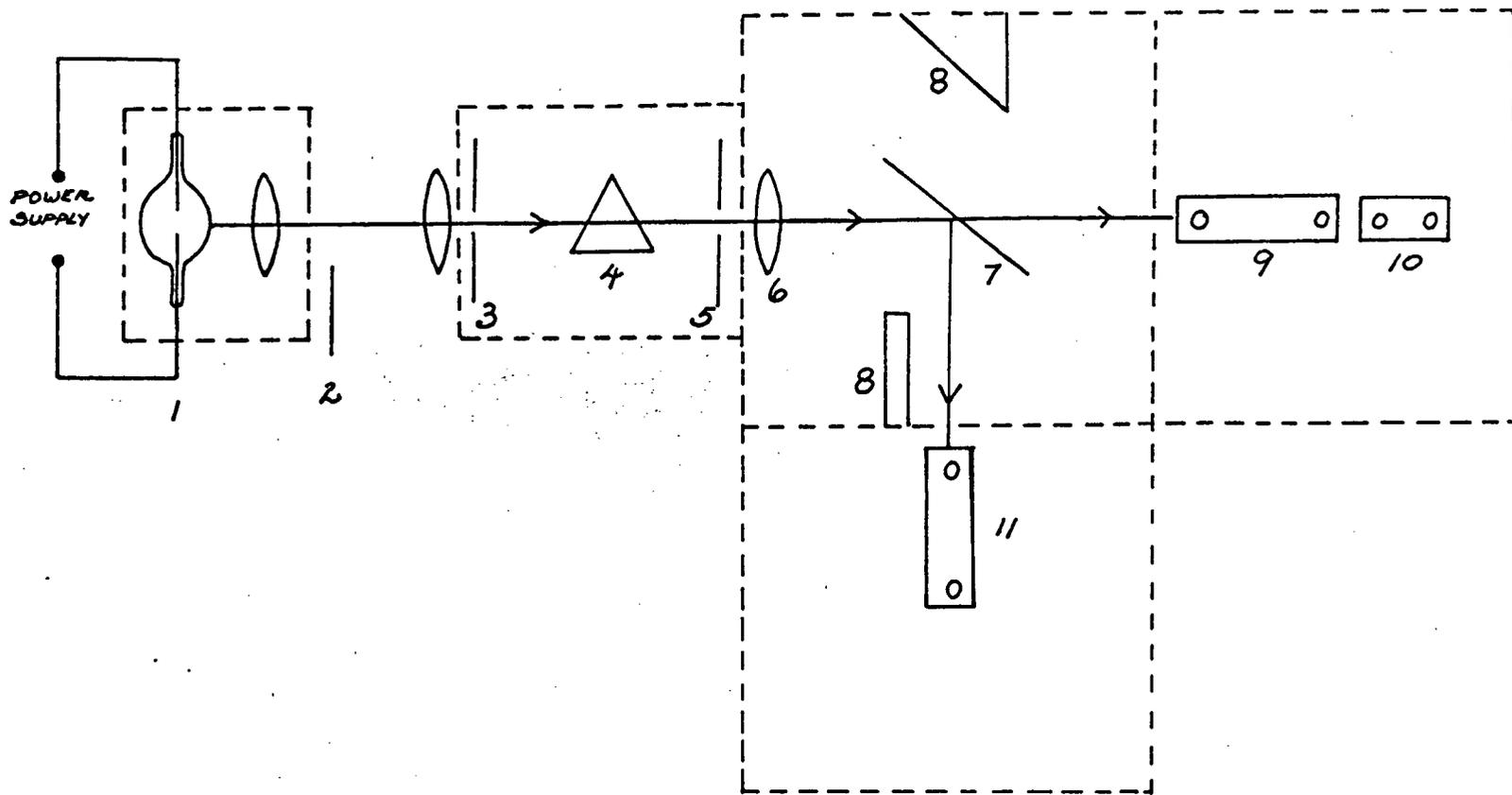


Figure 2. Quantum Yield Apparatus - " U.B.C. Blue Box"

- | | |
|---|--|
| 1- Osram HBO 200 super high pressure mercury lamp | 7- 2" x 2" x 1/16" quartz plate |
| 2- Aluminum plate used to block light during lamp warm up | 8- light baffles |
| 3- Monochromator entrance slit 5.36 mm | 9- 10 cm x 2 cm quartz cell (test solution cell) |
| 4- 1200 grooves/mm diffraction grating | 10- 5 cm x 2 cm quartz cell (5 cm reference cell) |
| 5- Monochromator exit slit 3.00 mm | 11- 10 cm x 2 cm quartz cell (10 cm reference cell) |
| 6- Achromatic quartz-fluorite condenser | |

and 16 cm from the condenser lens. At this distance the light beam comes to a focus 5cm into the 10 cm cell. The second 10 cm cell (reference cell) was placed at right angles to the light beam. A 2" x 2" x 1/6" quartz plate was placed in the light path at a 45° angle in such a way that some of the incident light was reflected into the 10 cm reference cell. Each of the 10 cm cells was equidistant from the quartz plate.

A box completely enclosed the apparatus, including the condenser lens but not the monochromator or light source. The box was designed to have three compartments: (a) containing the condenser lens, quartz reflecting plate and light baffles to eliminate stray light entering the cells, (b) containing the 10 cm test and 5 cm reference cells on a movable stage, (c) containing the 10 cm reference cell, also on a movable stage. Magnetic stirring motors were placed in compartments (b) and (c) to stir the solutions in the rear quarter of the 10 cm cells. The magnetic bars used were 1 x 0.2 cm and their speed of rotation was controlled by variable resistors located outside the photolysis box.

The solutions to be photolyzed were thoroughly degassed before photolysis by the freeze-pump-thaw method. For this purpose a 25 ml round bottomed flask was adapted to the 10 cm quartz cell as shown in figure (3). The solution to be photolyzed (26.8 ml) was introduced into the 25 ml round bottomed flask (fig. 3). All the joints were greased at their outer extremity by Apiezon N grease (such that no grease would find its way into the solution). The apparatus was then assembled. The round bottomed flask was immersed in liquid nitrogen for 15 minutes, vacuum (0.05 mm Hg) was applied in the cell and then purged four times with argon. The liquid nitrogen was removed and

the solution allowed to thaw. The solution was then frozen again and the cycle repeated. Four such cycles were considered sufficient to remove the oxygen from the cell.

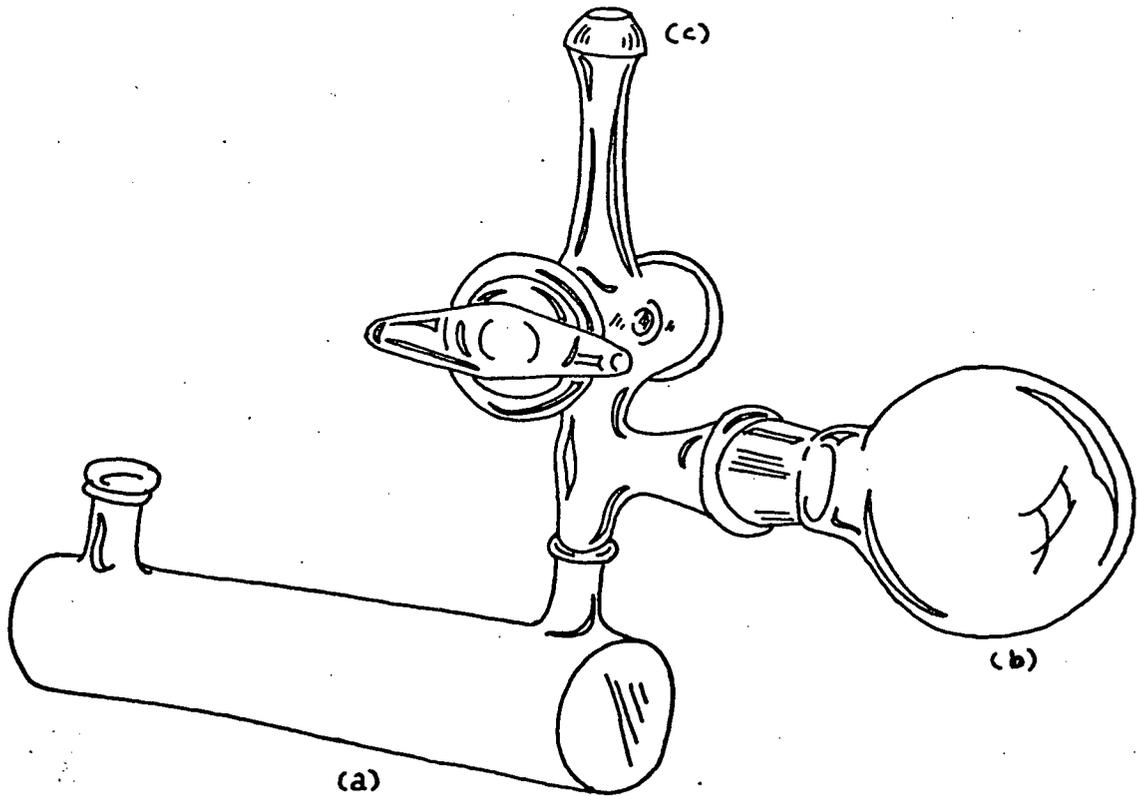


Figure 3 . Cell system for degassed solutions
(a) 10 cm x 2 cm quartz cylinder
(b) 25 ml Pyrex round bottom flask
(c) connection for vacuum manifold

Figure 4 represents the emission spectrum of the mercury light source used for quantum yield measurements. The very intense 366 nm mercury resonance line was selected for all the work described.

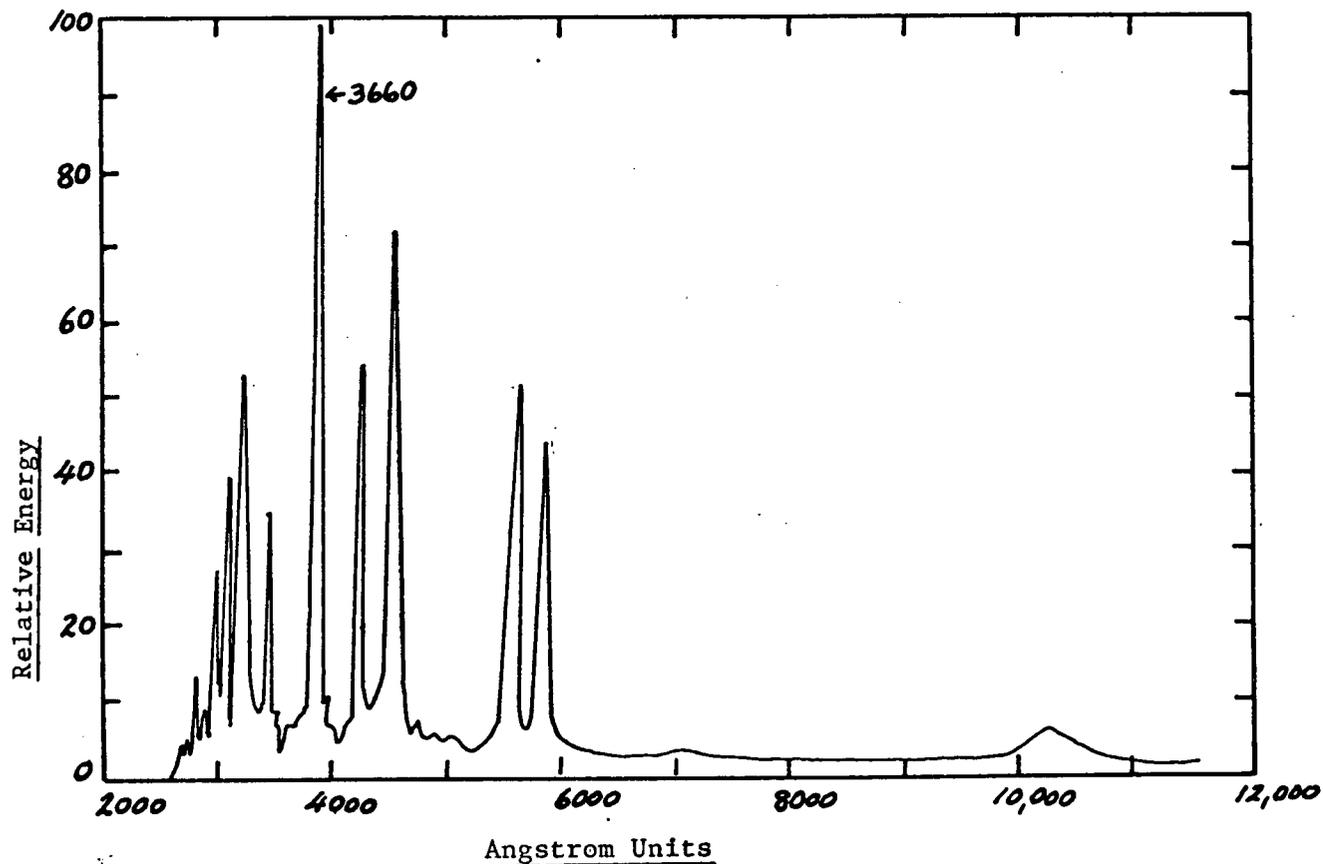


Figure 4. Emission spectrum of the Osram HBO 200 super high pressure mercury lamp. Adapted from J.G. Calvert and J.N. Pitts, Jr, "Photochemistry", John Wiley & Sons, Inc., New York (1967), p.704.

B. Actinometry

The basic requirement of quantum yield measurements is knowledge of the amount of light that entered and was absorbed in the reaction solution. This can be determined in several ways:

(a) Measure with the actinometer the light intensity before and after photolysis, then average those values to determine the incident light on the reaction solution.

(b) Monitor the amount of light entering the reaction solution in the test cell by using a quartz plate beam splitter which reflects a known amount of light into an actinometer solution in the 10 cm reference cell.

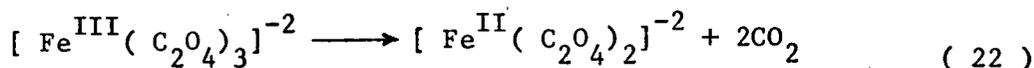
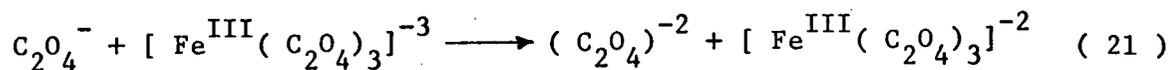
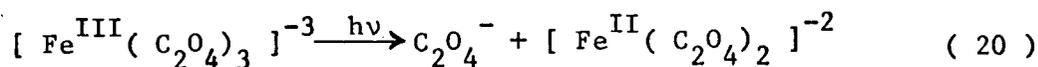
(c) Carry out the procedure described in (b) but also measure with actinometer in both test cell and 10 cm reference cell, the light intensity before and after photolysis to determine the splitting ratio of light by the beam splitter.

(d) One can perform any of the above methods using calibrated phototubes instead of actinometers.

The work described herein was done using procedure (b). The beam splitting caused by the quartz plate was determined and then assumed to remain constant.

Phototubes afford simplicity of operation once calibrated but they cost more than actinometers.

The actinometer used for all the work was potassium ferrioxalate.⁶⁰ This is a very sensitive actinometer and its usefulness ranges from 250 - 509 nm.⁶¹ The actinometer reacts photolytically as follows:⁶²



The amount of ferrous ion produced can be measured when an aliquot of the photolysis mixture is combined with 1,10-phenanthroline and the absorbance measured at 510 nm. All actinometry work was done under Kodak OB safelights and a ruby red lamp.

Potassium ferrioxalate [$\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot 3 \text{H}_2\text{O}$] was prepared by the method of Hatchard and Parker.⁶⁰ A solution of 600 ml of 1.5 M potassium oxalate (reagent grade) was mixed vigorously with 200 ml of 1.5 M ferric chloride (reagent grade). Beautiful green crystals were obtained. These were recrystallized three times from warm water and dried in an oven at 50° for 48 hours. Safelights were used during recrystallization. The solution used for actinometry was 9.82 gm (0.0999 moles/liter) of potassium ferrioxalate in 200 ml of 0.1N H_2SO_4 . The solution was kept sealed and in darkness.

A modification by Kurien⁶³ involved adding acetate buffer and 1,10-phenanthroline solution to the solution containing the actinometer before photolysis. This simplified the procedure of analyzing the actinometer after photolysis. The solution could simply be diluted a proper amount and measured directly in the spectrophotometer. However, it was found that the results were lower in value and less consistent than those obtained by the method of Parker. It could be that due to the fairly substantial amount of light absorbed during photolysis, the

ferrioxalate became somewhat depleted and that the 1,10-phenanthroline may have absorbed some of the incident light. Kurien's method was not adopted.

The solution showed little ferrous ion formation in the first four days after preparation. The solutions used were never older than this. In preparation for photolysis a 27.0 ml aliquot of solution was introduced into the 10 cm reference cell and a 13.5 ml aliquot introduced into the 5 cm reference cell. Both cells were then placed in the photolysis box.

There seemed to be no need to degas the solution since the results were comparable for degassed and non-degassed solutions.

After photolysis the solutions were diluted sufficiently with 0.1N H_2SO_4 to give an absorbance in the range of 0.3 to 0.7. A portion of this diluted solution was then combined with acetate buffer (600 ml 1N-sodium acetate and 360 ml 1N H_2SO_4 to 1 liter) and 1,10-phenanthroline monohydrate in water (0.1 %) in a ratio 5:3:2 respectively. The solution was stirred and allowed to stand for one hour, then it was analyzed in a Cary Model 15 spectrophotometer at 510 nm.

C. Calibration of the Cary Model 15 Spectrophotometer response to Fe^{++} -Phenanthroline complex.

A stock solution containing 1.1203 gms (4.030 mmol) of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ made up to 250 ml with 0.1N H_2SO_4 was prepared. A 25 ml aliquot was diluted to 1 liter with 0.1N H_2SO_4 . A series of eleven 20 ml solutions were prepared by combining from 0 to 5.0 ml of the diluted ferrous sulfate solution with 4 ml of 0.1% 1,10-phenanthroline monohydrate in water, 6 ml of acetate buffer and topped with 0.1N H_2SO_4 . The solutions were well mixed, allowed to stand for at least one hour and then analyzed at 510 nm on the Cary 15.

Graph 13

ABSORBANCE versus Fe⁺⁺ CONCENTRATION

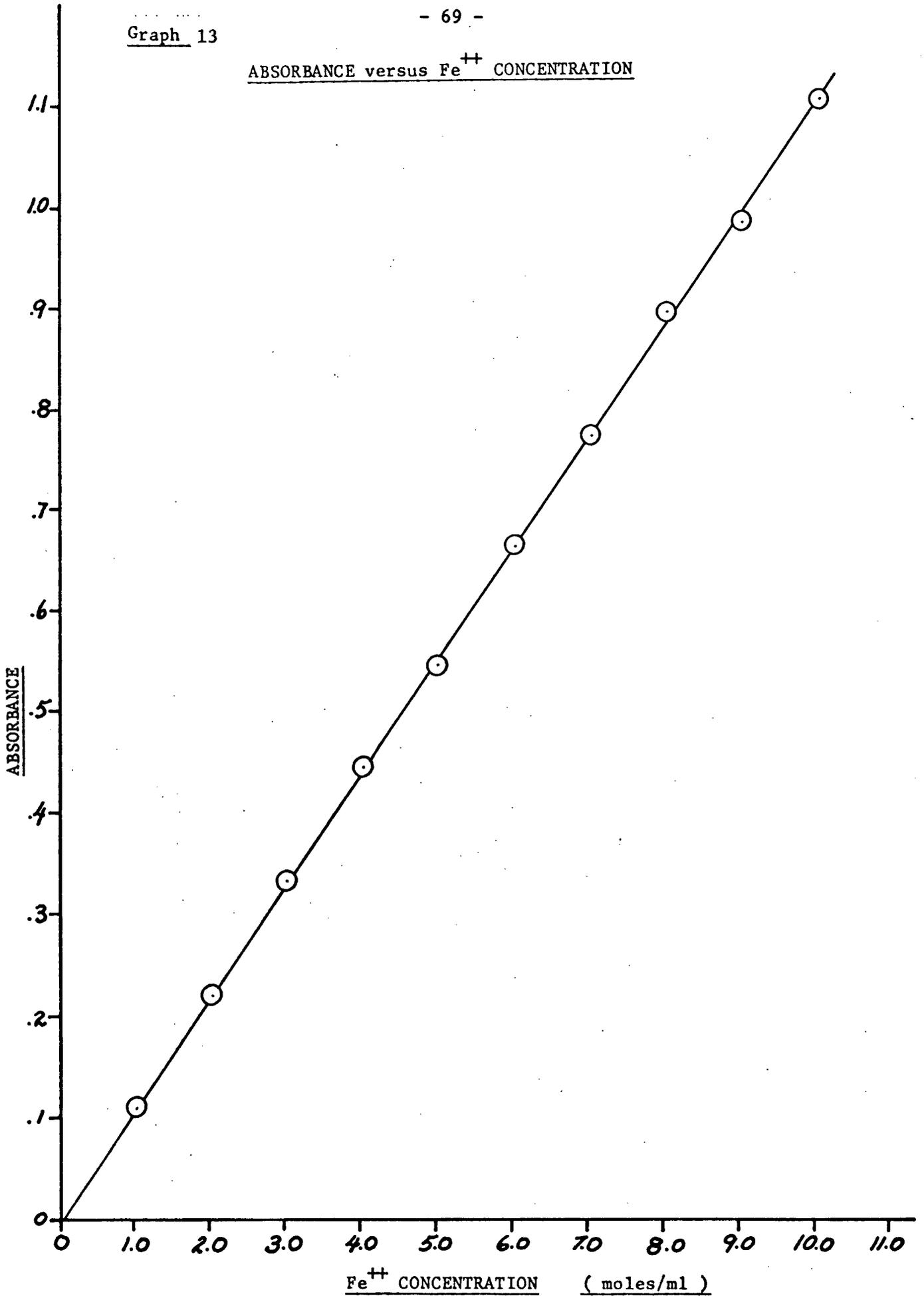


TABLE 4

<u>Concentration of Fe⁺⁺</u> (mole/ml)	<u>Absorbance 510 (nm)</u>
1.007 x 10 ⁻⁸	0.110
2.015 x 10 ⁻⁸	0.222
3.022 x 10 ⁻⁸	0.333
4.030 x 10 ⁻⁸	0.446
5.037 x 10 ⁻⁸	0.546
6.044 x 10 ⁻⁸	0.664
7.052 x 10 ⁻⁸	0.775
8.059 x 10 ⁻⁸	0.897
9.067 x 10 ⁻⁸	0.986
10.07 x 10 ⁻⁸	1.106

The data is plotted on graph 13.

The least squares slope for the points is 1.099×10^7 ml/mole and the standard error for the slope is 1.3×10^5 ml/mole. The callibration of the machine was carried out at six month intervals, however, the variation in the slope never exceeded the experimental error.

D. Determination of the Percentage Splitting Caused by the Quartz Plate Beam Splitter.

It was necessary to know the amount of light actually reflected by the Quartz plate in the quantum yield apparatus. For this purpose a series of experiments were performed in which all the cells were filled with $0.0999 \text{ M } \text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3$.

The mercury lamp was turned on but the beam block (2) Fig. was left in place for thirty minutes to assure that the lamp had warmed up and the arc stabilized before photolysis was permitted.

A ten minute 366 nm photolysis was performed. The solutions were stirred during photolysis and for another fifteen minutes after. The solutions were diluted with 0.1N H₂SO₄ except for the 5 cm reference solution, and the required amount of 1,10-phenanthroline solution and buffer was added, stirred, allowed to stand for one hour, and measured on the Cary 15 at 510 nm.

The results were:

7.76% , 7.88 , 7.72 , 7.92 , 7.57 , 7.62 , 7.84 , 7.80 ,
8.07 , 7.75 , 7.99 .

The mean value was 7.81 % and the standard error 0.14 %.

E. Formula for Calculating the Number of Quanta Absorbed by the Test Solution.

For each occasion that actinometer solutions were measured for ferrous ion content, the ferrous ion content of the unphotolyzed stock solution was measured.

No. of Einsteins absorbed by the solution photolyzed in the test cell =
$$\frac{[V_1 (d_1 A_1 - A_0) 11.8] - [V_2 (d_2 A_2 - A_0)]}{l \times \epsilon_{Fe^{++}} \times 10^3 \times \phi_{Fe^{++}}}$$

The first term represents the amount of light incident on the test solution cell and the second term represents the amount of light not absorbed by the test solution.

V₁ = volume of the 10 cm reference cell (27.0 ml)

d₁ = dilution factor for absorbance measurement of the 10 cm reference cell actinometer solution

A₁ = absorbance of the 10 cm reference cell actinometer solution.

A₀ = absorbance of the unphotolyzed solution.

11.8 = factor derived from the % light reflected into the 10 cm reference cell

$$[\text{light entering test cell}] = \frac{(\text{light entering 10cm ref. cell})(1-0.0781)}{0.0781}$$

V_2 = volume of the 5 cm reference cell (13.5 ml)

d_2 = dilution factor for absorbance measurement of the 5 cm reference cell actinometer solution

A_2 = absorbance of the 5 cm reference cell actinometer solution

l = path length of the cell used in the spectrophotometer (1cm)

$\epsilon_{\text{Fe}^{++}}$ = extinction coefficient of ferrous ion at 510 nm
($1.099 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$)

$\phi_{\text{Fe}^{++}}$ = quantum yield for the formation of ferrous ion at 366 nm
(1.15 is the value adopted here. This value was found by Hatchard and Parker,⁶⁰ however Lee and Selinger⁶⁴ found a value of 1.20)

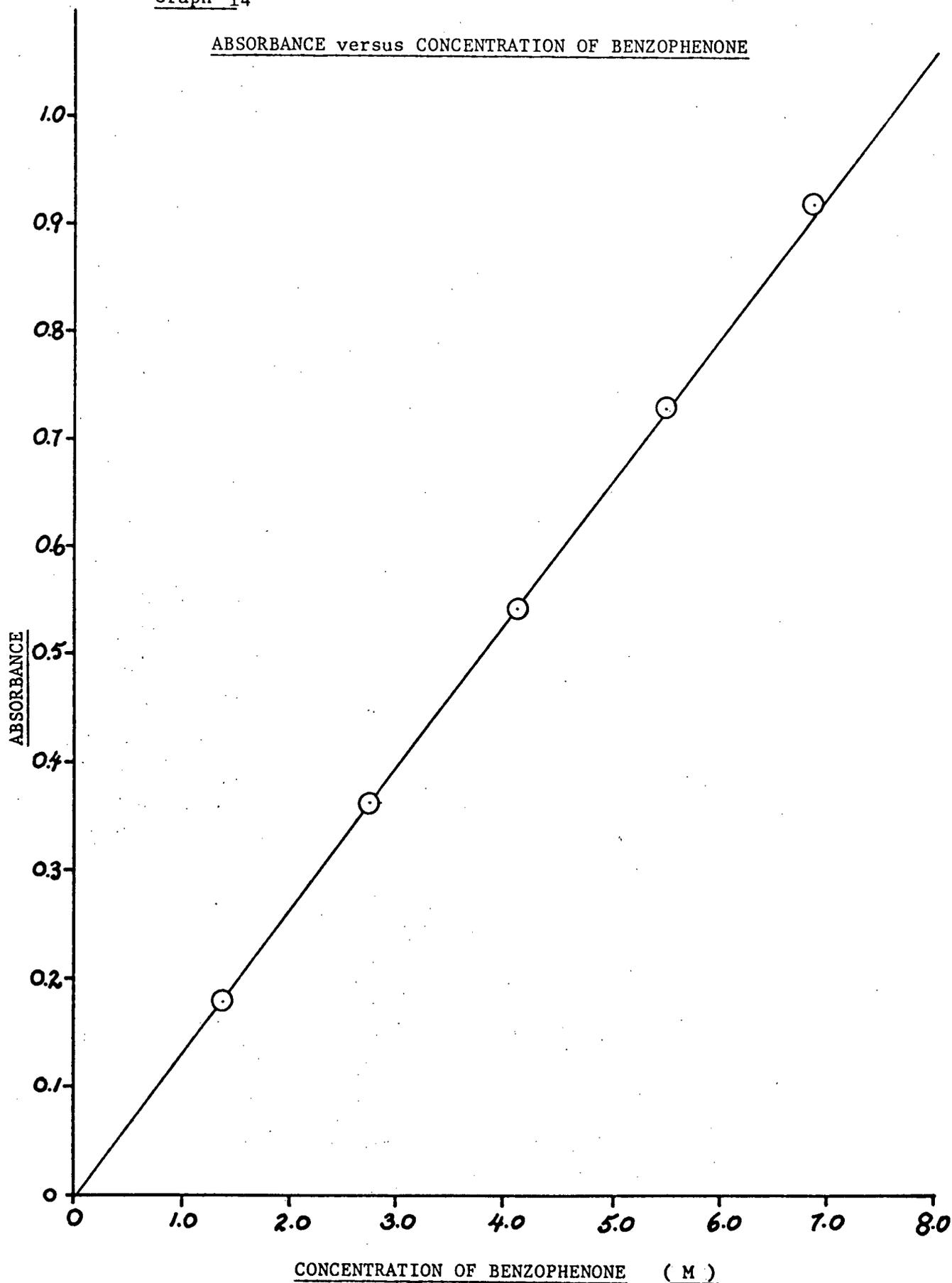
F. Cary 15 Response Calibration Curve to Benzophenone Concentration at 342 nm.

To determine the accuracy of the quantum yield apparatus, a series of experiments were designed to establish the quantum yield of 0.1M benzophenone with 0.1M benzohydrol in benzene. To this end a calibration curve of response of the Cary 15 spectrophotometer to benzophenone concentration was required. Benzophenone has a λ_{max} at 342 nm, and it was this absorption that the Cary 15 was calibrated to.

Two stock solutions were made: (a) 0.1998 M Benzhydrol (Aldrich reagent, twice recrystallized from ethanol, mp 65.5 - 66.0°) to 250ml in benzene ; (b) 0.2201 M Benzophenone (Aldrich reagent, twice distilled, mp 46.5 - 47.0°) to 100 ml in benzene. To each of six 50 ml volumetric

Graph 14

ABSORBANCE versus CONCENTRATION OF BENZOPHENONE



flasks, 25 ml of the benzhydrol solution (0.0999 M) and 0 to 25 ml of the benzophenone solution was added, then topped with benzene (spectrograde). Then 3 ml aliquots of these solutions were diluted with 45 ml of benzene and then analyzed in the uv machine.

TABLE 5

<u>Concentration of</u> <u>Benzophenone</u> (M) in the diluted 48 ml solution	<u>Absorbance</u> (342 ml)
6.872×10^{-3}	0.919
5.502×10^{-3}	0.730
4.127×10^{-3}	0.543
2.751×10^{-3}	0.362
1.372×10^{-3}	0.180
0	0

The points are plotted on graph 14.

The best fit to these points was a least squares slope of $132M^{-1}cm^{-1}$. This of course, represents the extinction coefficient of benzophenone at λ_{max} 342.

G. Quantum Yield of 0.1 M Benzophenone with 0.1 M Benzhydrol in Benzene.

Four experiments were made. One of these four involved using 25 ml of the 0.1998 M solution of benzhydrol and 25 ml of the 0.2201 M benzophenone solution from the calibration runs (previous section).

The other three experiments used two new stock solutions:

100 ml of 0.2000 M benzhydrol in benzene ;

100 ml of 0.2000 M benzophenone in benzene.

These were combined in equal parts as well. The 26.8 ml of each of these solutions were placed in the cell, degassed and then photolyzed for five hours at 366 nm.

TABLE 6

Absorbance Unphotolyzed Solution	Photolyzed Solution	Mole Benzophenone Reacted (m mol)	Light Absorbed mEinstein	Quantum Yield for Benzophenone disappearance
0.922	0.813	0.351	0.492	0.71
0.837	0.711	0.406	0.580	0.70
0.841	0.726	0.371	0.535	0.69
0.839	0.728	0.358	0.542	0.66

The mean value for the quantum yield of benzophenone disappearance is 0.69. This value is in good agreement with the values obtained by Hammond et al⁶⁵ 0.67 and by Moore et al⁶⁶ 0.68.

EXPERIMENTAL

A. General

Infrared (ir) spectra were recorded on a Perkin-Elmer Model 137 spectrometer, using sodium chloride cells. Nuclear magnetic resonance (nmr) spectra were recorded on the Varian Model T-60, HA-100, and XL-100 by Ms. Philis Watson and Mr. William Lee of this department. TMS was used as an internal standard in all cases. Melting points were determined on a Fisher-Johns melting point block and are all uncorrected. Ultraviolet (uv) spectra and visible measurements were recorded on a Cary Model 15 recording spectrophotometer. The 510 nm absorption of the σ -phenanthroline-Fe⁺⁺ complex was measured with wavelength control approaching 510 nm from higher wavelength. The gas liquid partition chromatography (glpc) other than quantum yield measurements were done on a Varian Aerograph Model 90P and Varian Aerograph Autoprep Model 700. Both were connected to Honeywell Elektronik 15 strip chart recorders. For all glpc operations involved in the measurement of quantum yields, a Varian Aerograph Model 1520B with a flame ionization detector was used. The carrier gas was helium. Pure grade air, hydrogen and oxygen were used to combust the materials isolated by glpc. The oxygen was fed into the hydrogen line at a point close to the detector, using a Y-tube. Each line was fitted with one-way valves opening under a pressure of 1 psi. The use of

oxygen⁶⁷ improved the sensitivity of the instrument almost threefold. The glpc was connected to a Honeywell Electronik 15 strip chart recorder with a 1 mvolt full scale sensitivity and fitted with a Disc Chart Integrator Model 201-B.

The columns used for all glpc measurements of the quantum yields were: (a) 10' x 1/8" stainless steel packed with 20% DEGS on 60/80 Chromosorb W (this material was carefully fluidized and then sieved to obtain a homogeneous support. The column was packed as a straight pipe under 45 psi pressure. The column was then bent to the desired shape after packing.). The column temperature was kept at 135° and the injector and detector at 190°. The carrier gas flowed at 30 ml/minute ; (b) 3' x 1/8" stainless steel packed with 20% DEGS on 60/80 Chromosorb W in the same manner as (a). The column operated at 145° and the injector and detector at 190°. The He carrier gas flowed at 30ml/minute. Column (a) was used for the isolation of the photoproducts of tetrahydronaphthoquinone 27 and column (b) for the isolation of the photoproducts of tetrahydronaphthoquinone 10.

Biphenyl (Aldrich reagent grade, twice recrystallized from ethanol, mp 67.8 - 68.0°) and 1,4-naphthoquinone (K & K Labs., Inc., recrystallized from petroleum ether (68°), decolorized with carbon, recrystallized again, mp 122-123°) were used as internal standards for the glpc measurements.

Internal standard was added after photolysis. A 15 ml portion of the photolysis mixture was combined with 2 ml of internal standard stock solution. This mixture was then immediately analyzed by glpc.

The two different internal standards used were selected for their glpc retention time, such that their peaks would not overlap with any other peak expected and yet have a retention time close to that

of the photoproducts studied.

Pipets and volumetric flasks were used for all the measurements of volume.

For all quantum yield measurements, spectro grade benzene was used. For those runs using tert-butanol, reagent grade material was used. A 95:5 mixture of tert-butanol-benzene was dried through a column packed with molecular sieves Linde Type 4A 1" x 16" mesh.

Preparation of 2,3,4a β ,6,7,8a β -Hexamethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (27).

The method proposed by Ansell et al²⁶ was followed. A slurry of 3.2008^m (19.5 mmol) of duroquinone [(prepared from durene according to the method of Smith⁶⁸, yield 81%, recrystallized from petroleum ether (68°C), mp 112 - 112.5°)], 4.0 gm (48mmol) of 2,3-dimethyl-1,3-butadiene (Aldrich, 98%), and a few crystals of hydroquinone were sealed in a Pyrex tube and heated for 27 hrs. at 197°C. The resulting pale yellow solution crystallized on cooling. The material was recrystallized from petroleum ether (68°) to give 4.593 gm (18.6 mmol, 96%) of faint yellow crystals of the desired quinone. The material was recrystallized four more times from petroleum ether (68°) which produced a material with a mp 114.5-115.5° (lit.²⁶ 115-117°); ir (CCl₄) 5.98 (C=O) μ ; nmr (CCl₄) τ 7.3-8.4 (m,4,methylene), 8.0 (s,6,C₂ and C₃ methyl), 8.4 (s,6,C₆ and C₇ methyl), 8.9 (s,6, bridgehead methyls); uv (hexane) ($\epsilon_{254 \text{ nm}}$ 1.20 x 10⁴), 275 - 340 nm, broad shoulder ($\epsilon_{285 \text{ nm}}$ 430), 345 - 475 nm, broad featureless absorption (ϵ_{366} 65).

Large Scale Photolysis of 27 in Benzene.¹⁷

A solution of 2.5 gm (10.1 mmol) of 27 in 300 ml benzene (reagent, distilled) was irradiated through a Corning glass filter No. 7380 (transmitting light of $\lambda > 340$ nm) using a 450 W Hanovia type L medium pressure mercury lamp fitted in a water cooled quartz jacket. Glpc (20% DEGS on 60/80 Chromosorb W as solid support in a 5" x 1/4" column) was used to follow the progress of the photolysis. The solution was

degassed for 30 minutes with argon before photolysis, and a positive argon pressure maintained during photolysis. Irradiation for 4.3 hrs was sufficient to convert ca. 95% of the starting material to two products. The photolysis mixture was concentrated to a yellow oil, and the compounds separated by column chromatography [15" x 1" column charged with 125 gm of Silica Gel (less than 0.08 mm) from E. Merck AG, 10% ethyl acetate/benzene as eluant was used and the passage of material assisted by a positive pressure of 5 - 10 psi nitrogen].

1,3,4,6,8,9-Hexamethyltricyclo[4.4.0.0^{3,10}]dec-8-ene-2,5-dione 29 was isolated as a pale yellow oil. Two Kugelrohr distillations at 80° and 0.02 mm Hg gave a colorless oil (1.34 gm, 5.4 mmol, 54% yield); ir (CCl₄) 5.67 μ (C=O, 4 membered ring), 5.85 μ (C=O, 6 membered ring); nmr (CCl₄) τ 7.57 (q, 1, J=7.5 Hz, C₄ methine), 7.90 - 8.10 (m, 3, C₁₀ methine and C₇ methylene), 8.25 - 8.40 (m, 6, vinyl methyls), 8.78 (s, 3, methyl), 8.95 (s, 3, methyl), 8.95 (d, 3, J=7.5 Hz, C₄ methyl), 9.03 (s, 3, methyl); uv λ_{max} (CCl₄) 256 nm (ε 6.3 x 10²), 295 nm (ε 110). The spectral data is identical to that reported by Gayler, et. al.¹⁷

1,3,4,6,8,9-Hexamethyl-5-hydroxytricyclo[4.4.0.0^{5,9}]deca-3,7-dien-2-one 28 was isolated as a colorless oil which crystallized readily. Recrystallization from petroleum ether (68°) yielded 0.67 gm (2.7 mmol, 27% yield) of the alcohol, mp 101-102° (lit.¹⁷ mp 101-102°) ; ir (CCl₄) 2.69 μ (OH), 5.98 μ (C=O); nmr (CCl₄) τ 4.62 (m, 1, vinyl), 7.79 (broad s, 1, OH), 8.12-8.16 (m, 3, C₃ or C₄ methyl), 8.20 - 8.26 (m, 6, C₃ or C₄ methyl and C₈ methyl), 8.43 (d, 1, J=12.5 Hz, one of C₁₀ methylenes), 8.92 (s, 3, methyl), 9.03 (d, 1, J=12.5 Hz one of C₁₀ methylenes), 9.14 (s, 3, methyl), 9.20 (s, 3, methyl); uv λ_{max} (CCl₄) 257 nm (ε 7.4 x 10³), 320 nm (ε 46).

GLPC Response to Photoproducts 29 and 28 Calibration Curve.

(a) Two stock solutions were prepared. One contained 76.2 mg of ene-dione 29 in 100 ml of benzene, the other contained 100.7 mg of biphenyl (internal standard) in 100 ml of benzene. These two solutions were mixed in predetermined proportions and diluted with benzene to 25 ml to yield the first four entries in Table 7. At this point the ene-dione 29 stock solution was diluted by one half with benzene. Combination of this diluted solution with the internal standard solution in exactly measured proportions and diluted to 25 ml with benzene yielded the rest of the entries of Table . All the solutions were analyzed three times by glpc (10' x 1/8", 20% DEGS, column a).

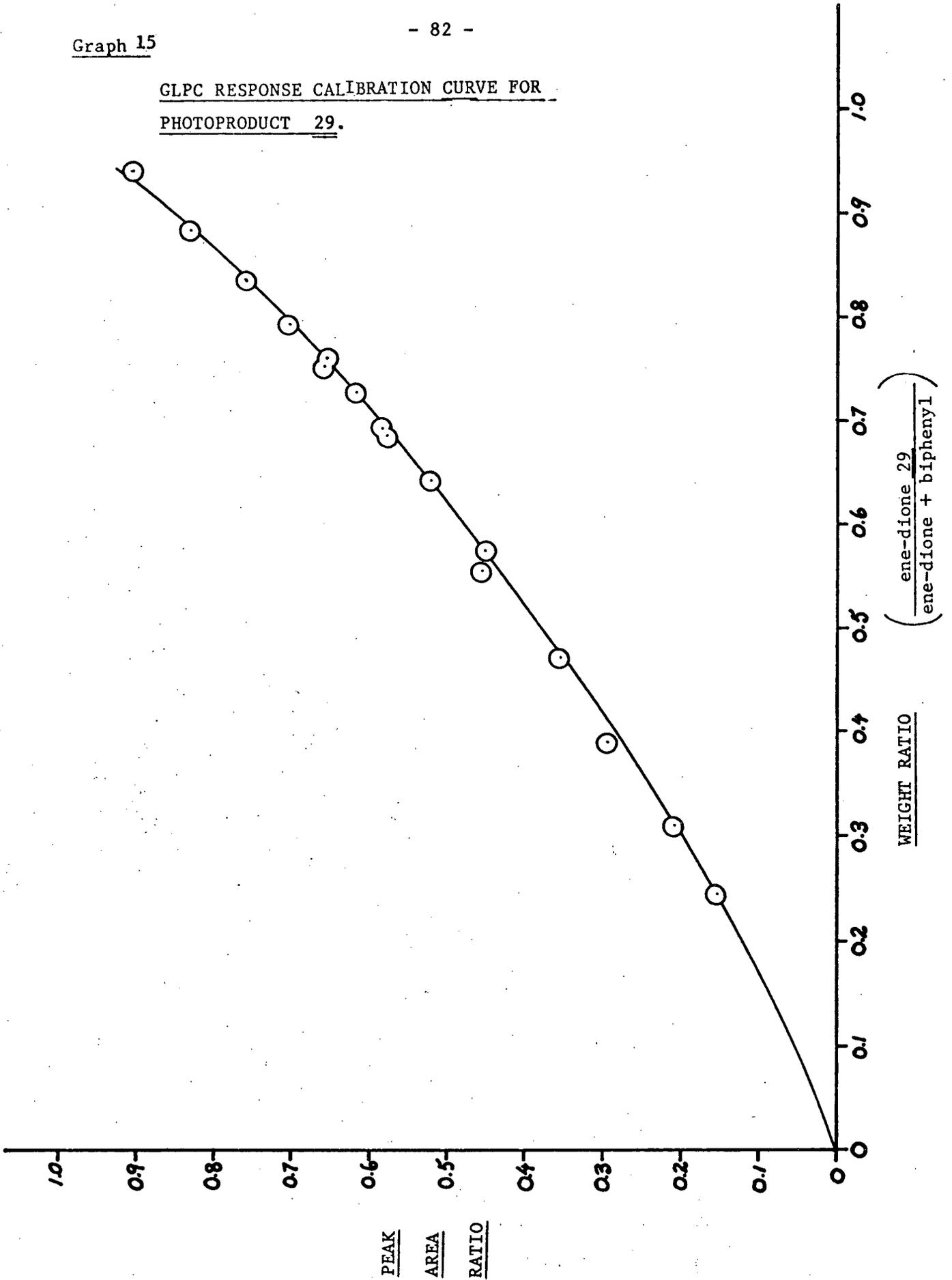
Peak area ratios [(Peak area of ene-dione)/(Peak area of ene-dione +Peak area of Internal Standard)] were measured for each analysis. The three values obtained for each solution were then averaged and plotted against the true weight ratios (Graph 15).

TABLE 7

Weight of ene-dione <u>29</u> in 25 ml (mg)	Weight of Biphenyl in 25 ml (mg)	Averaged Peak Area Ratio (ene-dione <u>29</u>) <hr/> (ene-dione <u>29</u> + IS)
15.20	1.01	0.902
7.60	1.01	0.829
5.45	1.01	0.759
3.80	1.01	0.703
3.17	1.01	0.655
3.05	1.01	0.658

Graph 15

GLPC RESPONSE CALIBRATION CURVE FOR
PHOTOPRODUCT 29.



(TABLE 7 continued)

Weight of ene-dione <u>29</u>	Weight of Biphenyl	Averaged Peak Area Ratio
2.67	1.01	0.617
2.27	1.01	0.582
2.18	1.01	0.578
1.80	1.01	0.520
1.36	1.01	0.452
1.25	1.01	0.455
0.900	1.01	0.356
0.638	1.01	0.294
0.450	1.01	0.208
0.325	1.01	0.156

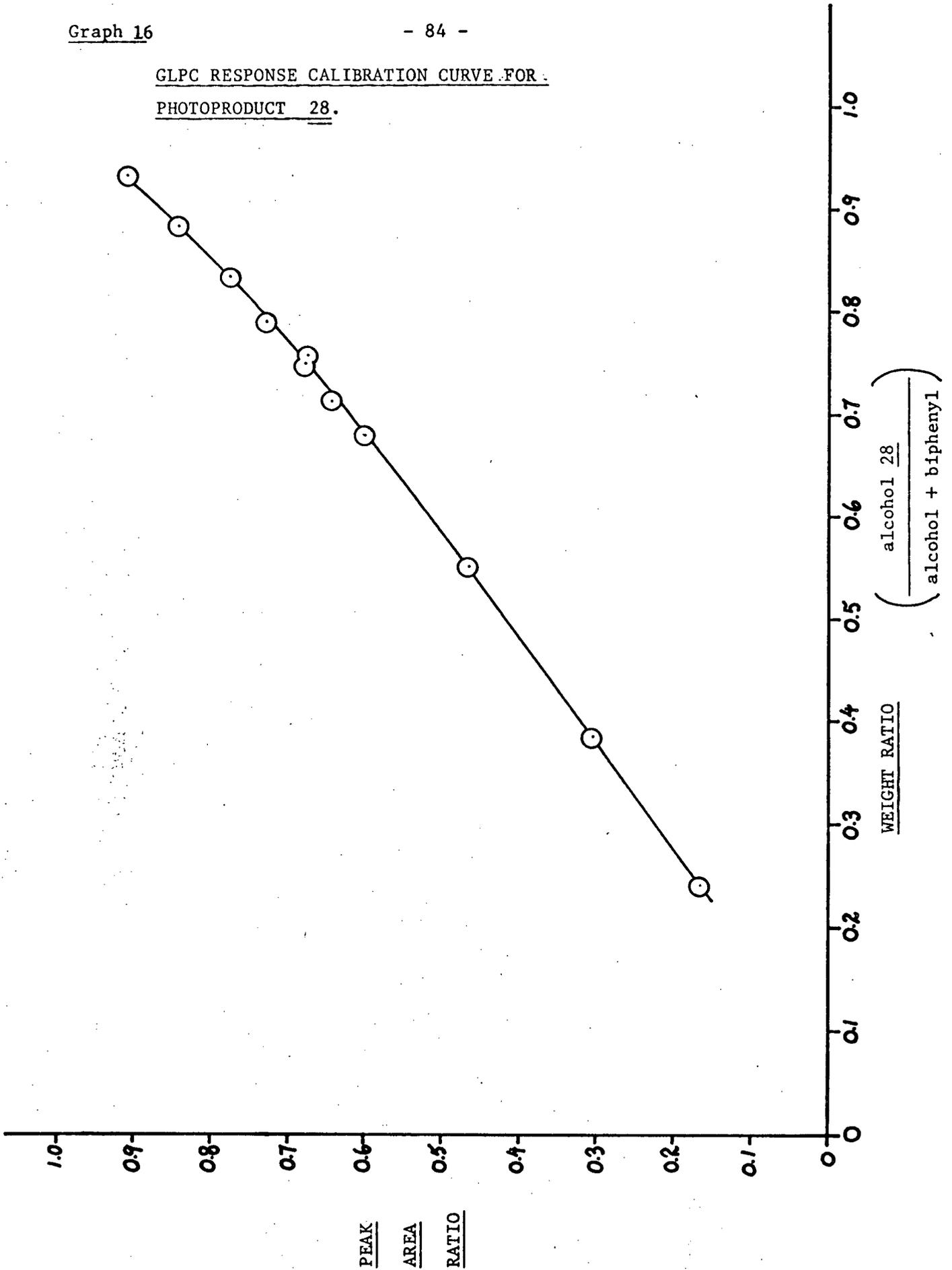
(b) Another stock solution was prepared, this time 74.6 mg of the enone-alcohol 28 was diluted to 100 ml with benzene. The internal standard solution used was the same as in section (a), (100.7 mg biphenyl in 100 ml of benzene). Once again the first four entries in Table 8 represent combinations in particular proportions of these two solutions. The rest of the entries represent combinations of the internal standard solution with a two times diluted enone-alcohol stock solution. All final solutions were made up to 25 ml with benzene. Graph 16 represents the calibration curve of the enone-alcohol 28.

TABLE 8

Weight of enone- alcohol <u>28</u> in 25 ml (mg)	Weight of biphenyl in 25 ml (mg)	Averaged Peak Area Ratio (alcohol <u>28</u>) <hr/> (alcohol <u>28</u> + IS)
14.91	1.01	0.910
7.45	1.01	0.842
4.99	1.01	0.775

Graph 16

GLPC RESPONSE CALIBRATION CURVE FOR
PHOTOPRODUCT 28.



(TABLE 8 continued)

Weight of enone- alcohol <u>28</u>	Weight of biphenyl	Averaged Peak Area Ratio
3.74	1.01	0.730
3.12	1.01	0.675
2.99	1.01	0.679
2.49	1.01	0.645
2.13	1.01	0.600
1.23	1.01	0.464
0.625	1.01	0.306
0.318	1.01	0.166

(c) Finally a standard solution of 30.5 mg of ene-dione 29, 29.9 mgm of enone-alcohol 28, and 25 ml of a solution of 38.7 mg of biphenyl in 100 ml of benzene was diluted with benzene 250 ml. The weight ratio of the ene-dione was 0.759 and the alcohol 0.756. This solution was used to check the response of the gc detector by injecting after every analysis of photolysis mixture.

The solution was at all times kept in the refrigerator to minimize any reactions. A new solution was prepared after every four weeks.

Quantum Yield Determinations of the Photolysis of 2,3,4a β ,6,7,8a β -Hexamethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone 27 in Benzene.

(a) Unquenched experiments:

A series of experiments were performed to determine the quantum yield of formation of photoproducts 28 and 29 in benzene. These consisted of introducing 26.8 ml of a ca. 1.55×10^{-2} M solution of 27 in benzene into the 25 ml round bottomed flask attached to the cell (see apparatus page 64). The solution was then degassed and

then photolyzed at 366 nm for a period sufficient to allow no more than a 15% total conversion, ca. 4 hrs.

After photolysis, a 15 ml aliquot of the solution was mixed with 2 ml of a stock solution of 30.3 mg biphenyl (internal standard) in 100 ml of benzene. The resulting solution was then analyzed by glpc. Table 9 gives the results for the quantum yield of formation of the ene-dione 29 and the alcohol 28.

TABLE 9

Naphthoquinone <u>27</u> Concentration (M)	Light mEinsteins	% Conversion	Quantum Yield of formation of ene-dione <u>29</u> *	Quantum Yield of formation of alcohol <u>28</u> **
0.0161	0.0392	1.4	0.086	0.069
0.0177	0.0389	1.2	0.084	0.066
0.0174	0.0351	1.2	0.088	0.066
0.0154	0.0978	3.6	0.088	0.064
0.0156	0.175	6.9	0.094	0.070
0.0153	0.343	13.3	0.093	0.066
0.0153	0.340	13.3	0.093	0.066
0.0153	0.393	14.3	0.089	0.060

* The mean value for the quantum yield is $0.089 \pm .003$.

** The mean value here is $0.066 \pm .003$.

(The errors expressed are standard errors for the data available.)

(b) Photolysis of 27 using Piperylene as Quencher.

cis & trans-1,3-Pentadiene (piperylene, K & K Labs, practical grade) was distilled (explosion hazard) from lithium aluminum hydride⁶⁹ behind a safety shield (bp 42.2°). A solution of 113.4 mgm (0.0154 M) of 27 with 1.8 ml (0.597 M) piperylene in 30 ml of benzene was prepared. As before, 26.8 ml of the solution was degassed and then

photolyzed at 366nm for ca. 4 hrs. The result was that there was some quenching of the formation of ene-dione 29, $\phi = 0.025$, and no quenching of the alcohol 28, $\phi = 0.064$.

(c) Photolysis using 1,3-cyclohexadiene as quencher.

A set of ca. 0.015 M solutions of compound 27 in benzene with varying concentrations of 1,3-cyclohexadiene (Aldrich 99%, twice fractionally distilled, bp 80.2°) in benzene were thoroughly degassed and photolyzed at 366 nm for approximately 2 - 4 hrs. depending on the age of the lamp.

TABLE 10

<u>27</u> Concentration (M)	1,3-cyclohexadiene Concentration (M)	Light mEinsteins	Quantum Yield of formation ene-dione <u>29</u>	Quantum Yield of formation alcohol <u>28</u>
0.0178	3.94×10^{-4}	0.0348	0.081	0.060
0.0166	3.94×10^{-4}	0.0353	0.085	0.063
0.0193	3.94×10^{-4}	0.0333	0.093	0.066
0.0164	7.88×10^{-4}	0.0299	0.080	0.074
0.0154	7.88×10^{-4}	0.114	0.078	0.070
0.0165	1.58×10^{-3}	0.0391	0.069	0.061
0.0155	1.58×10^{-3}	0.110	0.077	0.077
0.0154	1.58×10^{-3}	0.0960	0.071	0.069
0.0164	3.15×10^{-3}	0.0375	0.062	0.061
0.0155	3.15×10^{-3}	0.116	0.063	0.067
0.0153	4.73×10^{-3}	0.0574	0.052	0.066
0.0153	4.73×10^{-3}	0.103	0.054	0.093
0.0153	4.73×10^{-3}	0.100	0.056	0.070
0.0156	5.52×10^{-3}	0.0544	0.051	0.065
0.0169	6.30×10^{-3}	0.0372	0.045	0.062
0.0153	6.30×10^{-3}	0.408	0.046	0.065
0.0174	9.86×10^{-3}	0.0334	0.041	0.064

(TABLE 10continued)

Naphthoquinone <u>27</u> Concentration (M)	1,3-cyclohexadiene Concentration (M)	Light mEinsteins	Quantum Yield of formation ene-dione <u>29</u>	Quantum Yield of formation alcohol <u>28</u>
0.0153	9.86×10^{-3}	0.0963	0.045	0.073
0.0154	9.86×10^{-3}	0.273	0.048	0.069
0.0154	1.02×10^{-2}	0.109	0.034	0.062
0.0153	1.26×10^{-2}	0.321	0.030	0.065
0.0153	1.58×10^{-2}	0.110	0.028	0.059
0.0153	1.89×10^{-2}	0.137	0.019	0.060
0.0155	2.05×10^{-2}	0.115	0.022	0.061
0.0153	2.52×10^{-2}	0.329	0.017	0.061
0.0154	3.15×10^{-2}	0.116	0.016	0.086
0.0155	4.10×10^{-2}	0.107	0.012	0.065
0.0154	4.41×10^{-2}	0.160	0.011	0.058
0.0153	5.68×10^{-2}	0.133	0.0092	0.076
0.0153	7.57×10^{-2}	0.172	0.0059	0.075
0.0154	8.20×10^{-2}	0.142	0.0062	0.063
0.0154	9.15×10^{-2}	0.121	0.0052	0.080
0.0154	1.10×10^{-1}	0.164	0.0047	0.075
0.0153	1.26×10^{-1}	0.130	0.0039	0.063
0.0153	1.42×10^{-1}	0.188	0.0031	0.066
0.0154	1.58×10^{-1}	0.117	0.0022	0.065
0.0154	1.58×10^{-1}	0.124	0.0029	0.068

For each different quencher concentration, an average ratio was obtained for the ratio ϕ_0 / ϕ (ϕ_0 = unquenched quantum yield, ϕ with quencher). These results were then plotted as ϕ_0 / ϕ versus 1,3-cyclohexadiene concentration (see Graphs 1 & 2). For the ene-dione 29 quenching graph 2 , a least squares treatment was made of all the points up to and including that for 0.0441 M 1,3-cyclohexadiene to obtain the best straight line through these points. The slope was calculated to be 158 M^{-1} , the standard error for the slope was 19 M^{-1} and the error expected for a 99.9 % confidence limit (26 degrees of

freedom) for the points was $\pm 70 \text{ M}^{-1}$.

For the quenching of alcohol 28, a least squares treatment was made as well. The slope was calculated to be -0.03 M^{-1} and the 99.9 % confidence limit (26 degrees of freedom) of the slope was $\pm 10 \text{ M}^{-1}$, (the standard error for the slope was 2.8 M^{-1}).

(d) Photolysis of 27 using trans-stilbene as quencher.

trans-Stilbene (Aldrich 98 %) was twice recrystallized from ethanol, mp 123.5 - 124.0. As before, 0.0155 M solutions of compound 27 were photolyzed at 366 nm with varying amounts of quencher. The solution was first thoroughly degassed by the freeze-pump-thaw method.

It is important to realize that trans-stilbene does absorb some of the light at 366 nm that enters the test solution cell, ($\epsilon_{366\text{nm}} 0.2$) and that cis-stilbene (the product from the excited state of trans-stilbene) does too ($\epsilon_{366\text{nm}} 0.6$). The data for the quenching by trans-stilbene is presented in Table 11.

TABLE 11

<u>Naphthoquinone</u> <u>27</u> Concentration (M)	<u>trans-stilbene</u> Concentration (M)	Light mEinstein	Quantum Yield of formation ene-dione <u>29</u>	Quantum Yield of formation alcohol <u>28</u>
0.0153	5.22×10^{-4}	0.426	0.074	0.066
0.0153	1.04×10^{-3}	0.409	0.069	0.067
0.0154	2.08×10^{-3}	0.416	0.055	0.067
0.0153	1.05×10^{-2}	0.418	0.033	0.061
0.0154	2.11×10^{-2}	0.450	0.017	0.063
0.0153	4.19×10^{-2}	0.408	0.013	0.060
0.0157	6.35×10^{-2}	0.423	0.0065	0.060
0.0154	1.05×10^{-1}	0.420	0.0042	0.059

The data is plotted as ϕ_0 / ϕ versus trans-stilbene concentration in graph 3 and graph 4. Least squares treatment yielded the following

results: (a) ene-dione 29 quenching (graph 4):

slope 186 M^{-1} , standard error 20 M^{-1} , 99.9 % confidence limit on the slope (six degrees of freedom) $\pm 119 \text{ M}^{-1}$, 99.5 % confidence limit on the slope $\pm 86 \text{ M}^{-1}$.

(b) alcohol 28 quenching (graph 3):

slope 0.92 M^{-1} , standard error 0.85 M^{-1} , 99.9 % confidence limit on the slope (six degrees of freedom) $\pm 5.1 \text{ M}^{-1}$.

(e) Photolysis of 27 using Oxygen as Quencher :

The 0.0154 M solution of 27 in benzene was degassed twice and then flushed with the oxygen (Matheson, Ultra High Purity, 99.95 %) and pressurized to 760 mm Hg. The solution was allowed to thaw. The pressure in the cell was checked again and adjusted to 760 mm Hg. The gauge used was a simple U-tube half filled with mercury, open at one end, and connected to the vacuum system at the other end. The latter had a pinch-clamp attached so that the manometer was only open to the system two periods of about 4 seconds. The concentration of oxygen in the solution was ca. 0.01 M.

TABLE 12

<u>27</u> Concentration (M)	Oxygen Concentration (M)	Light mEinsteins	Quantum Yield of formation ene-dione <u>29</u>	Quantum Yield of formation alcohol <u>28</u>
0.0155	@0.01M	0.395	0.0015	0.044
0.0153	@0.01M	0.408	0.0013	0.042

(f) Study of the Effect of Changing Quinone 27 Concentration on the Quantum Yields of Photoproducts 29 and 28.

TABLE 13

Naphthoquinone <u>27</u> Concentration (M)	% Conversion	Light mEinsteins	Quantum Yield of formation ene-dione <u>29</u>	Quantum Yield of formation alcohol <u>28</u>
0.00769	20.7	0.266	0.093	0.066
0.0153	13.0	0.343	0.090	0.064
0.0229	9.1	0.364	0.086	0.066
0.0306	6.8	0.373	0.084	0.064
0.0383	5.6	0.371	0.088	0.065
0.0458	4.6	0.360	0.088	0.069
0.0611	3.3	0.354	0.087	0.063

The procedure in these experiments was the same as in the previous runs, however no quencher was added. The data is presented also in graph 5.

Synthesis of 6,7-Dimethyl-4a β ,5,8,8a β -tetrahydro-1,4-naphthoquinone 10.

Following the procedure of Mandelbaum and Cais⁴⁸, a mixture of 5.50 g of *p*-benzoquinone (50 mmol, Eastman, practical grade, recrystallized from petroleum ether (68°), decolorized with charcoal, and recrystallized twice more, mp 112.5 - 113.0°) and 9.45 g of 2,3-dimethyl-1,3-butadiene (116 mmol, Aldrich 98 %) was heated to 60° and stirred for one hour. The diene was removed and the residual solid was recrystallized from petroleum ether 68° and from ethanol to give 8.58 g (45 mmol, 91 % yield) of pale yellow needles. The material was recrystallized three more times

from petroleum ether to yield needles of mp 114.5 - 115.0° (reported mp 115 - 117°); ir (CHCl₃) 5.90 μ (C=O); nmr (CCl₄) τ 3.5 (s, 2, C₂ and C₃ vinyl), 6.9 (t, 2, J= 3 Hz, C_{4a} and C_{8a} methines), (m, 4, C₆ and C₈ methylenes), 8.4 (s, 6, vinyl methyls);
uv (n-hexane) λ_{max} 221 nm (ε 8720), 298 nm (ε 123),
shoulder 365 nm (ε 60).

Large Scale Photolysis of 6,7-Dimethyl-4aβ,5,8,8aβ-tetrahydro-1,4-naphthoquinone 10 in Benzene.¹²

Compound 10 (1.500 gm, 7.89 mmol) was dissolved in 400 ml of benzene (reagent grade, distilled). The solution after degassing by argon bubbling for 30 minutes, was photolyzed for 21 hrs with a 450 W medium pressure mercury Hanovia Type L lamp. A Corning 7380 filter allowed only wavelength longer than 340 nm to enter the solution.

The photolysis was followed by glpc, using a 5' x 1/4" column packed with 20 % DEGS on 60/80 Chromosorb W (column temp 150 °C, detector and injector temperature 200 °C, helium carrier gas at 60 ml/minute). Two products appeared. The starting material was heat labile and could not be detected. The photolysis was stopped when the photoproduct peaks on the gc did not increase in size any longer.

The two photoproducts were separated by column chromatography using 120 gm of Silica Gel (less than 0.08 mm) E Merck AG in a 15" x 1" column and chloroform as eluant. The two photoproducts overlapped in two of the thirteen fractions in which they eluted, and these two fractions were discarded. After the chloroform was removed,

crystals formed for each compound. These were recrystallized from ether-petroleum ether (30 - 60°) to yield:

(a) 450 mg (2.37 mmol, 30%) of white crystals of white crystals of 8,9-dimethyltricyclo[4.4.0.0^{3,9}]dec-7-ene-2,5-dione 12, mp 77-78° (lit.¹² mp 77-78°); ir (CHCl₃) 5.69, 5.81 μ (C=O); nmr (CDCl₃) τ 8.63 (s,3,C₉ methyl), 8.13 (d,3, J= 2 Hz, C₈ methyl), 4.48 (m,1, vinyl); uv (methanol) λ_{max} 292 nm (ε 220), shoulder 310 nm (ε 200).

(b) 378 mg (1.99 mmol, 25%) of white crystals of 8,9-dimethyl-5-hydroxytricyclo[4.4.0.0^{5,9}]dec-3,7-diene-2-one 13, mp 93-94° (lit.¹² mp 93-94°); ir (CCl₄) 2.8 (weak, OH), 5.90 μ (C=O); nmr (CCl₄) τ 8.90 (s,3,C₉ methyl), 8.50 (d,2,J=5 Hz, C₁₀ methylene),8.20 (d,3,J= 2 Hz, C₈ methyl), 7.76 (m,2, OH and methine), 6.98 (d,1, J=3 Hz, C₆ methine), 4.38 (m,1, C₇ vinyl), 4.15 (d,1,J=10 Hz, C₃ vinyl), 3.35 (d,1,J=10 Hz, C₄ vinyl); uv (methanol) λ_{max} 242 nm (ε 4000), shoulder 330 nm (ε 30).

Large Scale Photolysis of 6,7-Dimethyl-4aβ,5,8,8aβ-tetrahydro-1,4-naphthoquinone 10 in tert-Butanol.

Compound 10 (1.00 g, 5.26 mmol) was dissolved in about 400 ml of an 80:20 mixture of tert-butanol and benzene. The solution was photolyzed λ > 340 nm for 20 hrs after degassing with argon. The crude photolysate was distilled in a Kugelrohr apparatus at 90° and 0.01 mm Hg. The distillate crystallized on cooling to give beautiful white crystals, 0.789 g (4.15 mmol, 79%) of 8,9-dimethyltricyclo-[4.4.0.0^{3,7}]dec-8-ene-2,5-dione 11 was obtained this way.

Recrystallization from petroleum ether (68°) afforded a compound melting at 85-85.5° (lit. ¹² mp 84-85°); ir (CHCl₃) 5.69, 5.81 μ (C=O); nmr (CDCl₃) τ 8.63 (s,3, C₉-methyl), 8.13 (d,3,J= 2 Hz, C₈ methyl), 4.48 (m,1, vinyl); uv (methanol) λ_{max} 292 nm (ε 220), shoulder 310 nm (ε 200).

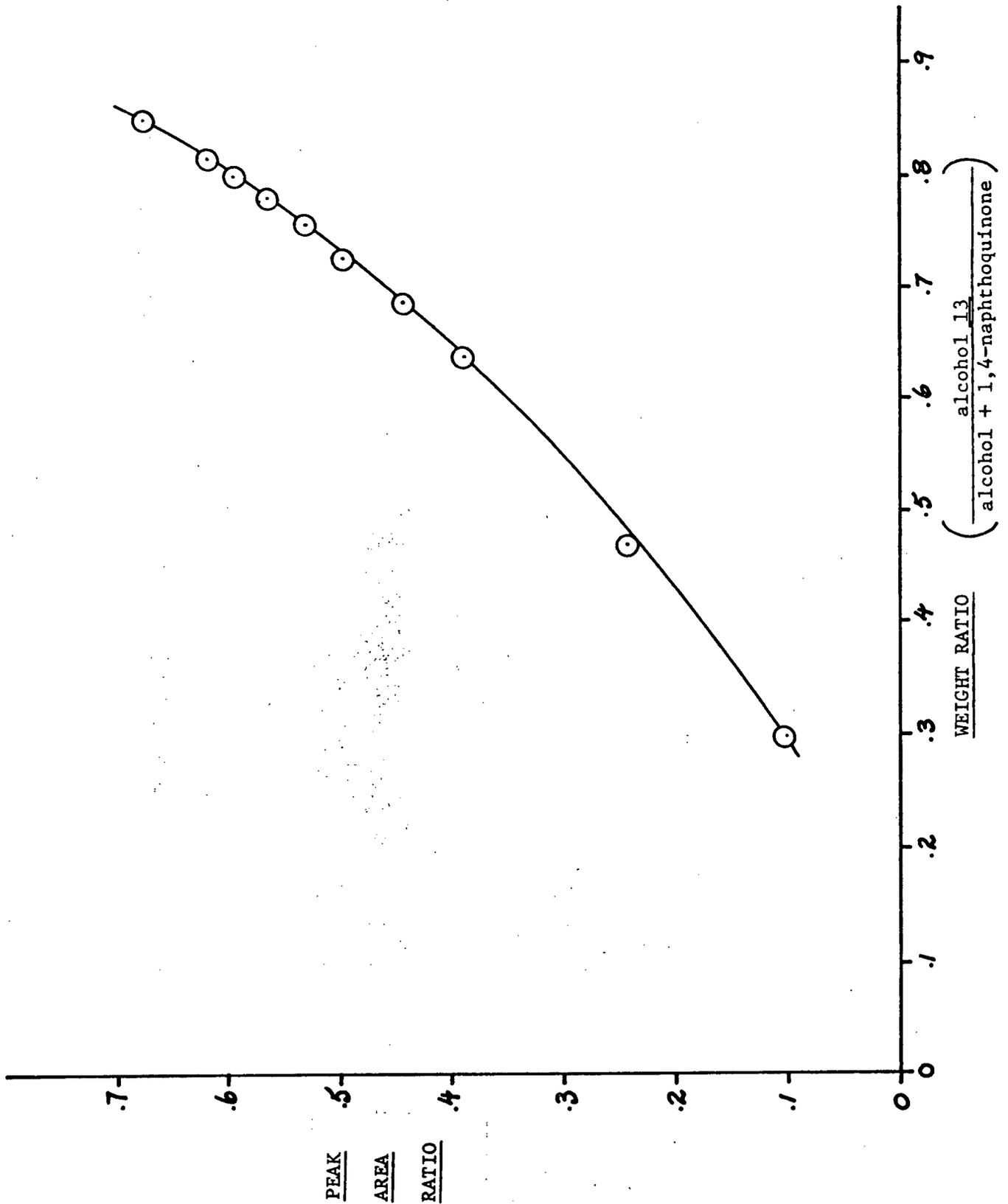
GLPC Response to Photoproducts 12, 13 and 11 Calibration Curve.

(a) A stock solution of 90.6 mg of photoproduct 13 in 100 ml of benzene was prepared. Another stock solution was made up with 103.2 mg of 1,4-naphthoquinone (internal standard) in 100 ml of benzene. These were mixed in predetermined ratios and diluted to 25 ml with benzene in volumetric flasks. Each solution thus made was injected three different times (4 μl injections, peaks separated using the 3' x 1/8 " column of 20% DEGS on 60/80 Chromosorb W, column b). For each run a weight ratio of peak size [(peak area product 13) / (peak area product 13 + peak area internal standard)] was obtained. The average of the three was then plotted against true weight ratio of product 13 [(weight product 13) / (weight product 13 + weight internal standard)], (graph 17). The data thus obtained is presented in Table 14.

TABLE 14

Weight of Product <u>13</u> in 25 ml.	Weight of 1,4-naphthoquinone in 25 ml.	Averaged Peak Area Ratio alcohol <u>13</u> alcohol <u>13</u> + IS
14.45 mg	2.75 mg	0.676
11.32	2.75	0.616
10.20	2.75	0.594

GLPC RESPONSE CALIBRATION CURVE FOR
PHOTOPRODUCT 13.



(TABLE 14 continued)

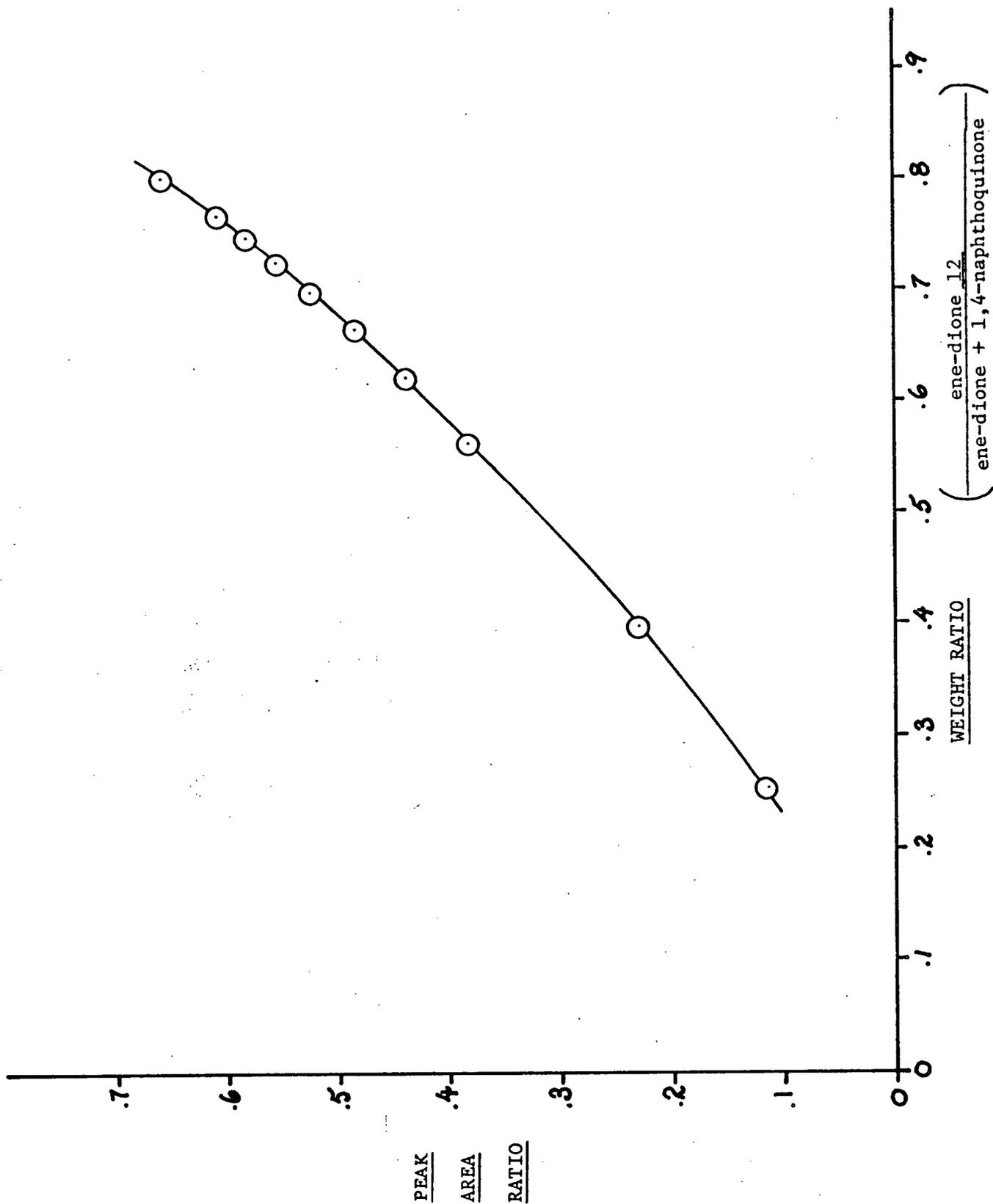
Weight of Product <u>13</u>	Weight of 1,4- naphthoquinone	Averaged Peak Area Ratio
9.05	2.57	0.563
7.92	2.57	0.529
6.80	2.57	0.495
5.65	2.57	0.442
4.52	2.57	0.388
2.26	2.57	0.242
1.08	2.57	0.100

(b) A third stock solution was prepared containing 67.6 mg. of photoproduct 12 in 100 ml of benzene. Varying aliquots were mixed with the internal standard stock solution and diluted to 25 ml. The solutions were analyzed as described in section (a) above. The results are plotted on graph 18 , and presented in Table 15 .

TABLE 15

Weight of Product <u>12</u> in 25 ml.	Weight of 1,4- naphthoquinone in 25 ml.	Averaged Peak Area Ratio <u>(dione 12)</u> <u>(dione 12 + IS)</u>
10.15 mg	2.57 mg	0.659
8.45	2.57	0.608
7.60	2.57	0.582
6.75	2.57	0.555
5.92	2.57	0.524
5.07	2.57	0.485
4.22	2.57	0.439
3.38	2.57	0.383
1.69	2.57	0.230
0.861	2.57	0.125

GLPC RESPONSE CALIBRATION CURVE FOR
PHOTOPRODUCT 12.



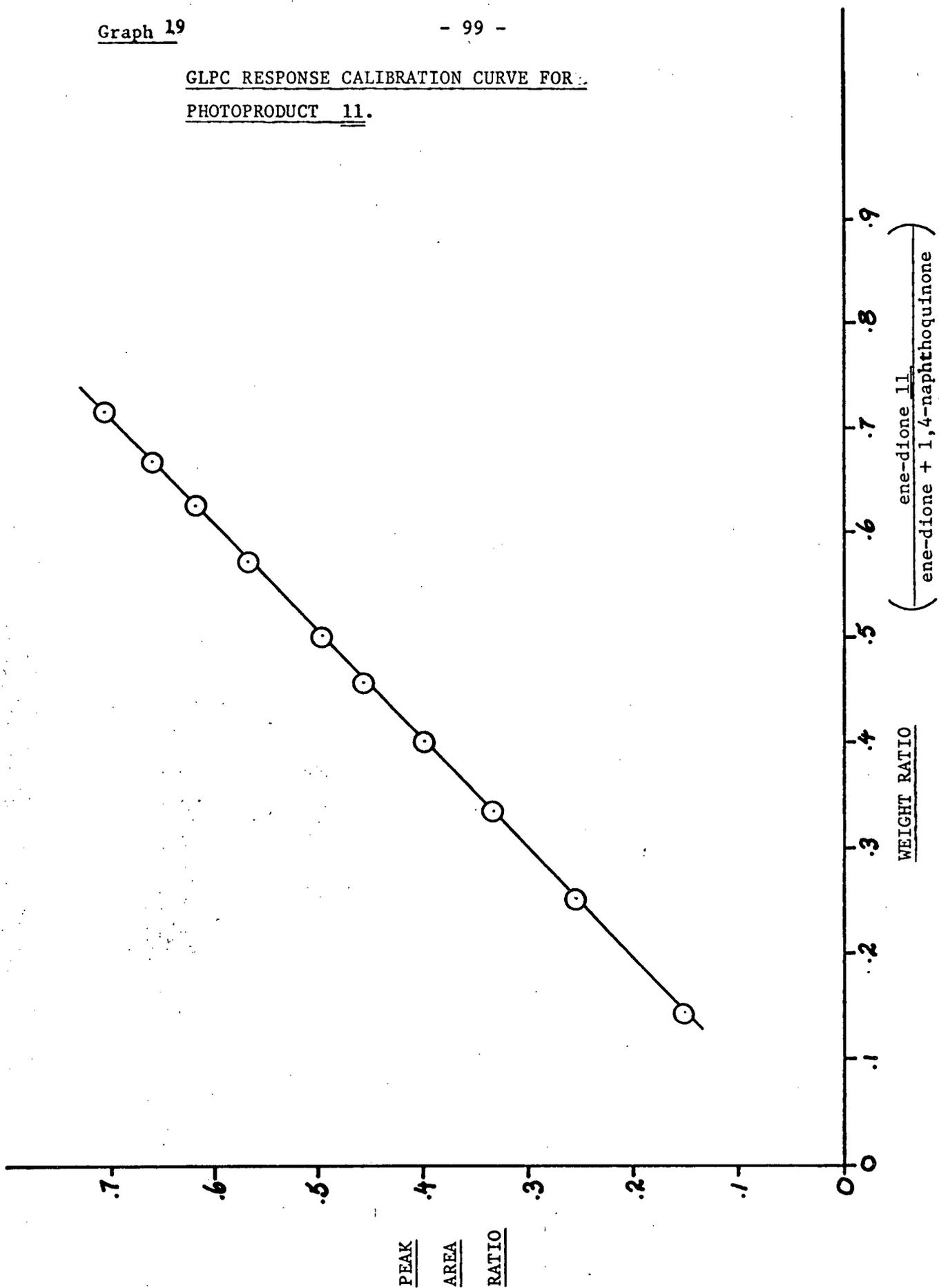
(c) A standard solution was prepared containing 30.4 mg of the alcohol 13, 30.4 mg of the dione 12 and 20.2 mg of 1,4-naphthoquinone (internal standard) and made up to 100 ml with benzene (weight ratio alcohol 13 = .601, weight ratio dione 12 = .601). This solution was kept refrigerated at all times and only kept for two weeks at which time a new solution was prepared. This solution was injected into the gc after every glpc analysis of the photolysis mixture of 10 in benzene.

(d) A stock solution of 94.0 mg of photoproduct 11 in 100 ml of benzene was prepared. A stock solution containing 140.4 mg of 1,4-naphthoquinone in 50 ml of benzene was also made. Once again, the solutions were combined in varying ratios, diluted to 25 ml in benzene, and analyzed by glpc in the same manner as described in section (a). Graph 19 represents the standard curve for the data in Table 16 .

TABLE 16

Weight of Product <u>11</u> in 25 ml	Weight of 1,4- Naphthoquinone in 25 ml	Averaged Peak Area Ratio (dione <u>11</u>) <hr/> (dione <u>11</u> + IS)
14.10 mg	5.62	0.706
11.28	5.62	0.659
9.40	5.62	0.618
7.52	5.62	0.568
5.64	5.62	0.496
4.70	5.62	0.457
3.76	5.62	0.397
2.82	5.62	0.332
1.88	5.62	0.253
0.94	5.62	0.150

GLPC RESPONSE CALIBRATION CURVE FOR
PHOTOPRODUCT 11.



(e) Finally, a standard solution of 37.9 mg. of dione 11 and 19.9 mg of 1,4-naphthoquinone (internal standard) in 100ml of benzene (weight ratio = 0.656) was prepared. This solution was kept cold, and used to check the response of the gc detector to the photolysis mixture of 10 in tert-butanol. This standard solution was kept only for two weeks before a new solution was prepared.

Quantum Yield Determinations of the Photolysis of 6,7-Dimethyl-4a β ,5,8,8a β -tetrahydro-1,4-naphthoquinone 10 in Benzene.

(a) Quantum Yield for the Formation of Alcohol 13 and Dione 12 -- Unquenched Photolysis.

The solutions of ca. 0.02 M of compound 10 in benzene were degassed and photolyzed for approximately 4.5 hrs at 366 nm. After photolysis a 15 ml aliquot of the photolysate was mixed with 2 ml of a stock solution of 1,4-naphthoquinone (internal standard) and this mixture was then injected into the gc for analysis. Each photolysis mixture was injected into the gc twice interspaced by an injection of the standard solution of alcohol 13 , dione 12, and 1,4-naphthoquinone (described earlier) and another injection of the standard solution at the end. Table 17 gives the quantum yield of formation of both products 12 and 13 in benzene.

TABLE 17

<u>Naphthoquinone <u>10</u></u> Concentration (M)	<u>Light</u> mEinsteins	<u>%</u> Conversion	<u>Quantum Yield</u> of formation alcohol <u>13</u> [*]	<u>Quantum Yield</u> of formation dione <u>12</u> ^{**}
0.0199	0.043	0.18	0.0149	0.0073
0.0198	0.102	0.51	0.0169	0.0091
0.0200	0.532	2.7	0.0180	0.0085
0.0201	0.548	2.3	0.0158	0.0070

* The mean quantum yield is 0.0164 ± 0.0012

** The mean quantum yield is 0.0080 ± 0.0008

(The errors represent standard errors for the data given.)

(b) Photolysis using Piperylene as Quencher.

Piperylene (3.4 ml, 33.8 mmol, to make a 1.27 M solution), purified by distillation from LAH, was added to a solution of 113.1 mg (1.98×10^{-2} M) of 10 in benzene to make up 30 ml of solution. The 26.8 ml of the solution was degassed and photolyzed at 366 nm. The quantum yield for the alcohol 13 was $\phi = 0.0104$ and for the dione 12 $\phi = 0.0040$.

(c) Photolysis using 1,3-Cyclohexadiene as Quencher.

Benzene solutions (26.8 ml) ca. 0.02 M in 10 containing various concentrations of purified 1,3-cyclohexadiene were degassed and photolyzed for ca. 5 hrs at 366 nm.

TABLE 18

Naphthoquinone <u>10</u> Concentration (M)	1,3-Cyclohexadiene Concentration (M)	Light mEinsteins	Quantum Yield of formation alcohol <u>13</u>	Quantum Yield of formation dione <u>12</u>
0.0199	3.94×10^{-3}	0.561	0.0162	0.0076
0.0198	9.86×10^{-3}	0.525	0.0156	0.0078
0.0198	1.97×10^{-2}	0.533	0.0153	0.0072
0.0198	2.96×10^{-2}	0.490	0.0152	0.0070
0.0199	3.94×10^{-2}	0.564	0.0145	0.0066
0.0198	5.91×10^{-2}	0.514	0.0137	0.0059
0.0198	9.86×10^{-2}	0.543	0.0128	0.0055
0.0198	1.97×10^{-1}	0.462	0.0115	0.0044
0.0199	3.94×10^{-1}	0.559	0.0110	0.0042
0.0198	7.88×10^{-1}	0.529	0.0100	0.0038
0.0198	1.18	0.508	0.0102	0.0040

A least squares treatment was made of all points up to and including that for a 1,3-cyclohexadiene concentration of 9.86×10^{-2} M for both photoproducts.

For the alcohol 13 an F test³³ of the points gave an $F = 9.8$ ($F_{5\%}(1,5) = 6.61$, $F_{1\%}(1,5) = 16.3$) indicating that the points do very likely make a straight line. The slope for this line was then calculated to be 3.0 M^{-1} , the standard error for the slope was 0.9 M^{-1} and the error expected for 99.9 % confidence limit (5 degrees of freedom) is $\pm 6.2 \text{ M}^{-1}$.

The data for the dione 12 gave an F test of $F = 28.4$ ($F_{1\%}(1,5) = 16.3$), thus this data does seem to lie in a straight line. The slope of this line was calculated to be 4.8 M^{-1} , the standard error for the slope was 0.9 M^{-1} , and the error expected for 99.9 % confidence limit is $\pm 6.2 \text{ M}^{-1}$.

(d) Photolysis using trans-Stilbene as Quencher.

Table 19 presents the data obtained from photolysis of 26.8 ml of a solution of ca.113 mg of compound 10 in 30 ml of benzene plus varying amounts of purified trans-stilbene. The degassed solution was photolyzed at 366 nm for approximately 5 hrs.

TABLE 19

Naphthoquinone <u>10</u> concentration (M)	<u>trans</u> -Stilbene concentration (M)	Light m Einsteins	Quantum Yield of formation alcohol <u>13</u>	Quantum Yield of formation dione <u>12</u>
0.0199	5.21×10^{-3}	0.496	0.0159	0.0078
0.0198	1.05×10^{-2}	0.538	0.0161	0.0073
0.0199	1.57×10^{-2}	0.511	0.0152	0.0074
0.0198	2.26×10^{-2}	0.515	0.0150	0.0067
0.0198	4.32×10^{-2}	0.547	0.0138	0.0062
0.0198	1.04×10^{-1}	0.508	0.0122	0.0048
0.0198	1.67×10^{-1}	0.522	0.0115	0.0044

The data is presented in a Stern-Volmer plot in graph 9 for the alcohol 13 and graph 8 for the dione 12. The slope for the graph of the alcohol 13 was determined by the least squares method for all points except for the trans-stilbene concentration of 0.167 M. An F test resulted in an $F = 39$ ($F_{1\%}(1,4) = 21.2$), indicating that there is a linear relationship of the points. Slope = 3.9 M^{-1} , the standard error was 0.6 M^{-1} and the 99.9 % confidence limit for the slope was (for 5 degrees of freedom) $\pm 5.2 \text{ M}^{-1}$.

A least squares treatment was made for all points of ene-dione 12 quenching, except for a quencher concentration of 0.167 M. An F test of the points resulted in $F = 26.1$ ($F_{1\%}(1,4) = 21.2$), thus the points again appear to form a straight line. The best line had a calculated slope of 6.6 M^{-1} , standard error 1.3 M^{-1} , and the 99.9 % confidence limit of the slope was $\pm 11.2 \text{ M}^{-1}$.

(e) Photolysis of 10 in Benzene : Effect of Variation of Compound 10 Concentration on Quantum Yield.

TABLE 20

Naphthoquinone <u>10</u> Concentration (M)	% Conversion	Light mEinstein	Quantum Yield of formation alcohol <u>13</u>	Quantum Yield of formation ene-dione <u>12</u>
0.00996	5.0	0.535	0.0168	0.0080
0.0198	2.2	0.518	0.0153	0.0072
0.0296	1.7	0.531	0.0170	0.0076
0.0396	1.3	0.540	0.0164	0.0089
0.0494	0.96	0.522	0.0154	0.0081
0.0593	0.82	0.529	0.0160	0.0085
0.0792	0.60	0.528	0.0165	0.0073

Quantum Yield Determinations of the Photolysis of 6,7-Dimethyl-4 α ,5,8,8 α -tetrahydro-1,4-naphthoquinone 10 in tert-Butanol.

(a) Quantum Yield for the formation of dione 11 -- Unquenched Experiments.

A series of 0.02 M solutions of 10 were thoroughly degassed by the freeze-pump-thaw method and photolyzed again at 366 nm.

TABLE 21

Naphthoquinone <u>10</u> Concentration (M)	Solvent used	Light mEinstein	% Conversion	Quantum Yield of formation dione <u>11</u> **
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0.0198	<u>t</u> -BuOH/Benzene*	0.072	0.11	0.0084
0.0199	<u>t</u> -BuOH/Benzene*	0.127	0.22	0.0091
0.0198	<u>tert</u> -BuOH	0.690	1.2	0.0095
0.0198	<u>tert</u> -BuOH	0.585	0.77	0.0069
0.0198	<u>t</u> -BuOH/Benzene*	0.480	0.68	0.0075
0.0199	<u>t</u> -BuOH/Benzene*	0.512	0.74	0.0076
0.0198	<u>t</u> -BuOH/Benzene*	0.567	0.85	0.0079

* A 95:5 ratio of tert-Butanol/benzene was used for the runs.

**Mean value $\phi_0 = .0081 \pm 0.0008$. The error is the standard

error for this data.

(b) Photolysis of 10 in tert-Butanol Using 1,3-Cyclohexadiene as Quencher.

Photolysis at 366 nm of degassed 0.02 M solutions of 10 in (95:5) tert-butanol-benzene with varying concentrations of 1,3-cyclohexadiene were performed. Again 15 ml aliquots of the photolysate were combined with 2 ml of standard 1,4-naphthoquinone (internal standard) solution and these mixtures analyzed by glpc. Table 22 represents the data obtained from these experiments.

TABLE 22

Naphthoquinone <u>10</u> Concentration (M)	1,3-Cyclohexadiene Concentration (M)	Light mEinstein	Quantum Yield of formation ene-dione <u>11</u>
0.0198	3.94×10^{-3}	0.566	0.0081
0.0198	7.88×10^{-3}	0.525	0.0079
0.0199	1.58×10^{-2}	0.470	0.0091
0.0198	3.15×10^{-2}	0.418	0.0082
0.0199	7.88×10^{-2}	0.518	0.0080
0.0199	2.37×10^{-1}	0.433	0.0079
0.0199	3.94×10^{-1}	0.627	0.0074
0.0198	3.94×10^{-1}	0.518	0.0090
0.0199	7.10×10^{-1}	0.526	0.0077
0.0198	11.04×10^{-1}	0.522	0.0080

The Stern-Volmer plot of this data is graph 11. The slope was calculated from a least squares treatment to be 0.047 M^{-1} , the standard error 0.16 M^{-1} and the 99.9 % confidence limit (8 degrees of freedom) 0.8 M^{-1} .

(c) Photolysis of 10 in tert-Butanol: Effect of Variation of 10 Concentration on Quantum Yield.

The solvent used was (95:5) tert-Butanol-Benzene (dried). Photolysis was at 366 nm for ca.5 hrs (depending on lamp age).

TABLE 23

Naphthoquinone <u>10</u> Concentration (M)	% Conversion	Light mEinstein	Quantum Yield of formation ene-dione <u>11</u>
0.0099	1.5	0.522	.0074
0.0198	0.80	0.554	0.0076
0.0297	0.53	0.508	0.0083
0.0396	0.44	0.567	0.0081

(TABLE 23 continued)

Naphthoquinone <u>10</u> Concentration (M)	% Conversion	Light mEinstein	Quantum Yield of formation ene-dione <u>11</u>
0.0496	0.37	0.547	0.0089
0.0594	0.28	0.524	0.0084
0.0791	0.19	0.516	0.0077

Photolysis of 1,3-Cyclohexadiene in Benzene with Benzophenone.

A solution of 2.521 gm (31.5 mmol) of 1,3-cyclohexadiene (Aldrich 98 %, twice fractionally distilled) and 0.920 gm (5.1 mmol) of benzophenone (Aldrich, reagent , twice distilled) in 50 ml of benzene was stirred & purged with argon for 15 minutes and then photolyzed for 27.0 hrs using a 450 W medium pressure mercury Hanovia Type L lamp, using a Corning 7380 filter to block light of wavelength shorter than 340 nm. Argon bubbling and stirring was continued during the photolysis.

After photolysis the benzene was removed and the remaining clear oil was analyzed by glpc, using a 5' x 1/4" column packed with OV-1 on 60/80 Chromosorb W (column temperature 120°, injector and detector kept at 170°, helium carrier gas flow at 30 ml/min.).

Several peaks of short retention time (less than six minutes) were observed; three major peaks were also detected. One of these, $t_R = 30$ minutes, was due to benzophenone (determined by co-injection of a fresh solution of benzophenone in benzene). The other two peaks, $t_R \underline{44} = 18$ minutes, and $t_R \underline{45} = 21$ minutes, were obtained in a 4:1 ratio respectively. However, the major peak had a shoulder at $t_R \underline{46} = 17$ minutes.

The isolation of the dimers by column chromatography, using 10 % silver nitrate-alumina (Al_2O_3 Woelm, neutral, activity grade I), described by Hammond⁷⁰ was attempted but failed to give a satisfactory separation.

Separation of the photolysis mixture was also tried with a 15' x 1/8" column of Apiezon L on 40/60 Firebrick (column 160°, injector and detector 180°, helium carrier gas flow 20 ml/minute). Once again, two major peaks were obtained: $t_{R\ 44} = 72$ minutes with shoulder peak at $t_{R\ 46} = 76$ minutes; and $t_{R\ 45} = 91$ minutes. The ratios of the two peaks were again 4:1 respectively, (44 + 46 / 45).

The two peaks (44 and 45) were collected by glpc from the OV-1 column. However, the major component 44, was collected, starting from a retention time above 17.5 minutes, thus avoiding a significant portion of the material 46 representing the shoulder peak.

The major product, cis,anti,cis-tricyclo[6.4.0.0^{2,7}]dodeca-3,11-diene 44 had the following nmr (CCl_4) τ 4.22 (m,4,vinyl), 7.64 (m,4, methines), 7.96 (m,4,C₅ and C₁₀ methylenes), 8.45 (m,4,C₆ and C₉ methylenes).

The minor product, cis,syn,cis-tricyclo[6.4.0.0^{2,7}]dodeca-3,11-diene 45, had the following nmr (CCl_4) τ 4.30 (m,4, vinyl), 7.26 (m,4,methines), 8.21 (m,8,C₅,C₆,C₉,C₁₀ methylenes).

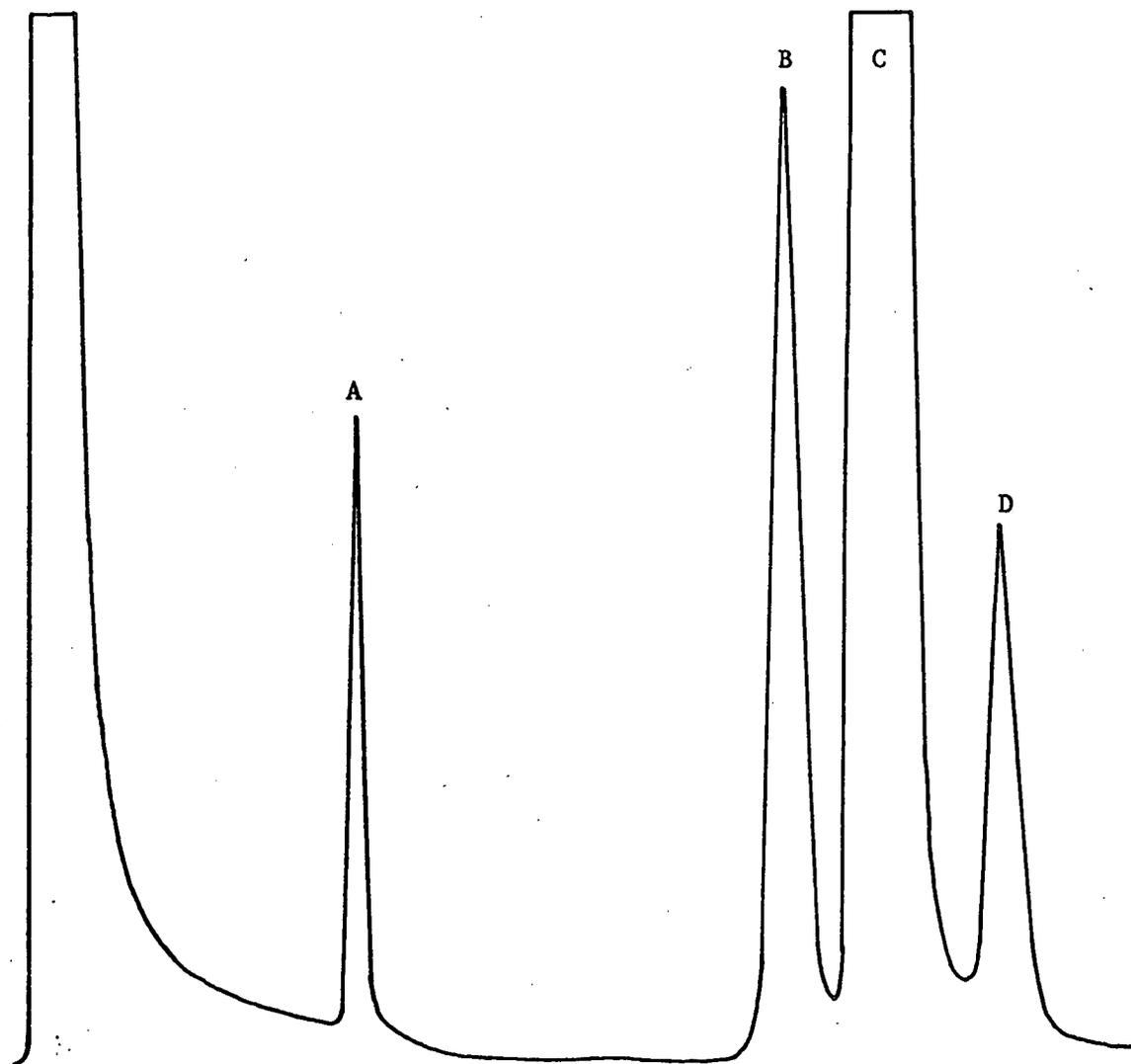
These two nmr spectra were identical to those published by Hammond and coworkers.⁷⁰

These two dimers of 1,3-cyclohexadiene were injected separately into the gc, using the 10' x 1/8" and the 3' x 1/8" 20% DEGS on 60/80 Chromosorb W columns used for quantum yield determinations, operating at a reduced temperature of 80°. The retention times of

the dimers corresponded with those of peaks appearing only when 1,3-cyclohexadiene was used as quencher.

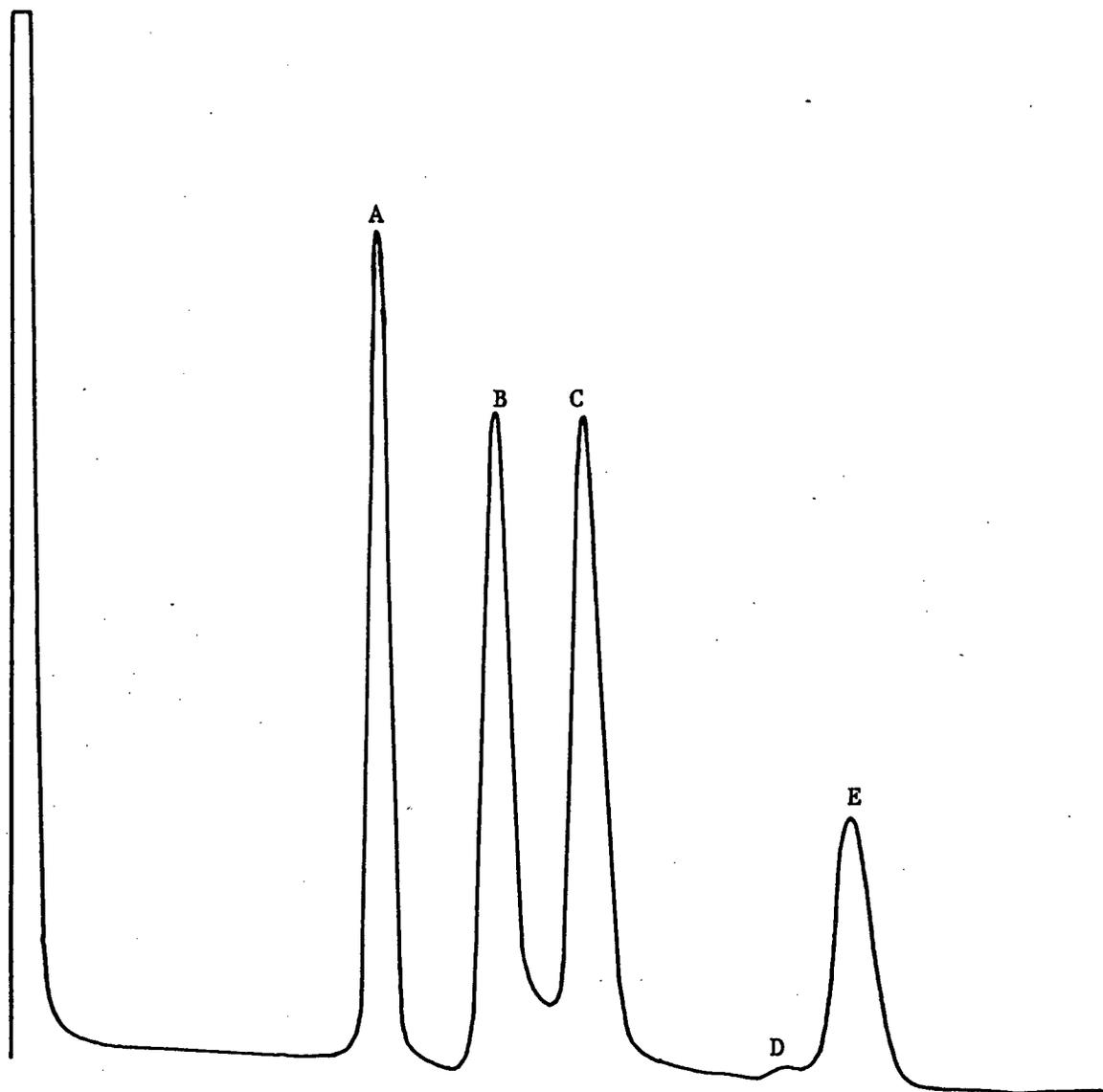
Coinjection of dilute samples of 44 and 45 in benzene, with photolysis mixtures of 10 and 27 (quenched with 1,3-cyclohexadiene), confirmed the assignment of these new peaks.

APPENDIX



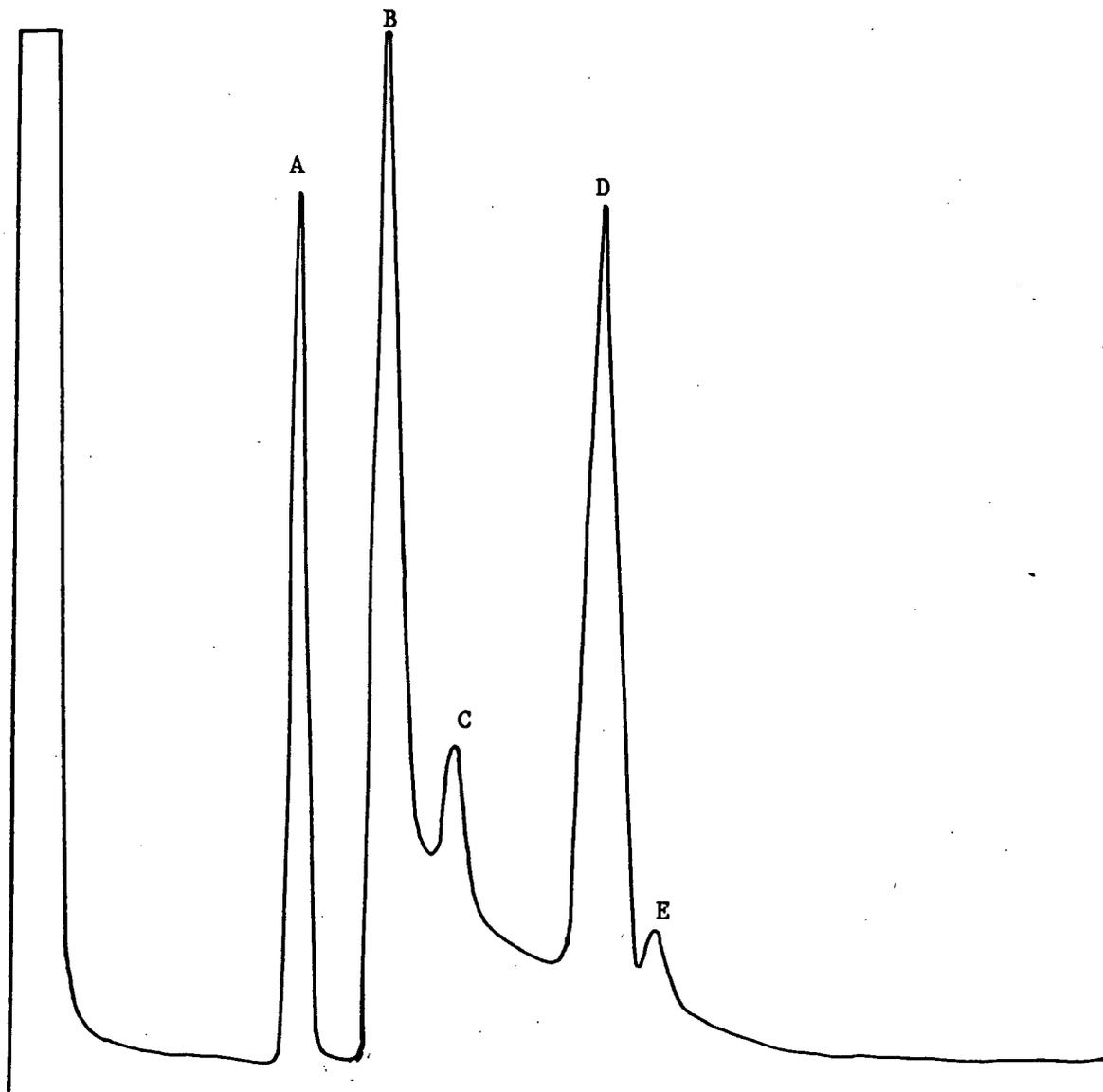
Gpc recorder trace of the photolysis products of 27 in benzene:

- A. Internal standard biphenyl ($R_t = 22$ min.),
- B. Photoproduct ene-dione 29 ($R_t = 52$ min.),
- C. Photoreactant 27
- D. Photoproduct alcohol 28 ($R_t = 66$ min.).



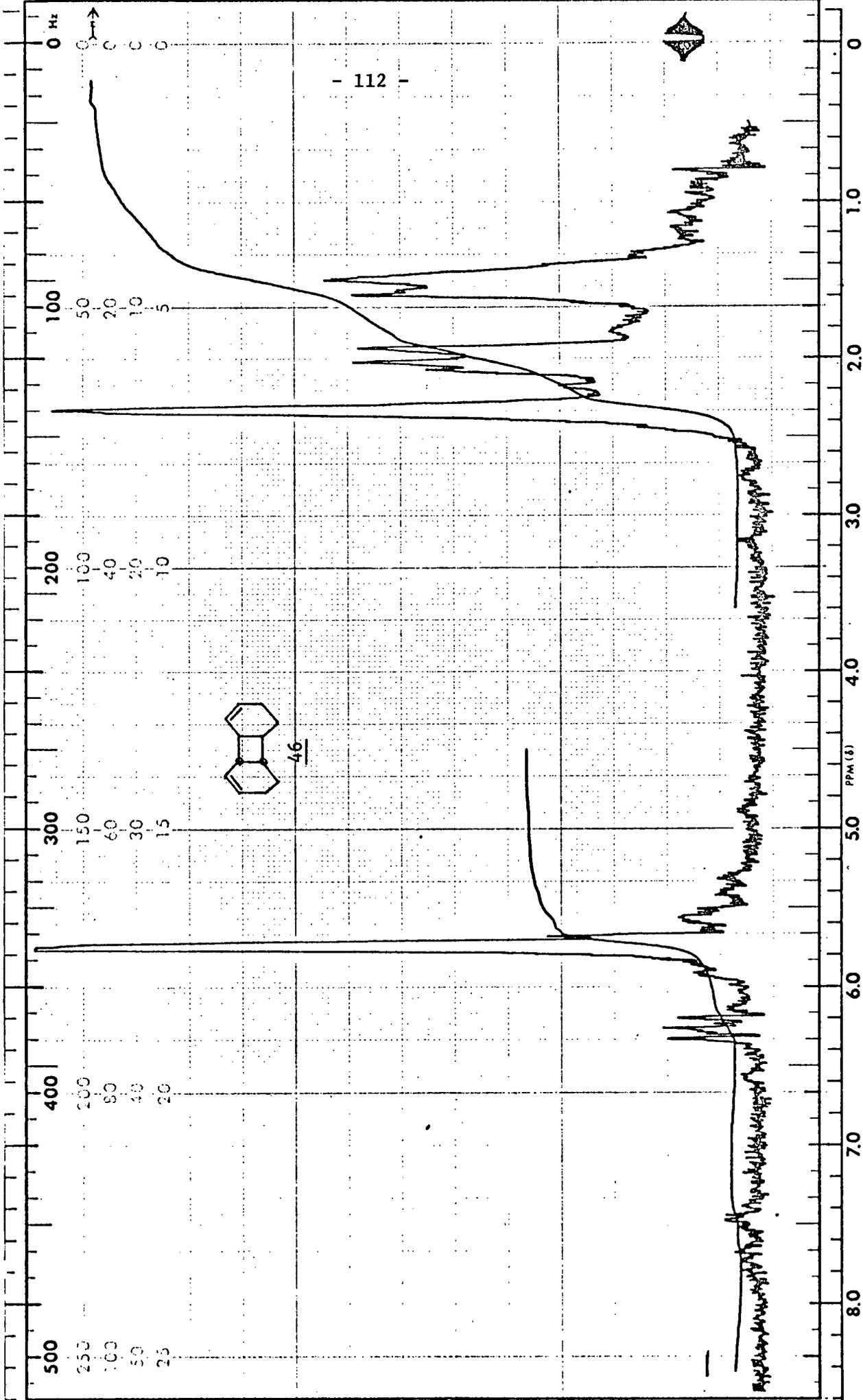
Glpc recorder trace of the photolysis products of 10 in benzene:

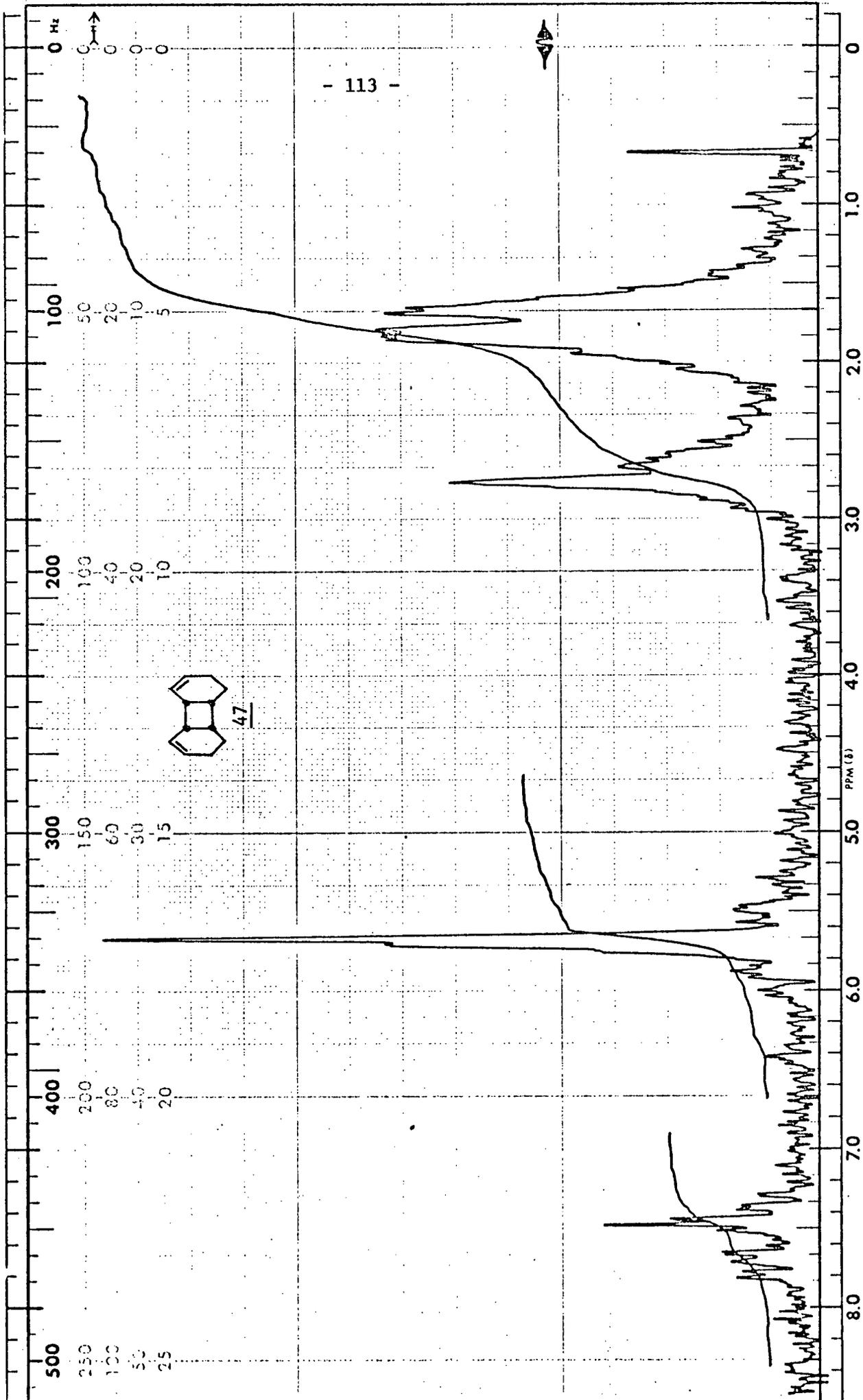
- A. Internal standard 1,4-naphthoquinone ($R_t = 26$ min.),
- B. Photoreactant 10 ($R_t = 34$ min., thermally decomposes),
- C. Photoproduct alcohol 13 ($R_t = 41$ min.),
- D. Photoproduct ene-dione 11
- E. Photoproduct ene-dione 12 ($R_t = 59$ min.).



Glpc recorder trace of the photolysis products of 10 in tert-butanol:

- A. Internal standard 1,4-naphthoquinone ($R_t = 19$ min.),
- B. Photoreactant 10 ($R_t = 28$ min., thermally decomposes),
- C. Photoproduct alcohol 13,
- D. Photoproduct ene-dione 11 ($R_t = 42$ min.),
- E. Photoproduct ene-dione 12.





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