

The University of Leicester

Department of Chemistry

Some Aspects of the Photoreduction of Carbonyl Compounds.

by

Paul Francis Lambeth

A thesis submitted for the degree of

Doctor of Philosophy

Oct., 1969.

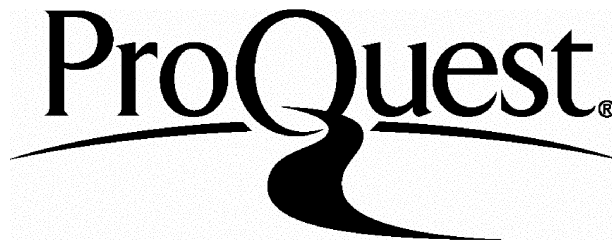
ProQuest Number: U371921

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



ProQuest U371921

Published by ProQuest LLC(2015). Copyright of the Dissertation is held by the Author.

All rights reserved.

This work is protected against unauthorized copying under Title 17, United States Code.  
Microform Edition © ProQuest LLC.

ProQuest LLC  
789 East Eisenhower Parkway  
P.O. Box 1346  
Ann Arbor, MI 48106-1346



X75301350 8



*Thesis*

*378115*

*1-6-1970*

*\* The author*

### Statement

The experimental work in this thesis has been carried out by the author in the laboratories of the Chemistry Department of the University of Leicester between October 1966 and August 1969. The electron paramagnetic resonance studies were carried out by Dr. R. Wilson at the National Physical Laboratory, Teddington and are included because of their particular relevance to the work described. This work has not been presented and is not being presented for any other degree. Some of the work has previously been published as follows:

The Photoreduction of Carbonyl Compounds by Amines,  
R. S. Davidson and P. F. Lambeth, Chem. Comm, 1265 (1967).  
A Study of the Effect of Quenchers upon the Photoreduction  
of Benzophenone by Amines and Alcohols.  
R. S. Davidson and P. F. Lambeth, Chem. Comm., 511, (1968).  
The Photoreactions of Aromatic Ketones with Arylamines.  
R. S. Davidson, P. F. Lambeth, J. F. McKellar, P. H.  
Turner and R. Wilson, Chem. Comms. 732, (1969).  
The Quenching of Excited States by Trivalent Phosphorus  
Compounds and Arylamines.  
R. S. Davidson and P. F. Lambeth, Chem. Comms. In press.  
The Photoreduction of Aromatic Ketones in Basic Solution.  
R. S. Davidson, P. F. Lambeth, Mrs. F. A. Younis and  
R. Wilson, J. Chem. Soc. (C). In press.

Paul Lambeth

### Acknowledgements

I wish to record my gratitude to the following people for their invaluable assistance. To Miss Phillpott and Mr. Jones for the nuclear magnetic resonance and mass spectrometry services provided and to Miss Lawson and Mrs. Banks for the typing and diagrams respectively. My particular thanks go to my supervisor, Dr. R. S. Davidson for his valuable tuition, criticisms and encouragement at all stages of this work, and to the Ipswich Education Committee for the provision of a maintenance grant.

### Abstract

The absorption of light by the carbonyl group has been reviewed as has been the different ways by which an excited carbonyl group can lose its excess energy. The photoreduction of carbonyl compounds by alcohols has also been reviewed.

The photoreduction of carbonyl compounds by tertiary alkylarylamines has been studied in detail and the evidence suggests the reaction proceeds via an initial interaction of the non-bonding electrons of the amine with excited carbonyl forming a charge transfer complex. With amines of low ionisation potential, the complex can dissociate into radical ions if these can be stabilised by solvation. The quenching of the fluorescence of biacetyl, fluorenone and anthracene by triphenylamine, triphenylphosphine and phenylsulphide occurs by a similar mechanism.

The photoreduction of fluorenone and benzophenone in ethanolic and aqueous amine solutions gives rise to the radical anion of the ketone, and the differing fate of the radical anion in both cases is discussed.

Photoreduction of the carbonyl group by tin alkyls has been studied and the greater activity of tri-n-butylstannane as a hydrogen donor is thought to be due to the weak tin-hydrogen bond.

The photoreduction of  $\alpha$ - $\beta$  unsaturated ketones by amines gave addition products but use of tri-n-butylstannane gave varying amounts of the saturated ketone.

## CONTENTS

<u>Introduction</u>	<u>Page</u>
Absorption and loss of energy from the excited carbonyl group	1
Energy transfer	4
The Stern-Volmer equation	7
Sensitisation	10
Intramolecular energy transfer	12
Quenching of photochemical reactions by charge transfer	13
Photoreduction of carbonyl compounds by alcohols	15
Photoreduction in basic media	24
Photoreduction of substituted benzophenones	25
Cleavage of pinacols	27
Photoreduction by amines	28
<u>Results and Discussion</u>	
Photoreduction of benzophenone by tertiary alkylarylamines	31
Photoreduction of ketones by N,N-dimethylaniline	32
Selectivity of attack by triplet benzophenone on tertiary amines	34
Energy transfer studies	41
Quenching of the photoreduction of benzophenone by benzhydrol by tertiary arylamines	45
Flash photolysis studies	51

Further studies of quenching by electron transfer	56
Photoreduction of fluorenone and benzophenone by amines in alcoholic or aqueous media	72
Photoreduction by tin alkyls	81
Photoreduction of $\alpha$ - $\beta$ -unsaturated ketones and diketones	87
Experimental	99
References	169

## Introduction

'And God said, Let there be light;  
and there was light.

And God saw the light, that it was  
good'.

Genesis Chap,I vv 3 and 4.

The molecular orbital description of the carbonyl group is  $(\sigma_{\text{CO}})^2 (\pi_{\text{CO}})^2 (n_{\text{O}} \uparrow \downarrow)^2$  and in the case of aliphatic ketones, two modes of excitation are possible: one corresponding to a  $\pi \rightarrow \pi^*$  excitation, and the other at longer wavelength to an  $n \rightarrow \pi^*$  excitation. Examination of the ultra-violet spectrum of diaryl ketones shows that at longer wavelength there is an  $n \rightarrow \pi^*$  excitation involving the non-bonding electrons on the oxygen, and also a  $\pi \rightarrow \pi^*$  excitation which involves the aromatic  $\pi$ -system. The involvement of the non-bonding electrons in the electronic transitions of carbonyl compounds was first suggested by Mulliken<sup>1</sup>. The act of absorption<sup>2,3</sup> and the electronic transitions due to non-bonding electrons have been the subject of a number of reviews<sup>4</sup>.

Promotion of a non-bonding electron on the oxygen atom to a  $\pi$  antibonding orbital in a quantised Franck-Condon allowed transition gives rise to an excited singlet state containing excess vibrational energy. Except in the gas phase at low pressure, the excess vibrational energy is rapidly transferred to the environment leaving a vibrationless excited singlet state. Loss of energy from this state

can take place in a number of ways.

A radiationless transition to the ground state can occur. This is known as internal conversion and may produce ground state molecules with sufficient vibrational energy to cause chemical reaction<sup>5</sup>.

The first excited singlet state can lose its excess energy by emission of light, and this emission of light during a transition between states of like multiplicity is known as fluorescence. Examination of the fluorescence spectrum of a compound can give information about the energy and life time of the first excited singlet state<sup>6</sup>.

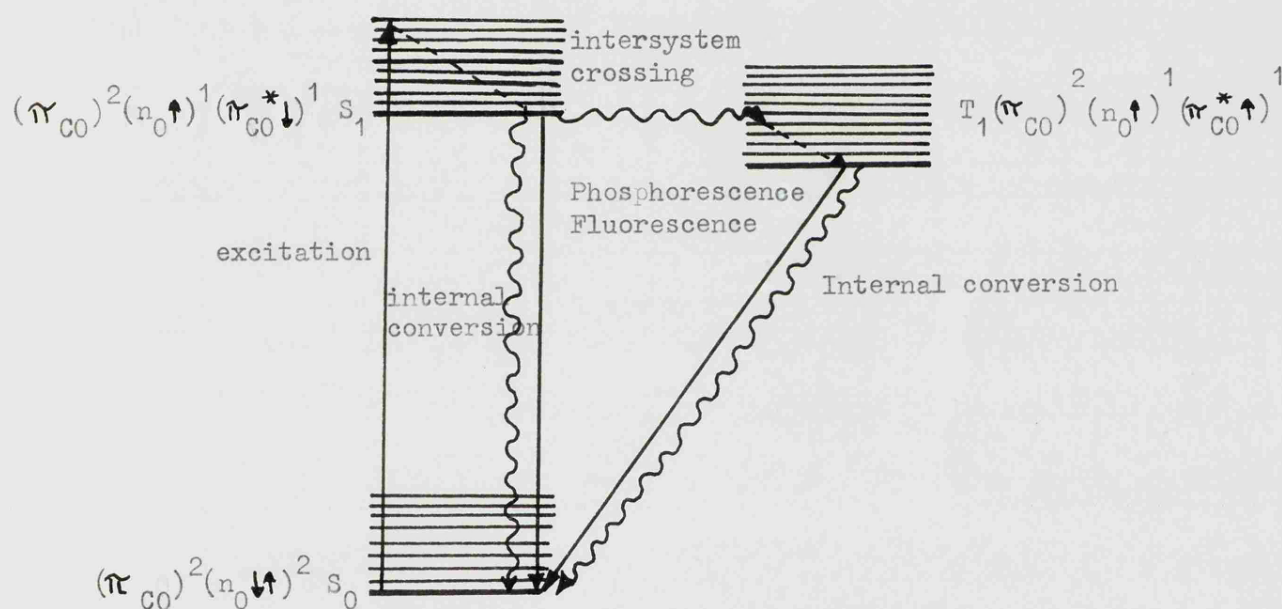
Another process which the first excited singlet state can undergo is spin inversion of an unpaired electron to give the first excited triplet state. This non-radiative process is known as intersystem crossing. A simple method of measurement of quantum yields of intersystem crossing has been developed by Lamola and Hammond<sup>7</sup> using the compound under investigation to sensitise the cis-trans isomerisation of olefins.

In an analogous manner to the singlet state, the triplet can lose its excess energy and return to the ground singlet state in a non-radiative or radiative process. The emission of light during a transition between states of differing multiplicity is known as phosphorescence. The  $T_1 \rightarrow S_0$  transition is a spin forbidden process and is consequently relatively slow. This greater lifetime of the triplet relative to the singlet state means that the former is more likely to undergo chemical reactions when intersystem crossing is efficient. The triplet state has been studied by flash photolysis<sup>8,9</sup> and paramagnetic



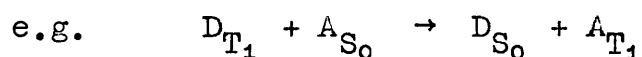
resonance spectroscopy<sup>10</sup> and has been the subject of a number of reviews<sup>11,12,13</sup>.

These processes are illustrated below in a Jablonski diagram. Radiative processes are indicated by straight lines, non-radiative or internal conversion processes by wavy lines. The vibrational fine structure is also shown and the diagram is confined to the first excited singlet and triplet levels.



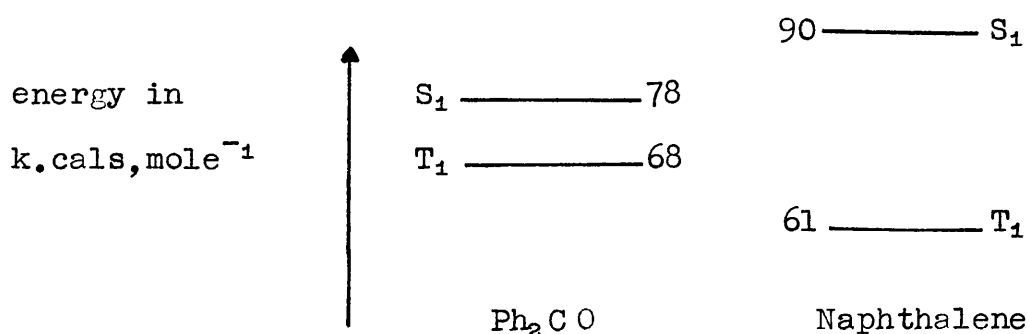
### Energy Transfer

Another important type of deactivation involves the direct transfer of electronic energy selectively to individual molecules present in relatively small concentrations in the system. The transfer occurs with spin conservation, the acceptor being produced in the same state that the donor originally had.



where D and A are donor and acceptor respectively.

Probably the best known example of energy transfer is the deactivation of excited benzophenone by naphthalene. This process was observed directly by Porter<sup>14</sup> using flash photolysis. Flashing of a mixture of  $\sim 10^{-2}M$  benzophenone and  $\sim 3 \times 10^{-3}M$  naphthalene in benzene with light that was only absorbed by the benzophenone produced the absorption spectrum typical of triplet naphthalene and the absence of any triplet or radicals derived from the benzophenone. Consideration of the relative energy levels shows that



transfer must have occurred between the two triplet levels since the first excited singlet of naphthalene is above that of benzophenone and transfer from singlet benzophenone to triplet naphthalene is a spin forbidden process.

Energy transfer between triplet benzophenone and naphthalene has also been observed by Moore and Ketchum<sup>15</sup> who studied the variation in quantum yield of benzophenone disappearance when reduction by benzhydrol was quenched by varying concentrations of naphthalene. They obtained a value of 455 for the ratio  $k_q/k_r$  (where  $k_q$  = bimolecular quenching rate constant and  $k_r$  = bimolecular hydrogen abstraction rate constant) and concluded that quenching was diffusion controlled.

Energy transfer between triplet benzophenone and naphthalene has also been observed by emission spectroscopy<sup>16</sup> and paramagnetic resonance spectroscopy<sup>17</sup>. In the former case Terenin and Ermolaev observed the phosphorescence typical of naphthalene and related compounds when carbonyl compounds were used to absorb the incident light, and in the latter, the paramagnetic resonance spectrum typical of triplet naphthalene was observed when irradiated with benzophenone at 366nm. In both cases, experiments were conducted at 77°K in EPA glass.

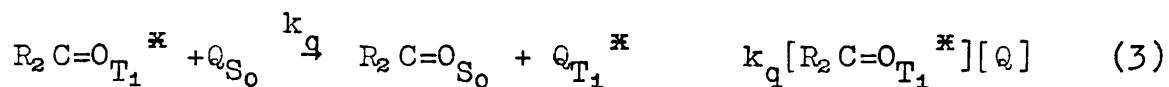
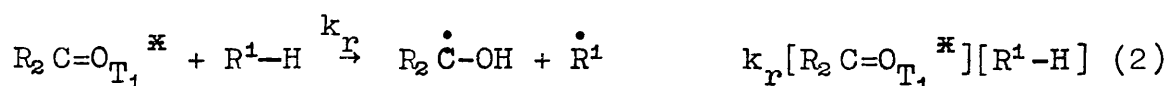
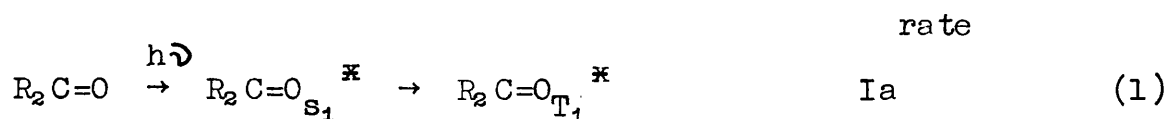
Triplet energy transfer between pairs of aromatic hydrocarbons has also been studied<sup>18</sup> and shown to be diffusion controlled when the energy of the acceptor triplet is considerably below that of the donor. As the energies became comparable, the transfer probability was reduced and did not occur when the acceptor energy was higher than that of the donor. Energy transfer was thought to occur during an encounter between donor and acceptor when the necessary orbital overlap for transfer occurred. There was no evidence for energy transfer via complex formation between

the donor and acceptor.

Another class of compounds which participate in energy transfer from excited benzophenone are transition metal chelates. A large variety of complexes containing ligands derived from  $\beta$ -diketones showed variable activity as quenchers of the benzophenone-benzhydrol photoreduction<sup>19</sup>. The presence of an unsaturated ligand was shown to be necessary as a solution of ferric chloride in t-butanol shows no quenching activity whilst other ferric complexes quenched the reaction effectively. The quenching efficiency also shows no correlation with the magnetic properties of the central atom. Two mechanisms are proposed to account for the quenching. First, a complex may be formed between quencher and triplet benzophenone, and within the lifetime of the complex, internal conversion occurs dissociating the complex, and producing ground state benzophenone. Alternatively, transfer of energy from triplet benzophenone to the quencher occurs. Support for the second alternative occurs in some instances where the chelates undergo decomposition although only light absorbed by benzophenone is used, suggesting that energy must be concentrated upon them at some stage. Tris(dibenzoylmethanato)iron III and -chromium III showed very high quenching activity and this was attributed to deactivation of excited singlet state as well as triplet state benzophenone<sup>20</sup>. That triplet energy transfer does take place was demonstrated by Bhaumik and El-Sayed<sup>21</sup> who observed the phosphorescence of a gadolinium chelate when benzophenone was used as a sensitiser. Use of benzophenone as donor and europium hexafluoroacetylacetonate as acceptor produced emission

typical of the rare earth ion suggesting that intermolecular energy transfer from the ketone to the chelate was followed by intramolecular energy transfer from the chelate to the central metal ion.

The effect of a number of triplet quenchers on the photoreduction of carbonyl compounds has been studied and the relationship between the quantum yield of photoreduction and concentration of quencher is given by the Stern-Volmer equation. Consider the following reaction sequence:



(1) is the excitation step using light of intensity

I. a is the yield of triplets.

(2) is the hydrogen abstraction step, rate constant  $k_r$

(3) is deactivation of triplet ketone by quencher molecule Q.

(4) is deactivation of triplet ketone by phosphorescence etc.

The rate of disappearance of triplet ketone is given by

$$\frac{d[R_2C=O_{T_1}^*]}{dt} = Ia - (k_r[R^1-H] + k_q[Q] + k_d)[R_2C=O_{T_1}^*]$$

∴ under steady state conditions

$$Ia = (k_r[R^1-H] + k_q[Q] + k_d)[R_2C=O_{T_1}^*]$$

The quantum yield for the disappearance of ketone is given

$$\text{by } \phi = \frac{k_r[R_2C=O_{T_1}^*][R^1-H]}{I}$$

$$\therefore \frac{1}{\phi} = \frac{1}{a} + \frac{k_d}{ak_r[R^1-H]} + \frac{k_q[Q]}{ak_r[R^1-H]}$$

if quenchers are excluded, the equation reduces to

$$\frac{1}{\phi} = \frac{1}{a} + \frac{k_d}{ak_r[R^1-H]}$$

Thus a plot of  $1/\phi \propto 1/[R^1-H]$  will give a straight line, slope  $k_d/ak_r$  and intercept  $1/a$ . If the value of  $[R^1-H]$  is kept constant and  $[Q]$  is varied, a plot of  $1/\phi \propto [Q]$  will give a straight line of slope  $\frac{k_q}{a \cdot k_r[R^1-H]}$ .

Using the method of actinometry developed by Moore and Ketchum<sup>15</sup> who employed a benzophenone-benzhydrol actinometer the equation becomes

$$\frac{\phi_{\text{act.}}}{\phi_{\text{quench.}}} = \left( \frac{1}{a} + \frac{k_d}{ak_r[R^1-H]} + \frac{k_q[Q]}{ak_r[R^1-H]} \right) \phi_{\text{act}}$$

since  $\phi_{\text{act.}}$  is constant.

The idea that triplet energy transfer was diffusion controlled was first suggested by Sandros and Backstrom<sup>22</sup> who studied the quenching of biacetyl phosphorescence by

a number of compounds. They noted a similarity of efficiencies over a range of quenchers and the fact that this was close to the calculated rate of diffusion. The quenching constant also varied with the viscosity of the solvent and it was concluded that energy transfer takes place on molecular encounters and not over large distances as is possible with singlet energy transfer.

Studies by Hammond and Leermakers<sup>23</sup> on the quenching of the benzophenone-benzhydrol photoreduction by a number of chemically unrelated compounds showed that efficiencies were very similar in a number of cases.

Quencher	$\phi$	$k_q/k_r$	$E_T^a$
2-Acetonaphthone	0.2	730	59
Naphthalene	0.2	750	61
cis-Piperylene	0.21	750	55-60
Benzil	0.31	436	62
Cyclohexene	0.67	30	?
Azulene	0.25	1100	?
1-Naphthaldehyde	0.17	880	57
Cyclooctatetraene	0.2	630	?

<sup>a</sup>Energy of lowest triplet state (k.cals.)

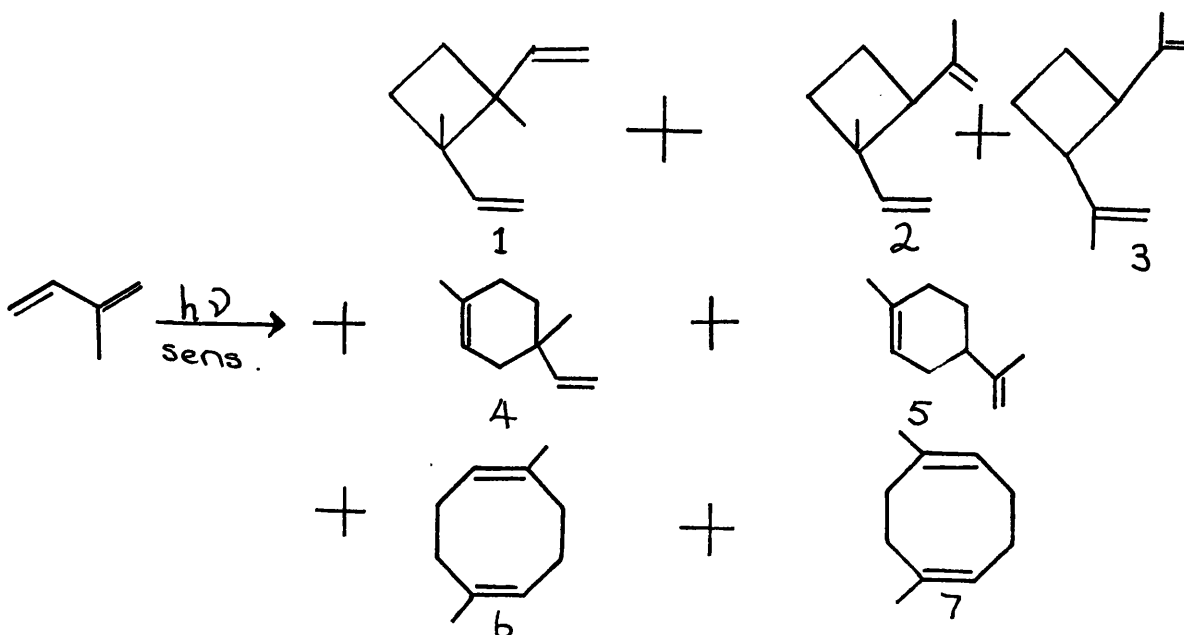
They concluded that there exists one common rate limiting factor, probably a diffusion controlled process, with energy transfer occurring at every collision of donor and acceptor molecules.

This theory has been modified by Wagner and Kochevar<sup>24</sup> as a result of their studies on the quenching of the triplet state photoelimination of valerophenone. They

concluded that in more viscous solvents ( $\eta > 3\text{cP}$ ) triplet energy transfer is diffusion controlled, but at lower viscosities, the rate of transfer is lower than that of the diffusion together of donor and acceptor and that energy transfer does not occur at every encounter. At high quencher concentrations in more viscous solvents, 'static' quenching should become increasingly important, i.e. if upon excitation a ketone molecule has a quencher molecule as its nearest neighbour, immediate quenching will result and it will not be able to enter into competition between reaction and diffusion controlled quenching, therefore Stern-Volmer quenching plots should curve upwards at higher quencher concentrations. This was found to be the case in the quenching of the photoelimination of valerophenone by hexadienol in t-butanol.

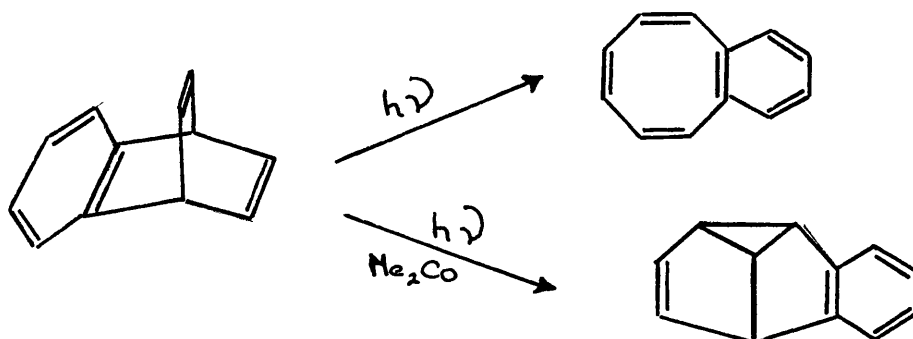
Energy transfer is also a good means of populating triplet levels which are normally inaccessible by intersystem crossing. This is known as sensitisation and a number of photosensitised reactions have been studied, for example, the cis  $\rightarrow$  trans isomerisation of piperylene<sup>25</sup> and stilbene<sup>26</sup>. The photodimerisation of dienes can also be accomplished by irradiation with a suitable sensitiser e.g. benzophenone. Triplet diene is produced which reacts with ground state diene to form an intermediate biradical which undergoes ring-closure<sup>27</sup>. The products obtained from the photosensitised dimerisation of isoprene are shown below<sup>28</sup>.





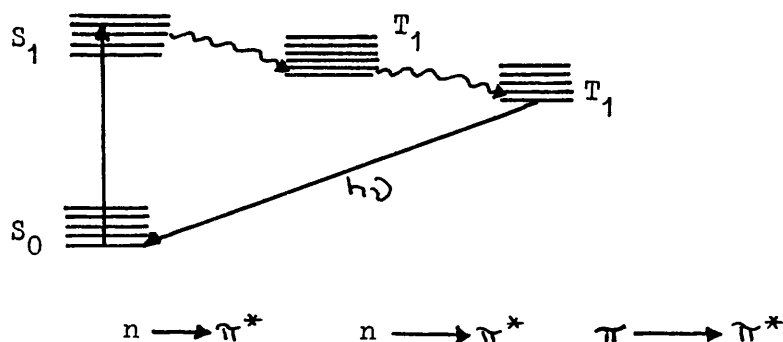
Variation in the triplet energy of the sensitiser creates a variation in the composition of the product mixture. High energy sensitisers produce mainly trans triplets which react with ground state isoprene giving mainly cyclobutanes and cyclooctadienes. As the triplet energy of the sensitiser falls below 60 kcal, increasing amounts of cis triplets are formed giving rise to cyclohexenes.

In a few cases the reaction pathway depends upon the multiplicity of the excited state. An example of this is the rearrangement of benzobarralene<sup>29</sup> to give benzosemibullvalene on sensitised photolysis (with acetone) and benzocyclooctatetraene on direct photolysis.



As well as taking place in an intermolecular manner, intramolecular energy transfer is known. p-Phenylbenzo-phenone can be considered as two separate chromophores

(a carbonyl and a biphenyl) and excitation of the carbonyl groups gives  $n \rightarrow \pi^*$  triplets in the normal manner, but since the  $\pi \rightarrow \pi^*$  triplet of the biphenyl moiety is of lower energy, intramolecular energy transfer occurs, so the lowest triplet state is of the  $\pi \rightarrow \pi^*$  type.



#### Electronic Energy levels of p-Phenylbenzophenone.

A similar transfer occurs in the case of  $\alpha$ -naphthaldehyde,  $\beta$ -acetylnaphthalene and fluorenone. In the latter case, molecular orbital calculations based on the absorption spectrum of fluorenone have confirmed this<sup>30</sup>.

Ketones in which the lowest excited state is of the  $\pi \rightarrow \pi^*$  type are photoreduced inefficiently by alcohols. This is thought to be due<sup>31</sup> to the fact that the unpaired electrons are delocalised in the  $\pi$ -system and the free radical character of the oxygen atom, which is responsible for hydrogen abstraction in the  $n \rightarrow \pi^*$  case, is substantially decreased. A further comparison of the properties of  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  excited states is given in the review by Sidman<sup>4</sup>.

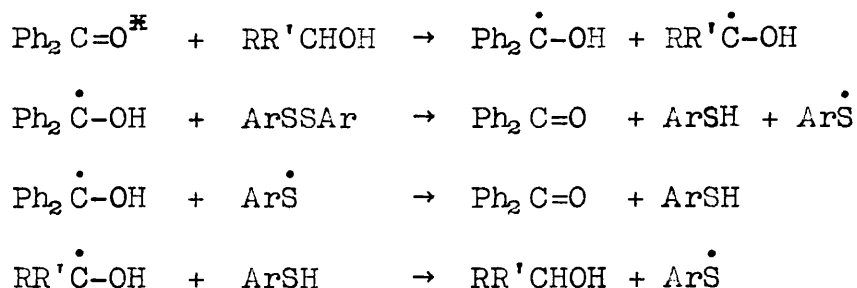
As well as quenching by direct energy transfer, excited states may be quenched by charge transfer. Such a

mechanism has been postulated to account for the quenching of perylene fluorescence by amines<sup>32</sup>. In solvents of low dielectric constant ( $\epsilon = 2.3-4$ ) charge transfer emission partly replaced the perylene fluorescence when amines were added. In solvents of high dielectric constant, no charge transfer emission was observed but flash photolysis investigations by Leonhardt and Weller<sup>23</sup> showed the formation of a transient  $\lambda_{\text{max}}$  580 nm, which was absent in solvents of low dielectric constant. This was attributed to the formation of the perylene mononegative ion. These results suggest that the complex formed between excited perylene and amine can either decompose into its ground state components, emit in the form of fluorescence, or in solvents of high polarity dissociate into its constituent radical ions which will then be stabilised by solvation. At 77°K, the interaction becomes much weaker because the rearrangement motions of the molecules which is necessary for charge-transfer complexing are hindered in the solid matrix<sup>34</sup>. A similar mechanism has been proposed<sup>35</sup> for the quenching of NN-dimethyl-2-naphthylamine fluorescence by a series of esters. The efficiency of quenching was toluate < benzoate < phthalate and an increase in efficiency was observed when DMF was used as a solvent in place of cyclohexane. In non-polar solvents a charge transfer emission occurred whilst in polar solvents<sup>36</sup> flash photolysis showed that the NN-dimethyl-2-naphthylamine radical cation was produced.

Analysis of the decay kinetics of this radical cation suggest that it exists as the solvent shared ion pair in

medium polar solvents (acetone, ethanol and D.M.F.) and as the free species in highly polar solvents (e.g. formamide).

The photoreduction of benzophenone is also inhibited by certain mercaptans and disulphides<sup>3,7</sup>, the mercaptan or disulphide initially present being converted into an equilibrium mixture of the two. Inhibited photoreductions in optically active 2-octanol lead to racemisation. It is suggested that the inhibition is not due to physical quenching but to interception of the radicals formed in the normal manner by the sulphur compounds, resulting in regeneration of the starting materials.



### Photoreduction by Alcohols

The photochemical reduction of benzophenone by primary and secondary alcohols to give benzpinacol in almost quantitative yield was first reported by Ciamician and Silber<sup>38</sup>. This has now become a standard method for the preparation of benzpinacol<sup>39</sup>. Numerous examples of the photoreduction of carbonyl compounds by alcohols have since been reported and much of this work has been reviewed by Schönberg and Mustafa<sup>40</sup>. As well as alcohols and amines, alkanes both aliphatic<sup>41</sup> and aromatic<sup>42</sup>, ethers<sup>43</sup>, tributylstannane<sup>44</sup> and ethyl orthoformate<sup>45</sup> are found to be efficient hydrogen donors to the excited carbonyl group.

The mechanism of the photoreduction of carbonyl compounds by alcohols has been extensively studied and the evidence that the excited species responsible for hydrogen abstraction is the first excited triplet state has been obtained by a number of techniques.

The majority of carbonyl compounds exhibit phosphorescence which is characteristic of the triplet state.

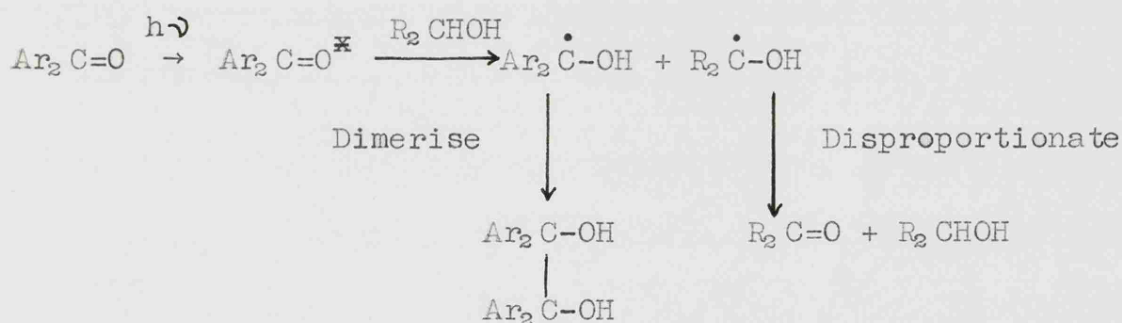
Kinetic measurements by Hammond and Moore<sup>46</sup> gave an upper limit of  $5 \times 10^7 \text{ sec}^{-1}$  as the rate constant for deactivation of excited benzophenone molecules when photo-reduced by benzhydrol. Since no fluorescence has ever been detected from benzophenone, and deactivation of the first excited singlet by internal conversion has a calculated rate constant of at least  $10^{10} \text{ sec}^{-1}$ , a relatively long lived state, probably the triplet must be responsible. Energy transfer from excited benzophenone to biacetyl resulted in only phosphorescent decay of the latter<sup>47</sup>,

showing that energy transfer occurred from the triplet state.

The deactivation of excited benzophenone by naphthalene, a known triplet quencher has been studied and shown to be diffusion controlled<sup>15</sup>.

Ultra-violet studies of benzophenone showed that the absorption maximum was shifted to the blue with increasing solvent polarity<sup>48</sup> which is considered to be characteristic of  $n \rightarrow \pi^*$  transitions<sup>49</sup>.

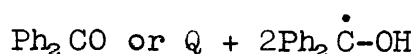
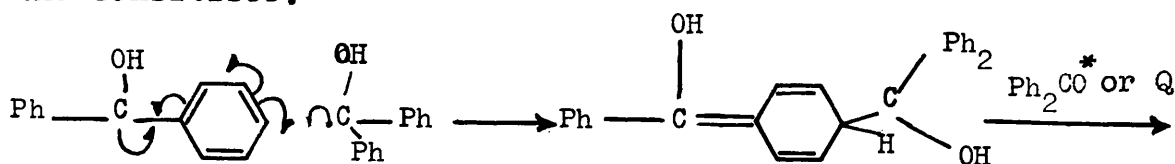
It was initially suggested<sup>50</sup> that the excited carbonyl abstracted a hydrogen atom from the alkane or from the  $\alpha$ -C-H bond of an alcohol to give  $\alpha$ -hydroxydiarylmethyl radicals as shown in scheme I.



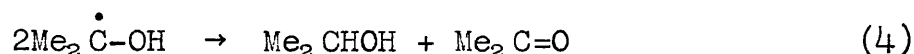
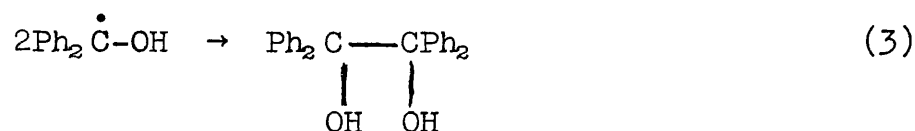
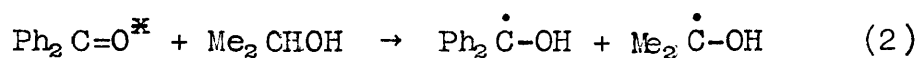
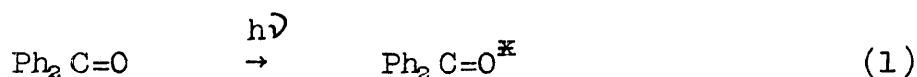
Scheme I

Studies on the photoreduction of benzophenone by benzhydrol<sup>48</sup> show that the quantum yield for the disappearance of benzophenone varies with the concentration of benzhydrol and approaches unity at high concentrations. This variation is in accordance with a simple competition between hydrogen transfer from the alcohol to the excited benzophenone and thermal deactivation of the latter. Replacement of benzhydrol by benzhydrol- $\alpha$ -d<sub>1</sub> gave a deuterium isotope effect  $\frac{k_H}{k_D} = 2.7$ , demonstrating that hydrogen abstraction is the rate controlling step.

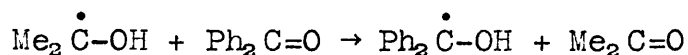
Deactivation of the excited benzophenone by paramagnetic quenchers is diffusion controlled. Wagner<sup>51</sup> has recently shown that reversible energy transfer can take place between quencher and triplet benzophenone if the triplet energy of the quencher is slightly less than that of benzophenone ( $E_T = 69.5 \text{ k.cals.}$ ). Examples of such quenchers of the benzophenone-benzhydrol reduction are biphenyl ( $E_T = 68.5 \text{ k.cals.}$ ), fluorene ( $E_T = 67.6 \text{ k.cals.}$ ) and triphenylene ( $E_T = 66.6 \text{ k.cals.}$ ). It was also suggested that a low steady-state concentration of some quenching species is produced, possibly by para coupling of 2  $\alpha$ -hydroxydiphenylmethyl radicals, which undergoes photo-sensitised decomposition to the original radicals. Triplet benzophenone or foreign quencher is envisaged as the sensitiser.



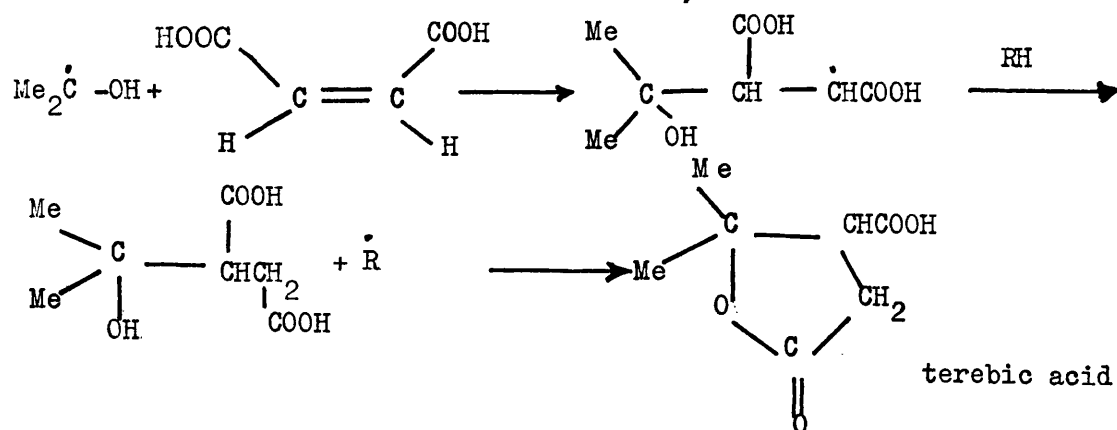
Photoreduction of benzophenone by isopropanol under normal preparative conditions to give benzpinacol and acetone showed that the quantum yield for benzophenone disappearance varied with concentration and tended towards a limiting value of  $2^{52}$ . The first mechanism for the photoreduction in the absence of oxygen was suggested by Backstrom<sup>53</sup>.



Pitts et al<sup>52</sup> replaced Backstrom's equation (4) with



This was more in accordance with their limiting value of 2 for the quantum yield and their finding that no racemisation occurred when optically active secondary butyl alcohol was used. Disproportionation of the planar radical intermediate would lead to racemisation of the remaining alcohol. The intermediacy of the  $\alpha$ -hydroxydiphenylmethyl radical was demonstrated by Porter<sup>54</sup> who obtained its absorption spectrum ( $\lambda_{\text{max}}$  545nm.) using a flash photolysis technique. The 2-hydroxy-2-propyl radical was shown to be produced by trapping it with maleic acid to form terebic acid<sup>52</sup>

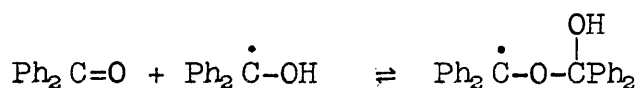
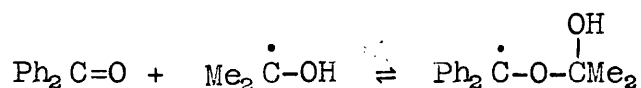


RH is thought to be the  $\alpha$ -hydroxydiphenylmethyl radical



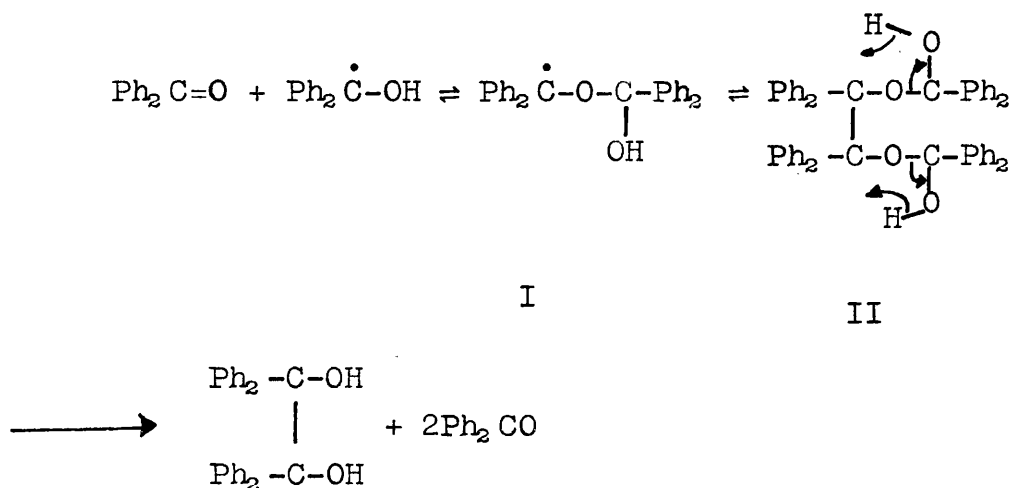
since benzophenone can be recovered almost quantitatively from the reaction, and no diphenyl analogue of terebic acid is formed.

The mechanism has been further modified by Schenck<sup>55</sup> who accounts for the fate of the two radicals as follows:

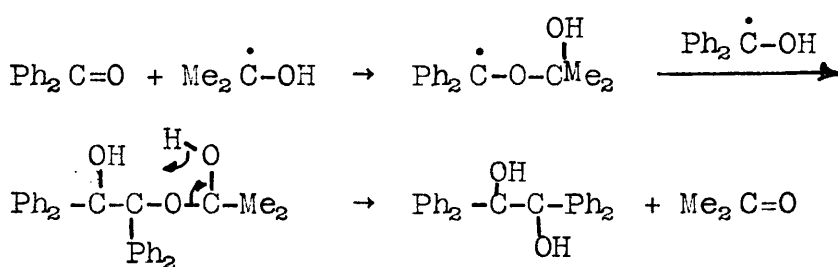


In the complete absence of oxygen the reaction is more complex. The quantum yield varies with the inverse square root of the light intensity,<sup>56,57</sup> approaching a limiting value of 1 at high intensity and 2 at low intensity<sup>56</sup>. Cohen<sup>58</sup> found that the quantum yield increased if the isopropanol was diluted with benzene reaching a value of 1.70 at 3.13M propanol. Stern-Volmer analysis leads to an extrapolated limiting quantum yield of  $\sim 1.9$  in neat isopropanol whilst that actually determined was 1.16.

The formation of a strongly absorbing long-lived intermediate ( $\lambda_{\text{max}}$  335nm.) was first demonstrated by Pitts<sup>52</sup> and its nature and role have been the subject of a number of investigations. It was initially suggested that the intermediate was formed from an  $\alpha$ -hydroxydiphenylmethyl radical and benzophenone to give I, the absorbing species, which dimerised to form the hemiketal II. Dissociation of this gives benzpinacol and benzophenone. (Scheme II)

Scheme II

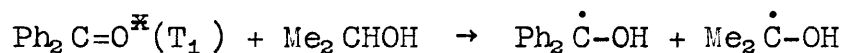
Testa<sup>56</sup> explained his quantum yield variation by assuming two possible modes of benzpinacol formation. At high light intensity, the dimerisation of  $\alpha$ -hydroxydiphenylmethyl radicals predominates and the quantum yield approaches 1. The 2-hydroxy-2-propyl radicals also dimerise to form the corresponding pinacol which presumably disproportionates to acetone and isopropanol. At lower light intensity, a mechanism involving the formation of a hemiacetal radical intermediate was envisaged. (Scheme III)

Scheme III

The quantum yield varies between 1 and 2 depending on the relative importance of each process.

Yang and Murov<sup>57</sup> also invoked the idea of two concurrent processes involving the reactive intermediate to

explain the variation of quantum yield. A first order hydrogen abstraction process:



and a competing deactivation step. This was held to be quenching of triplet benzophenone by the  $\alpha$ -hydroxydiphenylmethyl or 2-hydroxy-2-propyl radicals, which would act as paramagnetic quenchers.

Cohen<sup>58</sup> also observed the formation of an absorbing transient in neat isopropanol, but it was present to a much lesser degree upon dilution with benzene. He proposes that the increase in quantum yield on dilution is due partly to the absence of an absorbing intermediate, and partly to an increased value of  $k_r$  (the bimolecular rate constant for hydrogen abstraction) upon dilution.

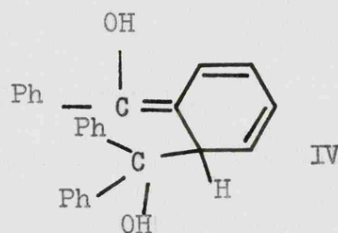
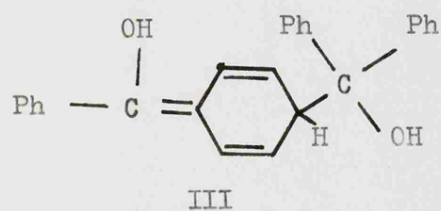
$$\frac{k_r(1.0\text{M Me}_2\text{CHOH in benzene})}{k_r(\text{Neat Me}_2\text{CHOH})} = 2.4$$

The intermediate has also been attributed to the formation of a charge transfer complex between the  $\alpha$ -hydroxydiphenylmethyl and 2-hydroxy-2-propyl radicals, or if irradiation is prolonged between the 2-hydroxy-2-propyl radical and  $\text{Ph}_2-\dot{\text{C}}-\text{O}-\overset{\text{OH}}{\underset{\cdot}{\text{C}}}-\text{Me}_2$ <sup>59</sup>.

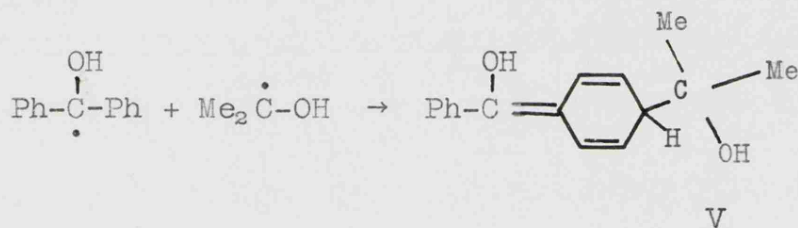
At room temperature, no signal from the free electron could be detected by paramagnetic resonance spectroscopy<sup>60</sup>, so the intermediate was assumed not to be of a free radical nature.

More recently, Schenck et al<sup>61,62</sup> have formulated the

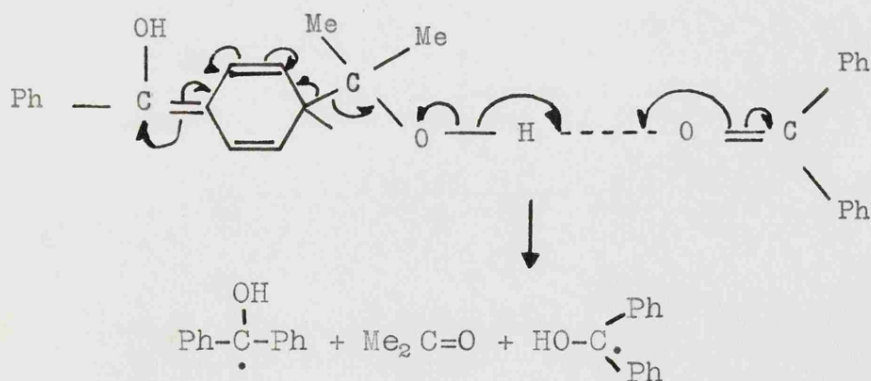
intermediate as an adduct of 2  $\alpha$ -hydroxydiphenylmethyl radicals, the isopinacols III and IV.



The investigations of Filipescu and Minn<sup>63</sup> have probably been most successful in elucidating the structure and breakdown of the intermediate. This, they propose, is the quinoid compound V resulting from para attack of the 2-hydroxy-2-propyl radical upon an  $\alpha$ -hydroxydiphenylmethyl radical.



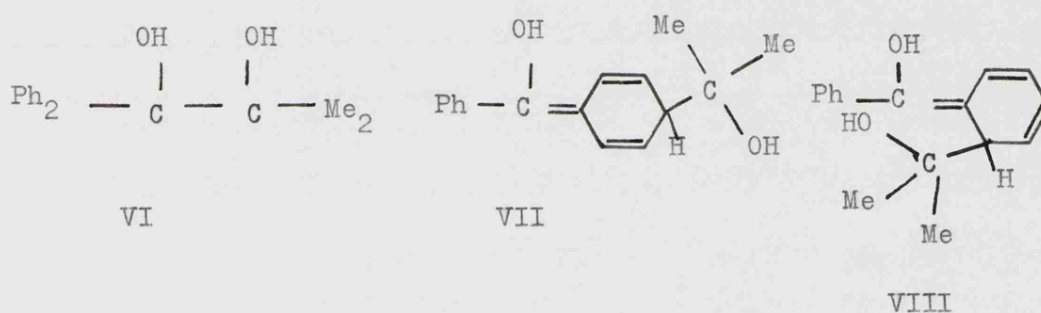
V then reacts with benzophenone in a concerted rate-determining dark reaction.



The kinetics of the dark reaction were studied and a value of  $2.75 \times 10^{-3} \text{ l.mol}^{-1}.\text{sec}^{-1}$  for the limiting rate constant was established. Structures III and IV for the intermediate were ruled out because they did not fit the

dark reaction kinetics, and the dark reaction stops before the intermediate is completely consumed if more than half the initial benzophenone is converted during the irradiation. Previous differing reports of quantum yield values were rationalised since the concentration of benzophenone and time of irradiation will affect the formation of the intermediate, which will be converted back to benzophenone if air is admitted before the slow dark reaction is completed.

In very dilute ( $\sim 10^{-4}M$ ) air-free solutions of benzophenone in isopropanol, the mixed pinacol (VI) is formed, together with the ortho and para isomers of the mixed isopinacol (VII + VIII)

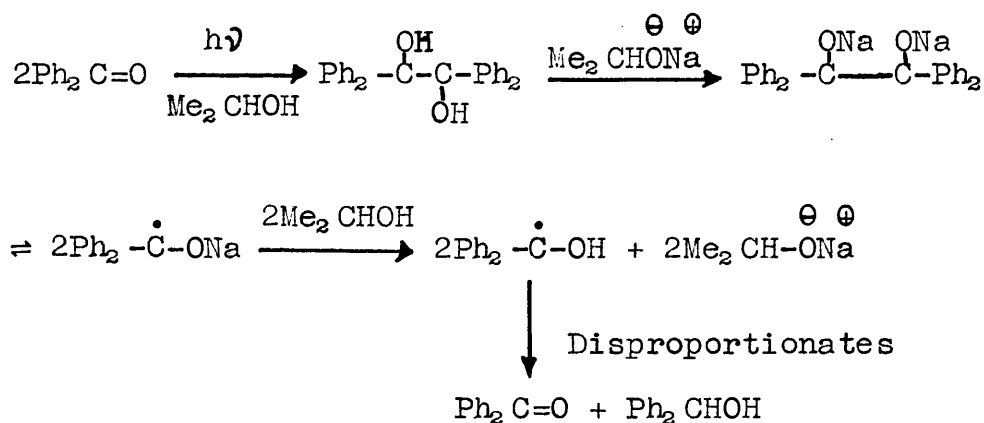


After formation of VII and VIII, continued irradiation at longer wavelength caused the absorbance due to the isopinacols to disappear. It was assumed that they were converted into the mixed pinacol via dissociation into the primary radicals.

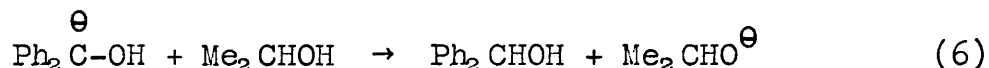
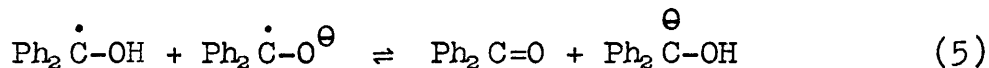
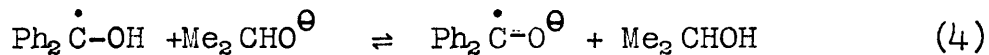
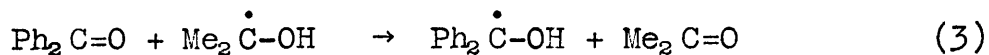
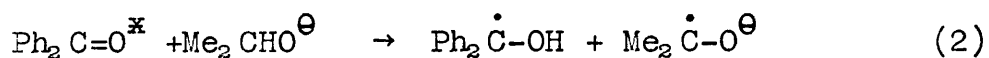
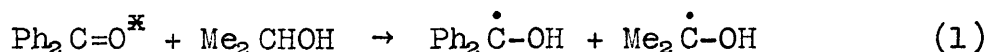
The photoreduction of carbonyl compounds by alcohols is a useful method of preparing the  $\alpha$ -hydroxydiphenylmethyl and related radicals for paramagnetic resonance studies<sup>65</sup>.

Photoreduction in Basic Media

The photoreduction of benzophenone and certain substituted benzophenones by isopropanol in the presence of sodium isopropoxide produces benzhydrol, not benzpinacol, in good yield<sup>66</sup>. The mechanism, according to Bachmann, involves initial formation of the pinacol and its decomposition by sodium isopropoxide to give  $\alpha$ -hydroxydiphenylmethyl radicals which disproportionate.



Cohen<sup>67</sup> found no evidence for the intermediacy of benzpinacol and proposes the following scheme:



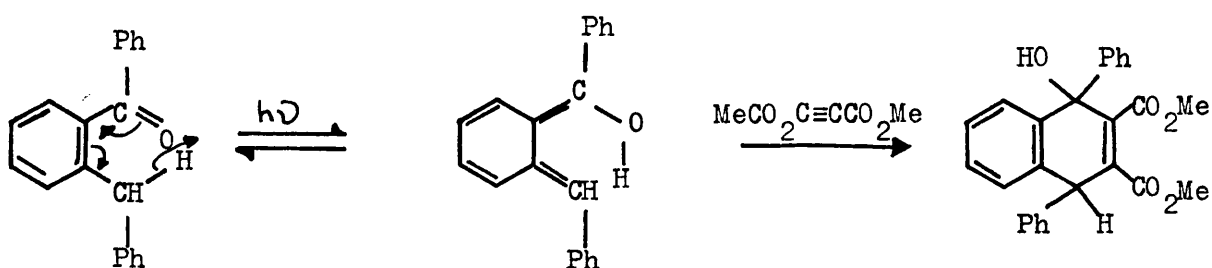
The formation of the radical anion has been demonstrated by paramagnetic resonance spectroscopy<sup>65</sup>.

Photoreduction of Substituted Benzophenones

The limiting quantum yield for the disappearance of substituted benzophenones in isopropanol varies, and some values are shown in the following table:

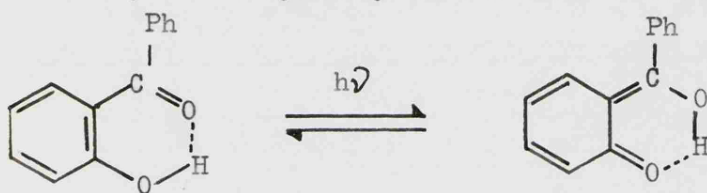
<u>Ketone</u>	$\phi_B$
Benzophenone	2.0
4,4'-Dimethoxybenzophenone	2.0
2-tert-Butylbenzophenone	0.5
4-Methylbenzophenone	0.5
4-Phenylbenzophenone	0.2
2-Methylbenzophenone	0.05
2-Ethylbenzophenone	0.02
4-Hydroxybenzophenone	0.02
2,4-Dihydroxybenzophenone	0.005
4,4'-tetramethyldiaminobenzophenone	0
4-Aminobenzophenone	0
3-Nitrobenzophenone	0
Fluorenone	0

The lack of reactivity of 2-alkylbenzophenones is attributed to photoenolisation occurring via a six-membered transition state which competes effectively with intermolecular photoreduction<sup>69</sup>. The photoenol, which reverts back to the keto form in the dark, has been trapped in the case of orthobenzylbenzophenone with dimethylacetylenedicarboxylate.

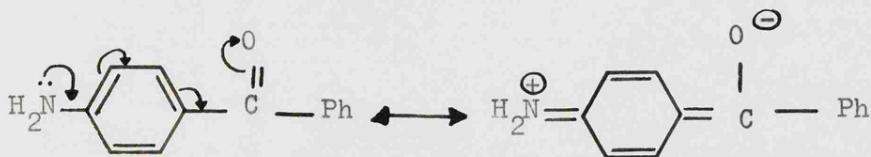


Since 2-*tert*-butylbenzophenone undergoes normal photo-reduction, the low reactivity is not due to steric hindrance to intermolecular hydrogen abstraction. A six-membered transition state is required for the photoenolisation step, a requirement which cannot be fulfilled in the 2-*tert*-butyl case. Flash spectroscopic investigations<sup>70</sup> have shown that the triplet state of the carbonyl is the reactive species.

A similar sort of intramolecular hydrogen abstraction, via a six-membered transition state made available by hydrogen bonding is postulated to account for the low reactivity of 2-hydroxy and 2-aminobenzophenones<sup>71</sup>.



*p*-Aminobenzophenone is not photoreduced by isopropanol<sup>72</sup> but is photoreduced with low quantum yield (0.2) in cyclohexane. It has been shown that intramolecular charge transfer occurs, giving rise to a high intensity band at longer wavelength, designated a charge transfer band.



This more polar species is stabilised by isopropanol, so that in this solvent, the lowest excited state is the charge transfer state. In cyclohexane, the energy of the charge transfer state is slightly above that of the first triplet level, so photoreduction can occur. The increase



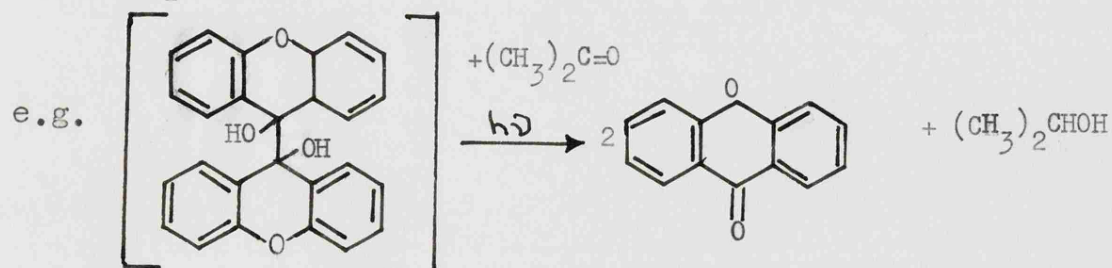
in electron density on the oxygen in the charge transfer state also causes a decrease in reactivity since electrophilic attack is more difficult. In the presence of hydrogen chloride, p-dimethylaminobenzophenone undergoes normal photoreduction in isopropanol to give the pinacol<sup>73</sup>,  $\phi_B = 0.5 - 0.6$  in 1-2N HCl. The lone pair of electrons on the nitrogen are involved in bonding and not available for release into the aryl ring.

A similar charge transfer effect is thought to account for the low reactivity of p-hydroxy benzophenone in isopropanol. It too undergoes efficient photoreduction in cyclohexane.

The cases of 4-phenylbenzophenone and fluorenone, where the lowest excited state is of the  $\pi \rightarrow \pi^*$  type have been dealt with previously.

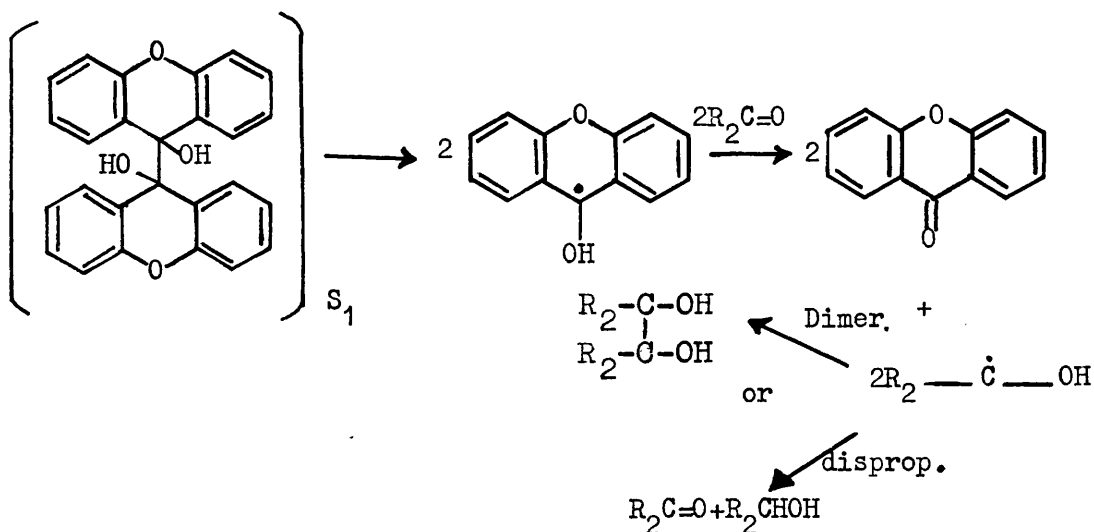
#### Photochemical Cleavage of Pinacols

It has been reported<sup>74</sup> that certain pinacols form the ketone when photolysed in the presence of a suitable hydrogen acceptor. This is the reverse of the photopinacolisation process.



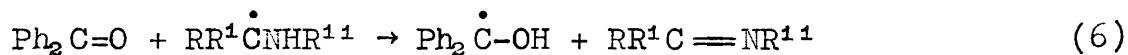
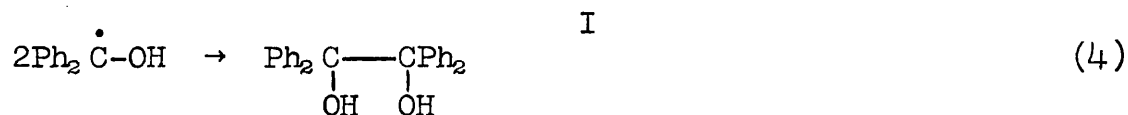
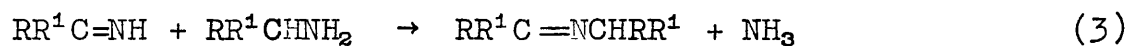
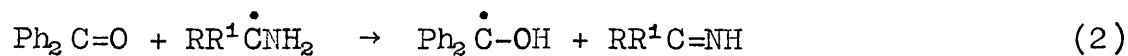
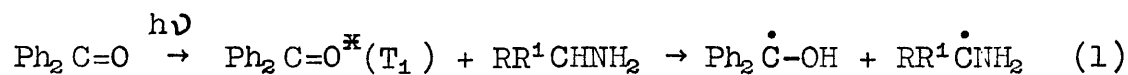
This reaction has been studied<sup>75</sup> and is thought to involve singlet pinacol since the reaction could not be sensitised by known triplet sensitisers, and triplet

quenchers had no effect. A possible mechanism for the reaction is



### Photoreduction by Amines

The photoreduction of benzophenone by amines was first reported by Cohen and Baumgarten<sup>77</sup>. Reduction by primary and secondary amines produced benzpinacol in high yield and the relative imines I and II.



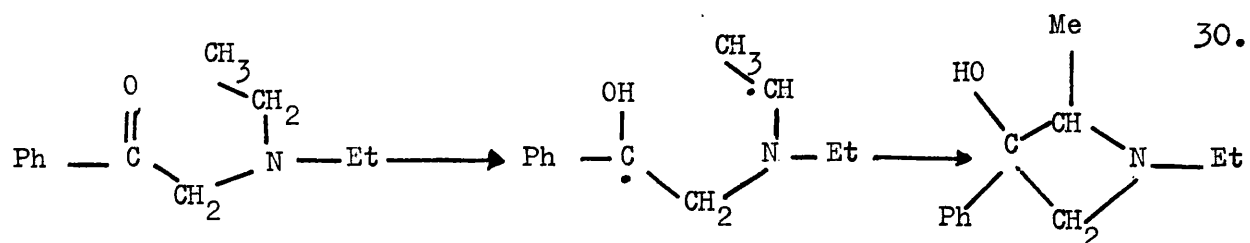
### II



The rates of photoreduction varied depending on the amine as is shown in the following table<sup>77</sup>.

Reducing Medium	Rate M hr <sup>-1</sup>	RelRate
2-Propanol	0.12	1.0
2-Butylamine	0.16	1.3
Cyclohexylamine	0.13	1.1
1M Cyclohexylamine in benzene	0.13	1.1
n-Butylamine	0.12	1.0
1M n-butylamine in benzene	0.12	1.0
n-Hexylamine	0.11	0.9
Isobutylamine	0.15	1.3
t-butylamine	0.020	0.17
Di-n-propylamine	0.055	0.46
Di-n-butylamine	0.064	0.53
Di-isopropylamine	0.042	0.35
1:4 Di-isopropylamine in benzene	0.066	0.55
Triethylamine	0.023	0.19
0.5M Trimethylamine in benzene	0.070	0.58
Tributylamine	0.047	0.39
Di-isopropylethylamine	0.058	0.48
0.5M Di-isopropylethylamine in benzene	0.096	0.80

Benzophenone is also photoreduced by N-alkylarylamines<sup>78</sup> and intramolecular abstraction of hydrogen from amines has been utilised in the formation of azetidin-3-ols<sup>79</sup>.



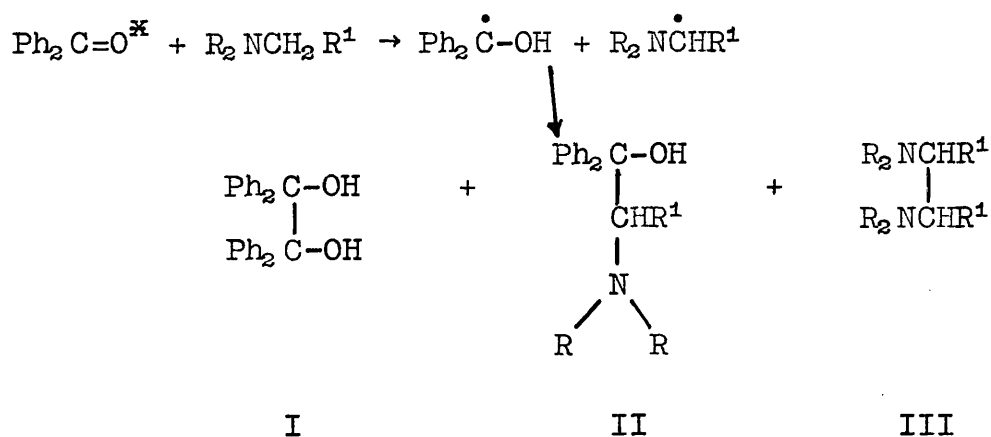
Yields are generally low due to a competing elimination reaction giving acetophenone and the trimer of the expected imine.

### Results and Discussion

Initial studies in this laboratory<sup>78</sup> showed that benzophenone was photoreduced by tertiary alkylarylamines giving benzpinacol (I), hydroxyamines(II) and 1,2-diamines (III). The photolysis was also carried out using N-methylcarbazole and N-benzylidiphenylamine, resulting in similar products. The yields are given in the following table.

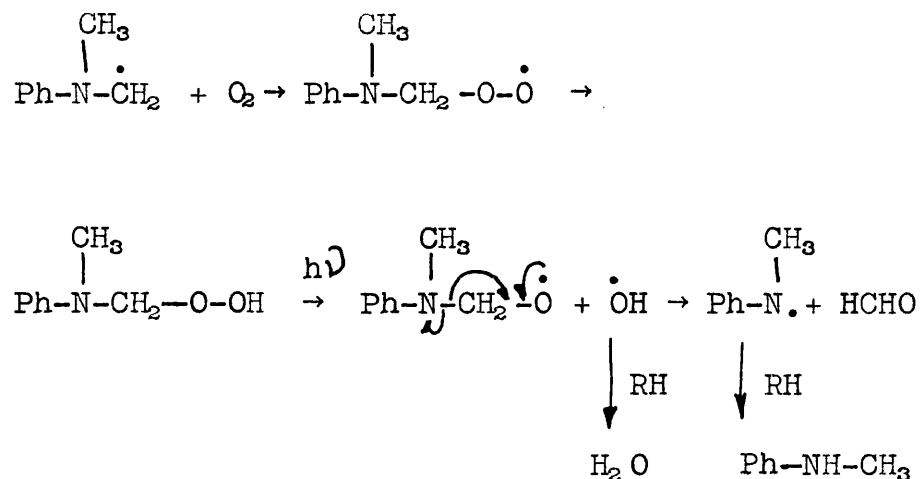
Amine	I	II	III
PhNMe <sub>2</sub>	60%	12%	12% PhNHMe formed also.
Ph <sub>2</sub> NMe	30%	7%	8%
Ph <sub>2</sub> NCH <sub>2</sub> Ph	36%	7.5%	15%
N-methylcarbazole	40%		12.5%

This is consistent with simple abstraction of hydrogen from the  $\alpha$ -carbon by triplet benzophenone giving two radicals which can either dimerise or combine giving the observed products.



The N-methylaniline formed in the case of reduction by NN-dimethylaniline may be due to oxidation of the methylamino radical. Although photolyses were carried out under

nitrogen, there may have been sufficient oxygen present to cause the following



Initial attempts to photoreduce fluorenone and xanthone, both of which are examples of ketones not photoreduced by alcohols<sup>67,74</sup> with NN-dimethylaniline proved successful. The reaction was carried out with a series of carbonyl compounds and the amounts of pinacols formed where photo-reduction took place are summarised in the following table. In all cases except benzaldehyde, 0.1M NN-dimethylaniline was photolysed with 0.05M carbonyl compound in benzene.

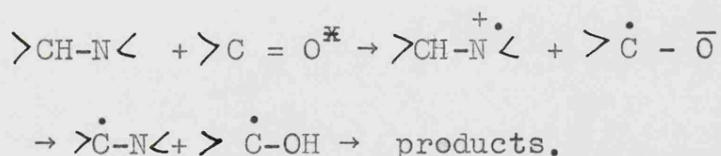
Carbonyl Compound	% pinacol
Xanthone	43
Fluorenone	58
2-Aminobenzophenone	0
4-Aminobenzophenone	59
2,4'-Dimethoxybenzophenone	40
4-Phenylbenzophenone	60
Thioxanthone	0
Acetophenone	33
Benzaldehyde <sup>a</sup>	50

Cyclohexanone	0
Isophorone	0
$\beta$ -Acetylnaphthalene	36

<sup>a</sup>Benzaldehyde was photolysed with 0.1M triethylamine.

This is a useful method for the preparation of pinacols which cannot be synthesised by photoreducing the corresponding ketones by alcohols. Such pinacols were previously prepared by reducing the ketone with a mixture of magnesium and magnesium iodide in ether-benzene (1:2)<sup>80</sup> or with aluminium foil which has previously been sandpapered and to which is added a small amount of mercuric chloride for amalgamation<sup>81</sup>.

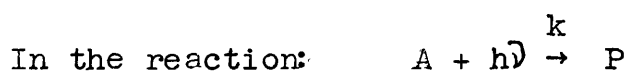
On the basis of their results on the photoreduction of p-aminobenzophenone by tertiary amines, Cohen and Cohen<sup>82</sup> proposed that photoreduction by amines proceeded via an initial electron transfer from the nitrogen atom to the triplet ketone giving a radical cation/anion pair. Proton transfer followed by electron redistribution gave the radicals which accounted for the observed products.



Since photoinduced electron transfer is known (see section on quenching of excited states in the introduction) the mechanism seemed feasible and a series of experiments was designed to test its validity.

It has previously been reported<sup>41</sup> that triplet benzophenone shows great selectivity in its attack on C-H bonds, the relative reactivities of the primary,

secondary and tertiary C-H bonds of alkanes being 1:50:300. The selectivity of excited benzophenone in its attack on the  $\alpha$  C-H bonds of a number of N-methyl and N-benzyl substituted tertiary amines was ascertained by photolysis of 0.1M amine and 0.05M benzophenone in benzene. The progress of the reaction was followed by measuring the decrease in the infra-red carbonyl absorption and comparing it with a previously obtained standard.



the rate of disappearance of A is given by

$$-\frac{d[A]}{dt} = k[A]I \quad (I) \text{ where } I = \text{light intensity}$$

The fraction of light absorbed by unreacted A at time t is  $\frac{[A]}{[A_0]}$  where  $[A_0]$  is the initial concentration of A.

The quantum yield of disappearance of A is given by

$$\phi = \frac{[A_0] - [A]}{I[1-10^{-D}]t \frac{[\bar{A}]}{[A_0]}} \quad (2)$$

where  $[\bar{A}]$  is the average amount of reactant present during the time of irradiation t

$$[\bar{A}] = \frac{[A_0]}{t} \int_0^t e^{-kIt} dt$$



from equation (1) and substituting in equation (2)

$$\phi = \frac{[A_0] \ln \frac{[A_0]}{[A]}}{I_{\text{abs}} t} \quad \text{where } I_{\text{abs}} = \text{rate of absorption.}$$

$$\therefore \ln \frac{[A_0]}{[A]} = \frac{\phi I_{\text{abs}} t}{A_0}$$

A plot of  $\ln \frac{[A_0]}{[A]}$  versus  $t$  will give a straight line of

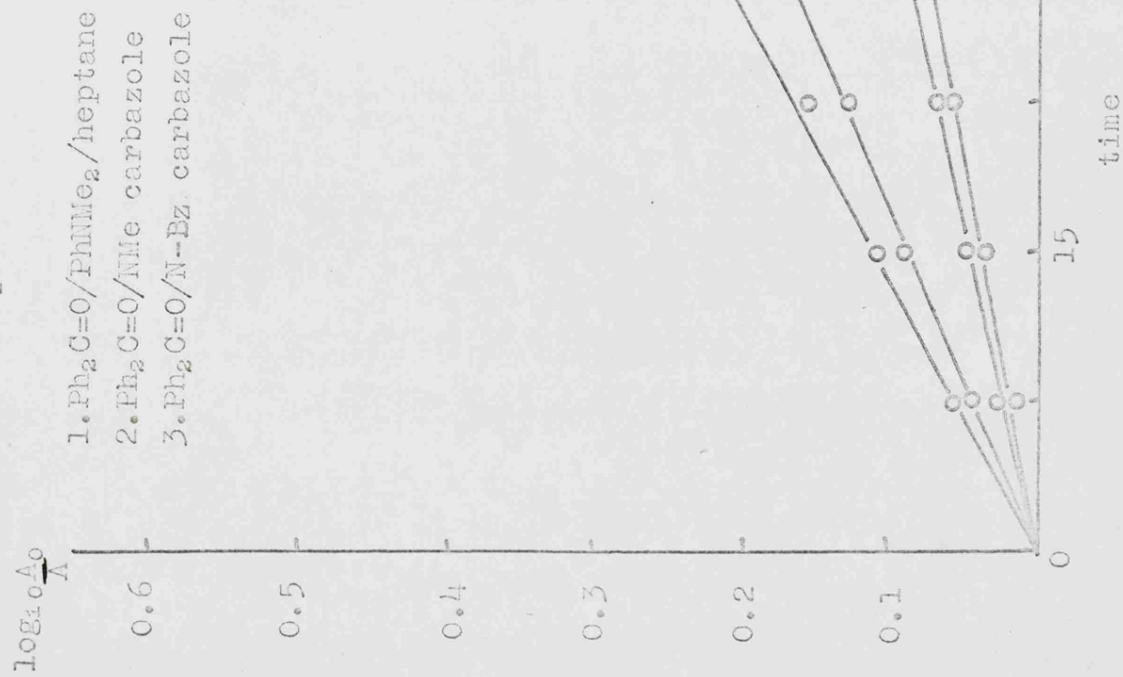
slope  $\frac{\phi I_{\text{abs}}}{[A_0]}$  therefore, for a series of reactions done under

constant conditions and constant initial concentration of reactant A, comparison of the slopes will give a direct comparison of quantum yields. The graphs A-D show plots of  $\log_{10} \frac{[A_0]}{[A]}$  versus time for the series of amines and ketones

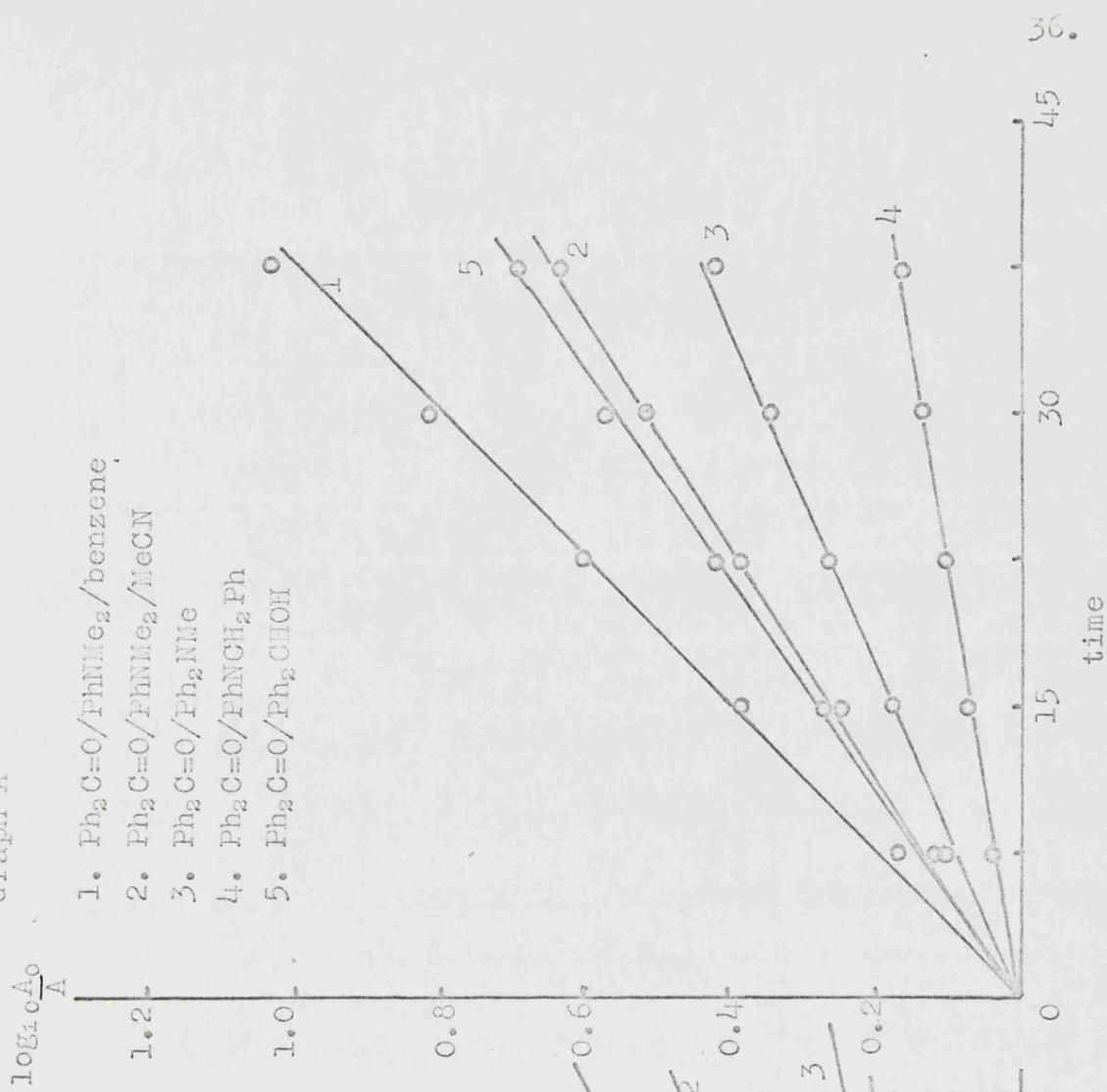
studied and the reactivity of the amines compared with the photoreduction of benzophenone by benzhydrol is given in Table 1.

If direct hydrogen abstraction is taking place as in photoreduction by alcohols and alkanes, one would expect the benzylic C-H bonds to be much more reactive than the methyl C-H bonds. As can be seen from the table, in contrast to the results of Walling and Gibian, the benzylic C-H bonds are not significantly more reactive than the methyl ones. Comparisons must be limited to the same

Graph B



Graph A



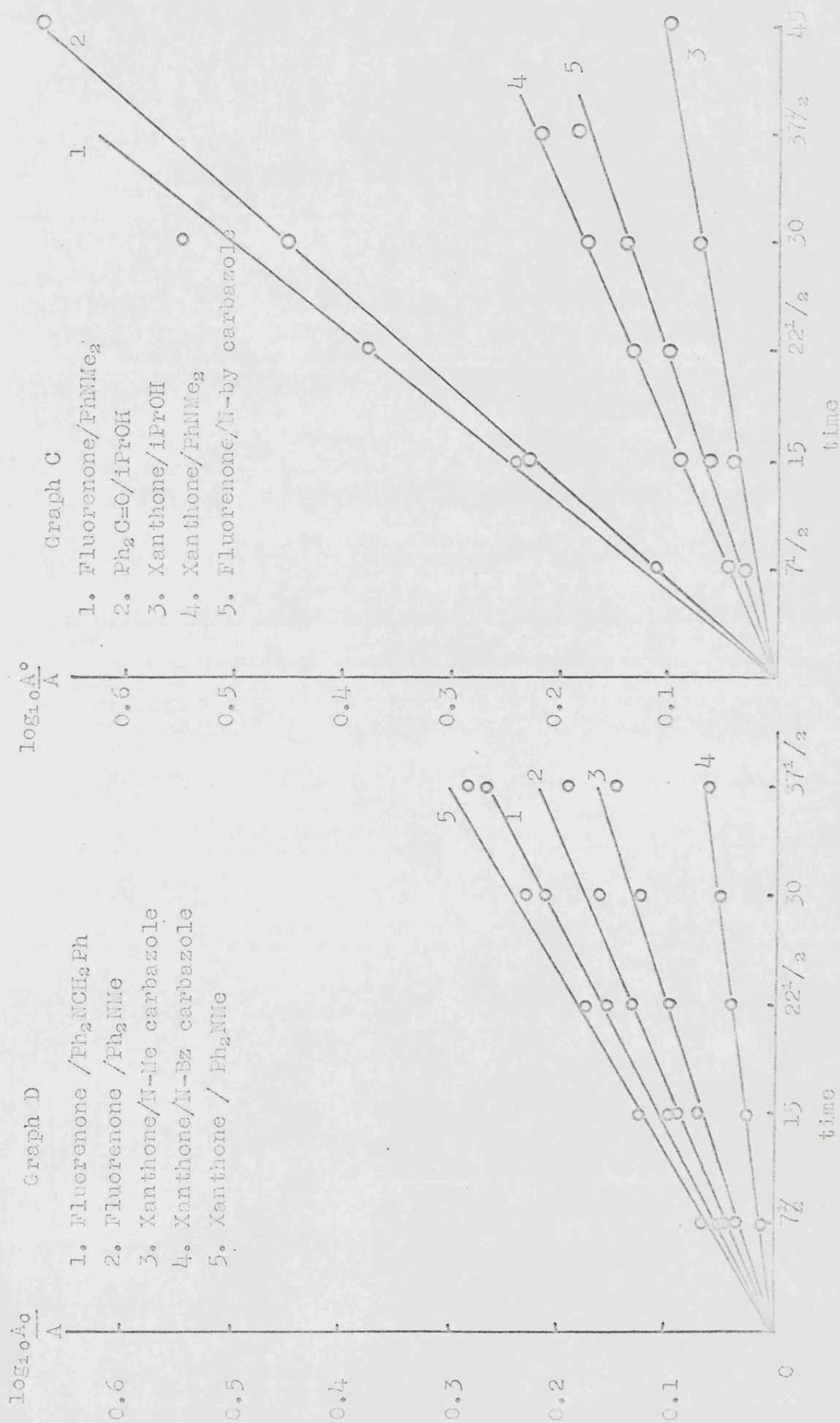


TABLE I

Ketone	Amine or alcohol	Relative Slope	Slope Relative to $\text{Ph}_2\text{CHOH}$ as 1	Reactivity per hydrogen.
Benzophenone	$\text{PhNMe}_2$ in benzene	0.78	1.39	0.231
	$\text{PhNMe}_2$ in $\text{CH}_3\text{CN}$	0.51	0.91	0.151
	$\text{PhNMe}_2$ in heptane	0.22	0.393	0.0655
	$\text{Ph}_2\text{CHOH}$	0.56	1	1
	iPrOH	0.46	0.82	0.82
	$\text{Ph}_2\text{NMe}$	0.35	0.625	0.208
	$\text{Ph}_2\text{NCH}_2\text{Ph}$	0.14	0.25	0.125
	N-Mecarbazole	0.175	0.312	0.104
	N-Bzcarbazole	0.1	0.178	0.089
Xanthone	iPrOH	0.07	0.125	0.125
	$\text{PhNMe}_2$	0.18	0.322	0.054
	$\text{Ph}_2\text{NMe}$	0.245	0.437	0.146
	$\text{Ph}_2\text{NCH}_2\text{Ph}$	0.075	0.134	0.067
	N-Mecarbazole	0.185	0.33	0.11
	N-Bzcarbazole	0.065	0.116	0.058

TABLE I continued

Fluorenone	PhNNMe <sub>2</sub>	0.51	0.91	0.151
	Ph <sub>2</sub> NMe	0.18	0.322	0.107
	Ph <sub>2</sub> NCH <sub>2</sub> Ph	0.21	0.374	0.187
	N-Mecarbazole	-	-	-
	N-Bzcarbazole	0.14	0.25	0.12

amine type photoreducing the same ketone. This lack of selectivity on the part of excited ketone suggests the possibility of a different mechanism to that occurring in the case of photoreduction by alcohols. If electron transfer does occur as suggested, this lack of selectivity would entail the proton transfer step being particularly exothermic. It was also found that contrary to previous reports<sup>7 4</sup> xanthone could be photoreduced by isopropanol, xanthopinacol being formed. This approach involving the comparison of quantum yields has recently been criticised by Wagner<sup>8 3</sup> who studied the quenching of the type II photoelimination of valerophenone by 2,5-dimethyl-2,4-hexadiene, triethylamine and NN-dimethyl-t-butylamine. Quenching by the amines corresponds to photoreduction of valerophenone and the comparable efficiencies measured by comparing the values of  $k_q$ , the bimolecular quenching constant showed that secondary C-H bonds were no more reactive than primary C-H bonds. Comparison of quantum yields is valid if it is restricted to comparing the reactivities of similar amines, e.g. the methyl and benzyl carbazoles. Since photoreduction by NN-dimethylaniline always produces small amounts of N-methylaniline which may also participate in photoreduction, the reactivity of this amine cannot be taken into account. The assumption has also to be made that the yield of triplets is the same in each case when comparisons are made. The fact that use of a more polar solvent, acetonitrile does not increase the rate of photoreduction of benzophenone by NN-dimethylaniline as might be expected if radical ions are formed may be due to the hydrogen abstraction step being so rapid that the radical ions do not have a chance to separate, or that complete electron transfer does not occur.

Instead an excited charge transfer complex may be formed. Diminished reactivity in n-heptane is due to the non-polar solvent being a poor stabiliser of charged or partially charged species.

Some energy transfer studies were performed using compounds which are known to deactivate excited benzophenone. The photoreduction of benzophenone by NN-dimethylaniline was carried out in the presence of varying concentrations of quencher, the progress of the reaction being followed as before. Stern Volmer plots of  $\frac{\phi_{act.}}{\phi_{qu.}}$  versus

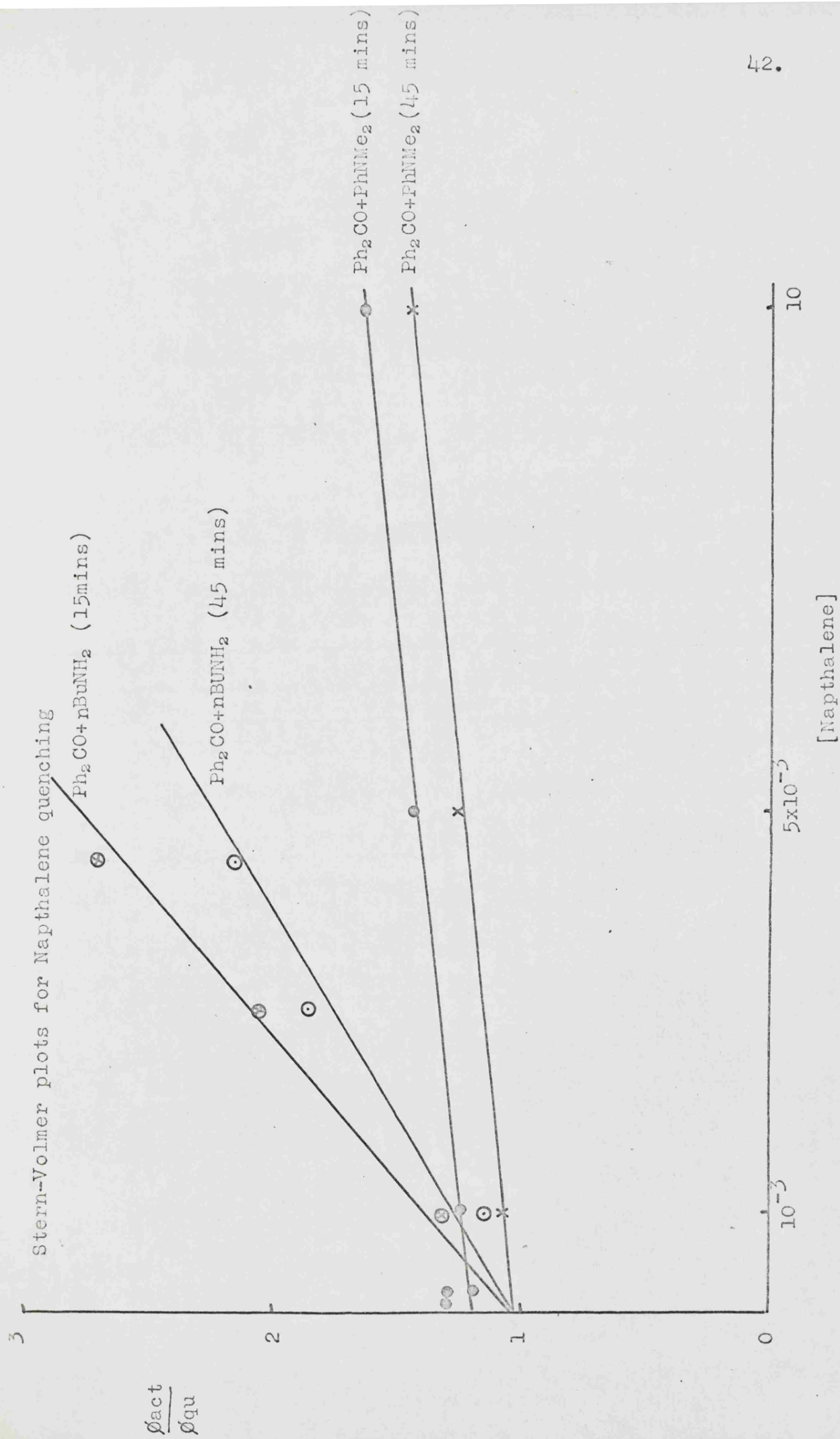
concentration of quencher were drawn, the actinometer being the benzophenone-benzylidene actinometer of Moore and Ketchum<sup>15</sup>, and the ratio  $\frac{k_q}{k_r}$  where  $k_q$  is the bimolecular quenching

constant and  $k_r$  is the bimolecular hydrogen abstraction rate constant, was calculated from the slope of the graph.

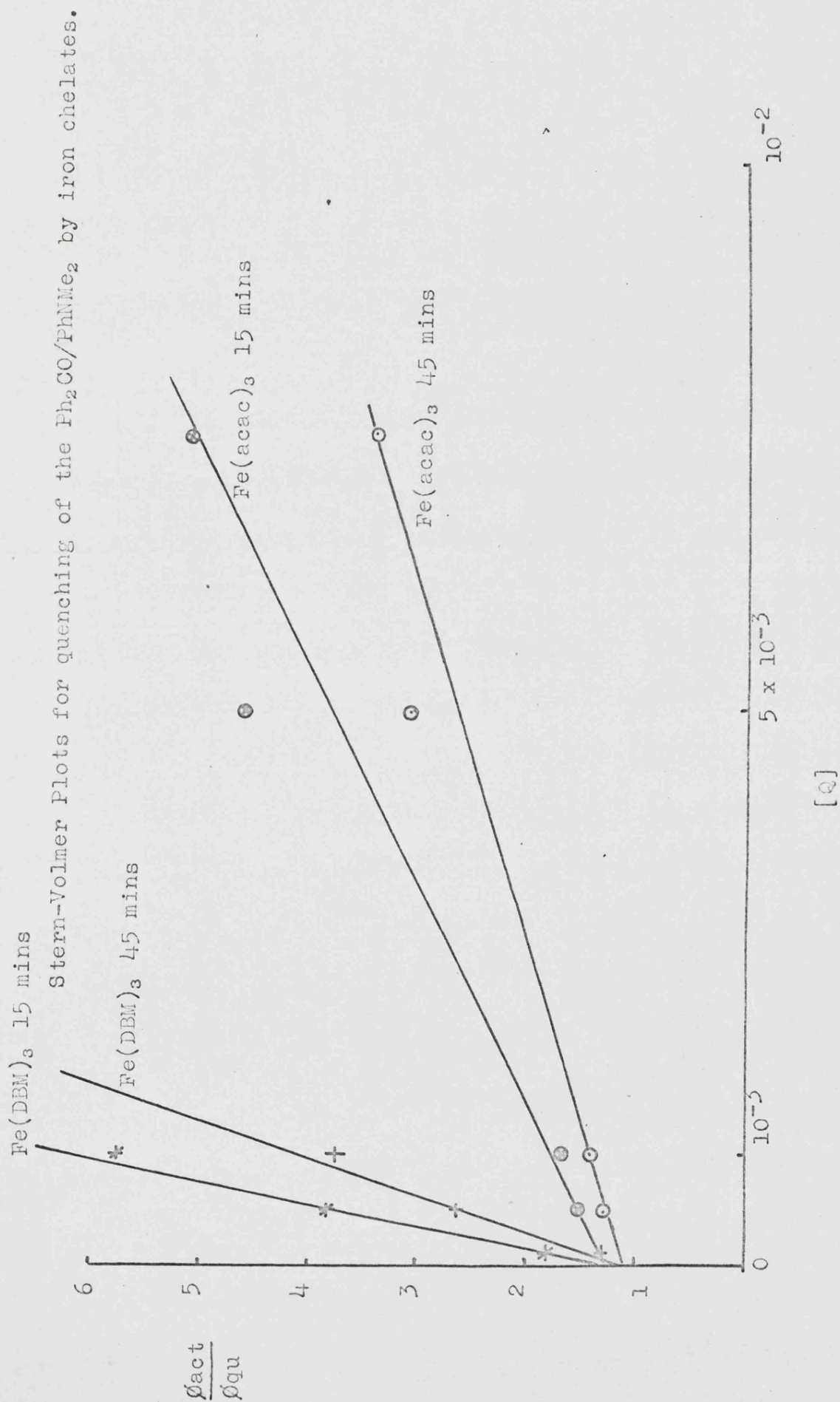
The quenching action of naphthalene, ferric tris-acetylacetonate [Fe(acac)<sub>3</sub>] and ferric tris-dibenzoylmethanate [Fe(DBM)<sub>3</sub>] upon the photoreduction of benzophenone by NN-dimethylaniline was studied and also that of naphthalene on the photoreduction of benzophenone by n-butylamine.

The relevant Stern-Volmer plots are shown overleaf and the  $\frac{k_q}{k_r}$  values obtained for the different quenchers are given

in the following table and compared with values obtained using benzhydrol as reductant<sup>19,20</sup>.







Quencher	$k_q/k_r$	
	PhNMe <sub>2</sub>	Ph <sub>2</sub> CHOH
Naphthalene	4.5	435
Fe(acac) <sub>3</sub>	38	540
Fe(DBM) <sub>3</sub>	330	3400

The  $\frac{k_q}{k_r}$  value for quenching of the benzophenone n-butylam-

ine photoreduction by naphthalene was 32.8. The effect of variation of concentration of NN-dimethylaniline was studied and the value of  $\frac{k_d}{k_r}$  (where  $k_d$  is the unimolecular rate

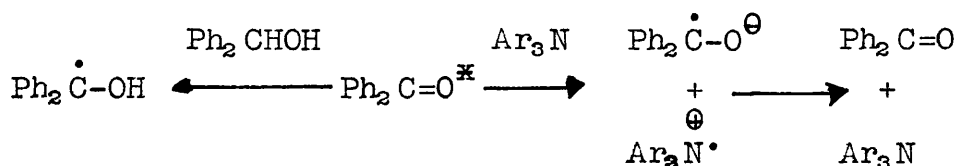
constant for deactivation of excited benzophenone by phosphorescence etc. and  $k_r$  is the rate constant as before) was calculated from the slope of the Stern-Volmer plot. The value of  $\frac{k_d}{k_r}$  obtained was 0.0243 compared with that of 0.05

for photoreduction by benzhydrol<sup>48</sup>. If the assumption is made that quenching by the compounds studied occurs by the same mechanism when amine or alcohol is the hydrogen donor, the value of  $k_r$  for photoreduction by NN-dimethylaniline can be calculated. From the work of Hammond<sup>19</sup>, the values of  $k_q$  for quenching by Fe(acac)<sub>3</sub> and Fe(DBM)<sub>3</sub> are  $2.7 \times 10^9$  and  $1.7 \times 10^{10}$  l.mol<sup>-1</sup> sec<sup>-1</sup> respectively. Substitution of these values into the  $\frac{k_q}{k_r}$  values obtained above for

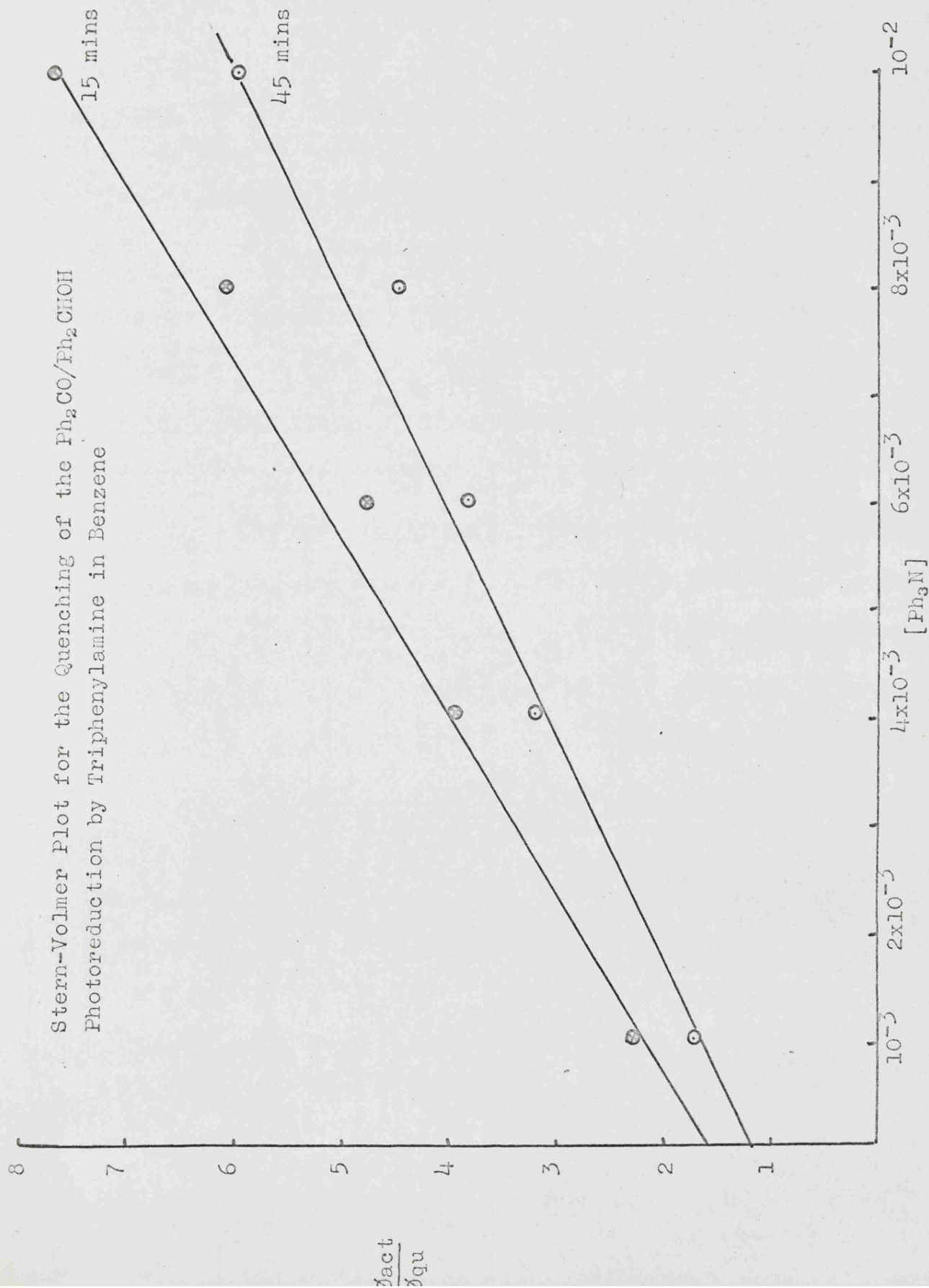
quenching of the photoreduction by NN-dimethylaniline gives values of 7.1 and  $5.15 \times 10^7$  l.mole<sup>-1</sup> sec<sup>-1</sup> for  $k_r$  respectively. These values are higher than that of  $5 \times 10^6$  l.mole<sup>-1</sup> sec<sup>-1</sup> obtained by Hammond<sup>48</sup>. If the average value of  $k_r$  is substituted, the value of  $k_d$  can

be obtained. This value is  $1.5 \times 10^6$  which is also much higher than that obtained in the benzhydrol case. If photoreduction by amines does occur by way of an excited charge transfer complex an additional mode of deactivation is possible, namely, dissociation of this complex to give ground state reactants which may account for the higher value of  $k_d$ . The greater efficiency of the ferric chelates, particularly ferric dibenzoylmethanate compared with naphthalene, of quenching the photoreduction by NN-dimethylaniline may be due to their ability to quench the excited complex. If the photoreduction does occur by the proposed mechanism, the concentration of triplet ketone will be rapidly diminished and unless quencher molecules can compete effectively with the rapid initial interaction of an electron with the excited carbonyl group, their quenching efficiency will be reduced.

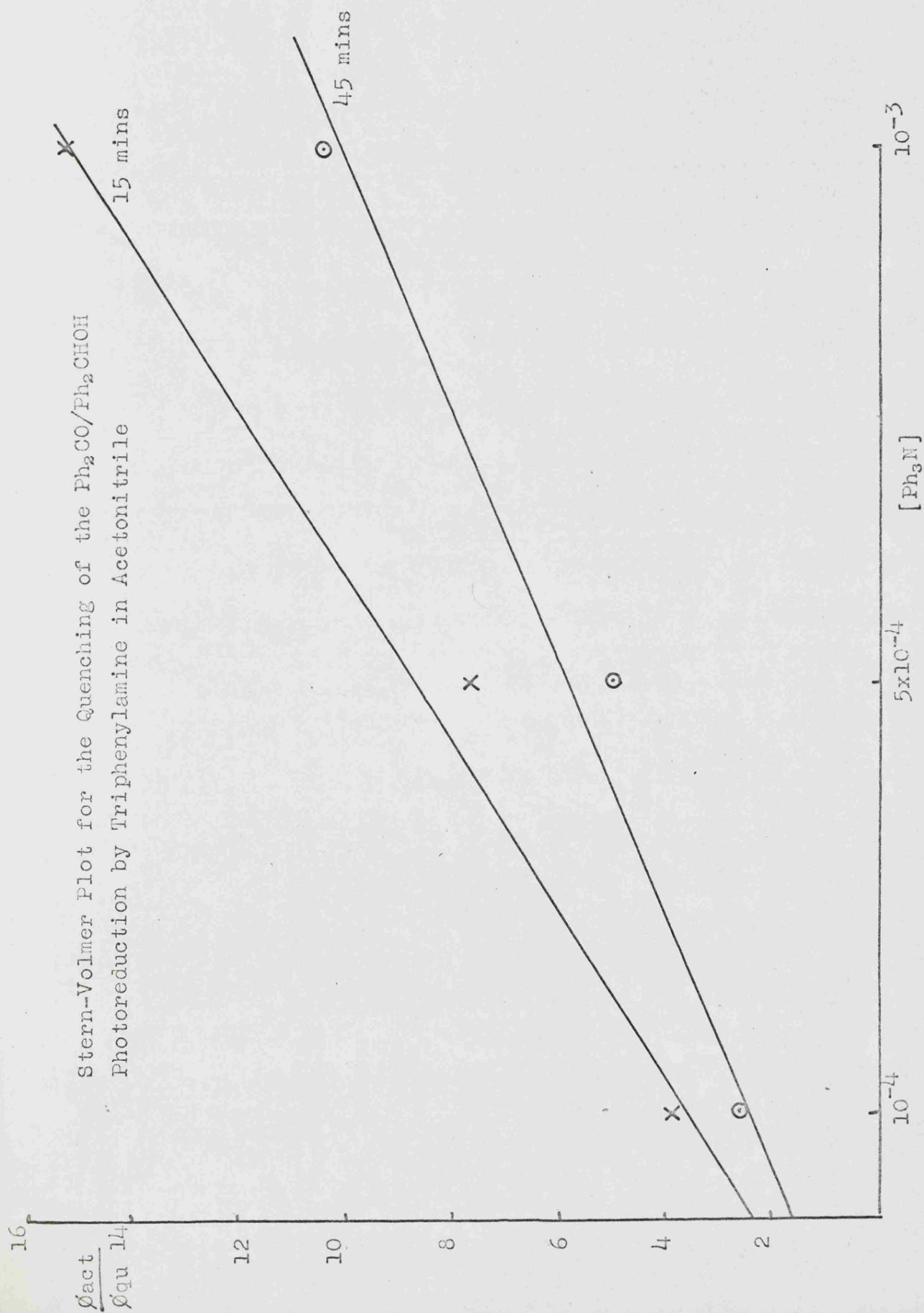
If such an electron transfer mechanism does operate then tertiary amines which do not contain abstractable hydrogen, if added to the benzophenone-benzhydrol system will compete for the excited benzophenone to form a radical ion pair. This would then breakdown into reactants resulting in quenching of the photoreduction.



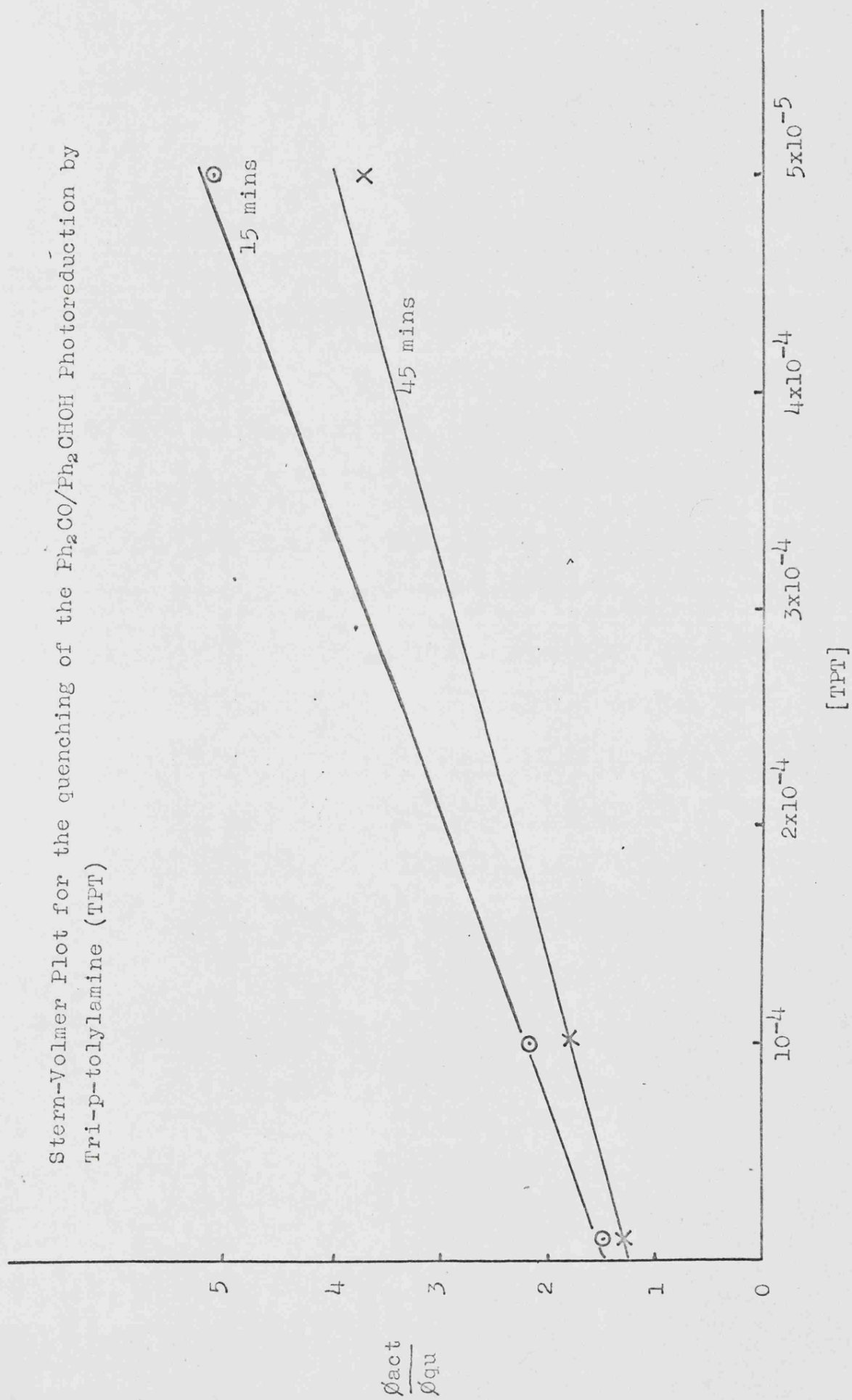
The quenching action of triphenylamine and tri-p-tolylamine on the photoreduction of benzophenone by benzhydrol was studied in an analagous manner to that used previously



Stern-Volmer Plot for the Quenching of the  $\text{Ph}_2\text{CO}/\text{Ph}_2\text{CHOH}$   
 Photoreduction by Triphenylamine in Acetonitrile



Stern-Volmer Plot for the quenching of the  $\text{Ph}_2\text{CO}/\text{Ph}_2\text{CHOH}$  Photoreduction by  
Tri-p-tolylamine (TPT)



Analysis of the Stern-Volmer plots gave the following values for  $\frac{k_q}{k_r}$  ;

Triphenylamine in benzene	44
Triphenylamine in acetonitrile	620
Tri-p-tolylamine in benzene	525

If deactivation does take the form of electron transfer, tri-p-tolylamine would be expected to quench more efficiently since its radical cation has been shown to be much more stable than that of triphenylamine on the basis of oxidation potential measurements<sup>36</sup>. The assumption must be made that the mode of solvation is the same in both cases. The very pronounced solvent effect observed when acetonitrile was used in place of benzene has been noted previously when quenching involves electron transfer<sup>33</sup>. The increase in efficiency is due to the separation of any charge-transfer complex formed into solvent stabilised radical ions. Deactivation of excited benzophenone by direct energy transfer is ruled out because of the unfavourable disposition of the relevant energy levels, ( $E_T(\text{Ph}_2\text{C}=\text{O})$  68.5 k.cals.mol<sup>-1</sup>,  $E_T(\text{Ph}_3\text{N})$  70.1 k.cals.mole<sup>-1</sup>) and the solvent effect. Recently, Turro and Engels<sup>87</sup> have suggested that quenching of both the fluorescence and phosphorescence of biacetyl by amines and phenols occurs by electron transfer. Quantum yields for the disappearance of benzophenone in some neat amines have been measured by Cohen and Chao<sup>85</sup> and are shown overleaf.

Amine	$\phi_\beta$
2-BuNH <sub>2</sub>	1.13
2-BuNHMe	0.31
2-BuNMe <sub>2</sub>	0.12

Studies using excess optically active 2-butylamine and NN-dimethyl-2-butylamine<sup>3 5</sup> showed that no racemisation was observed in the recovered amine indicating that reversible hydrogen abstraction from the asymmetric  $\alpha$ -carbon does not occur.

The photoreduction by primary amines was shown<sup>3 5</sup> not to involve initial rate determining abstraction of hydrogen from the nitrogen atom since use of 2-butylamine-NN-d<sub>2</sub> and cyclohexylamine-NN-d<sub>2</sub> gave a small inverse deuterium isotope effect,  $\frac{k_H}{k_D} = 0.86$  and  $0.9$  respectively.

Abstraction of hydrogen on the  $\alpha$ -carbon seems to be involved in rate determination since use of cyclohexylamine-1-d led to  $\frac{k_H}{k_D} = 1.6$ . This value is smaller than

that for photoreduction by benzhydrol,  $\frac{k_H}{k_D} = 2.7^{48}$ .

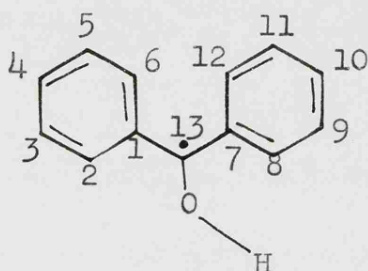
If the reaction does involve the non-bonding electrons of the nitrogen as suggested there will be less C-H bond breaking in the transition state than in the case of photoreduction by benzhydrol and consequently the deuterium isotope effect will be lower. Back transfer of the electron would regenerate starting materials without racemisation of the amine and account for the lower than



anticipated quantum yield. Studies on the photoreduction of p-aminobenzophenone by triethylamine<sup>88</sup> support an initial electron interaction between the amine and excited ketone. The bimolecular hydrogen abstraction rate constant,  $k_r$  for the photoreduction of p-aminobenzophenone by 1M triethylamine in cyclohexane was found to be  $4.2 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$  compared with  $5 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$  for the photoreduction of benzophenone by benzhydrol in benzene. Physical quenchers were inefficient at retarding the reaction and deactivation of triplet ketone by ground state ketone was observed.

To see if complete electron transfer could take place under optimum conditions, a solution of tri-p-tolylamine and benzophenone in acetonitrile was subjected to a flash photolysis study. In both nitrogen saturated and air saturated solution, a transient was formed which had maximum absorbance at 670nm. In the absence of benzophenone this absorption spectrum was very much weaker. This result is similar to that obtained by Granick and Michaelis who produced the radical cation by lead tetraacetate oxidation of tri-p-tolylamine and recorded its absorption spectrum<sup>89</sup>. The intensity and absorbance maxima were such as to obscure any absorbance due to concomitant formation of the benzophenone ketyl radical. Change of the amine to NN-dimethylaniline and the exclusion of oxygen produced the  $\alpha$ -hydroxydiphenylmethyl radical,  $\lambda_{\text{max}} 545\text{nm}$  and another transient having  $\lambda_{\text{max}} 500\text{nm}$ . This may be the radical derived from the NN-dimethylaniline after hydrogen abstraction.

The  $\alpha$ -hydroxydiphenylmethyl radical produced by the photolysis of benzophenone in either triethylamine or NN-dimethylaniline was also characterised by its paramagnetic resonance spectrum, the isotropic hyperfine coupling constants being given in the following table for a 0.2M solution of benzophenone in triethylamine at 22°C.



$$a_2 = a_6 = a_8 = a_{12}$$

$$3.21\text{G}$$

$$a_3 = a_5 = a_9 = a_{11}$$

$$1.22\text{G}$$

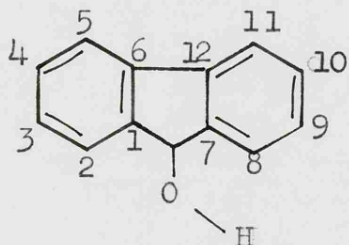
$$a_4 = a_{10}$$

$$3.66\text{G}$$

$$a_{\text{OH}}$$

$$5.48\text{G}$$

Similarly reduction of fluorenone by triethylamine or NN-dimethylaniline produced the 9-hydroxyfluorene radical which has not previously been characterised by electron paramagnetic resonance spectroscopy. The relevant coupling constants are given in the following table.



$$a_2 = a_8$$

$$2.95\text{G}$$

$$a_3 = a_9$$

$$0.56\text{G}$$

$$a_4 = a_{10}$$

$$3.52\text{G}$$

$$a_5 = a_{11}$$

$$0.77\text{G}$$

$$a_{\text{OH}}$$

$$0.77\text{G}$$

Photoreduction by amines is a useful method for preparing

hitherto unobtainable ketyl radicals for paramagnetic resonance spectroscopy studies.

To see if there was any preferential solvation of the carbonyl group by amines in the ground state the proton magnetic resonance spectrum of a 5% solution of acetophenone was run in a number of solvent systems and the chemical shift of the acetyl protons was recorded.

Solvent System	-CO-CH <sub>3</sub> in c.p.s.
Neat	148
Chloroform	156
Benzene	126
Pyridine	151
Aniline	129
t-Butylamine	152
Triethylamine	148
10% t-Butylamine/benzene	129
10% Aniline/benzene	129
10% Benzylamine/chloroform	152
10% Benzene/chloroform	151

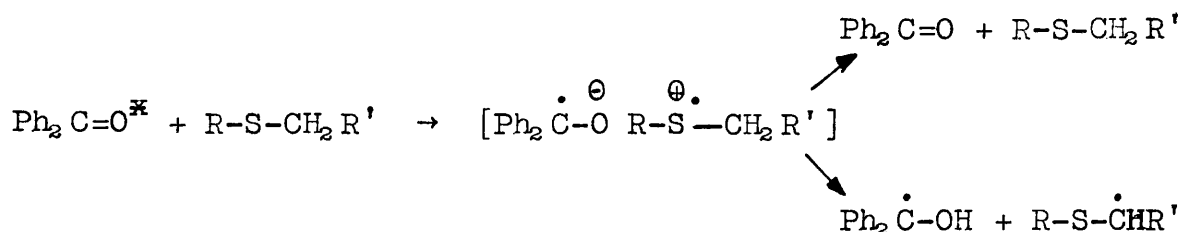
The results show that only aromatic solvents have any marked effect on the chemical shift of the acetyl protons. From this it can be concluded that solvation of the carbonyl group by aromatic rings is more favourable than by amine groups in the ground state. If preferential solvation by the amino group did occur, the activation energy for photoreduction would be decreased which could account in part for the greater reactivity of the amines.

The evidence presented here indicates that photoreduction by amines proceeds by an initial fast interaction of the non-bonding electrons of the nitrogen with excited ketone with which physical quenchers compete ineffectively. This is followed by proton transfer and electron redistribution to give the radicals which account for the observed products. With amines of low ionisation potential, the charge transfer complex formed by this electronic interaction may dissociate into radical ions if these can be stabilised by solvation. This was demonstrated by the formation of the tri-p-tolylamine radical cation in acetonitrile. In the case of primary, secondary and possibly tertiary aliphatic amines, where the ionisation potential is higher (sec.  $\text{BuNH}_2$  8.98eV,  $\text{Et}_2\text{NH}$  8.44eV  $\text{Et}_3\text{N}$  7.9eV<sup>90</sup> compared with 6.86eV for  $\text{Ph}_3\text{N}$ <sup>91</sup>) the intermediate probably takes the form of a charge transfer complex. Despite its low ionisation potential (7.14eV)<sup>90</sup> NN-dimethylaniline did not give rise to the radical cation upon flash photolysis with benzophenone in acetonitrile. This is probably due to the proton transfer step being very fast and competing effectively with the dissociation into solvated radical ions. In the case of amines of high ionisation potential there is the possibility that photoreduction of benzophenone does not involve formation of an intermediate but a transition state in which some electron transfer and breaking of the  $\alpha$  C-H bond occurs. Comparision of the quenching abilities of naphthalene upon reduction of benzophenone by n-butylamine (ionisation potential 9.19eV)<sup>90</sup> and NN-dimethylaniline (ionisation potential 7.14eV)<sup>90</sup> shows that the  $\frac{k_q}{k_r}$  values are 32.8

and 4.5 respectively. If such a transition state is formed in the former case it will have considerable triplet benzophenone character and thus naphthalene would be a more efficient quencher.

Further Studies of Quenching by Electron Transfer.

In addition to various quenching studies previously mentioned which are believed to involve electron transfer, aliphatic sulphides have also been shown to be physical quenchers of excited benzophenone whilst simultaneously acting as weak reducing agents<sup>92</sup>. It is postulated that the non-bonding electrons on the sulphur interact with the excited ketone leading to a complex of the two species which can react in two ways. It can either breakdown to give ground state reactants leading to quenching or transfer hydrogen to the ketone leading to photoreduction.



Intramolecular interaction of an excited carbonyl group with a phosphorus atom has also been postulated to explain the observed photorearrangement of dimethyl- $\beta$ -ketoethylphosphites to dimethylvinylphosphates<sup>93</sup>. Previous attempts to photoreduce methylphenylsulphide and dimethylphenylphosphine with benzophenone were unsuccessful so the reactions of trivalent phosphorus compounds with excited carbonyl groups was studied since complex and radical ion formation may occur as they do in the photoreductions by amines.

The effect of triphenylphosphine and trimethylphosphite

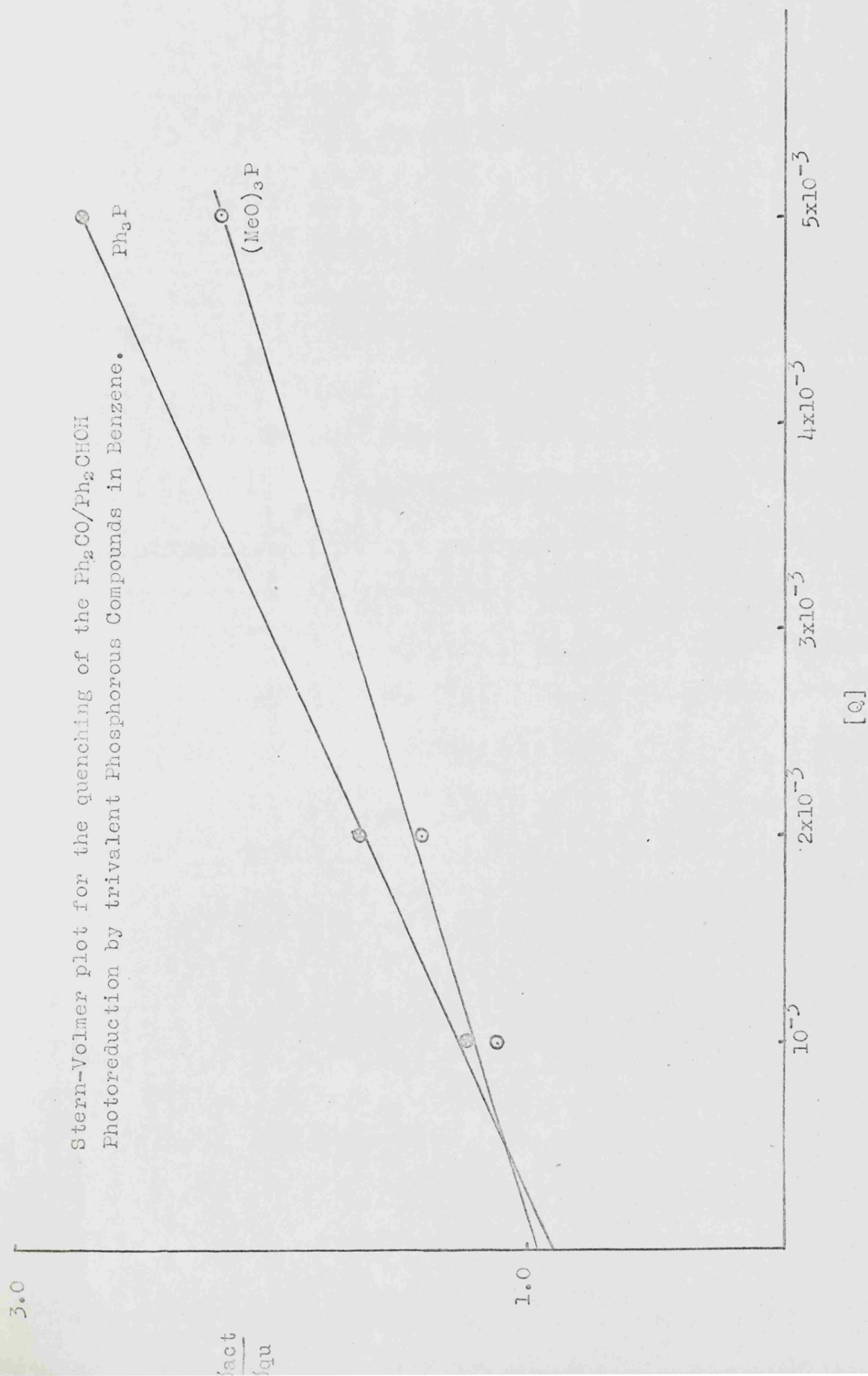
upon the photoreduction of benzophenone by benzhydrol was investigated. The method of investigation was the same as previous studies on the quenching of the same photoreduction by triphenylamine and tri-p-tolylamine. The values obtained from the slope of the Stern-Volmer plots for the ratio  $\frac{k_q}{k_r}$

are shown in the following table.

Triphenylphosphine in benzene	41
Triphenylphosphine in acetonitrile	35
Trimethylphosphite in benzene	26
Trimethylphosphite in acetonitrile	29

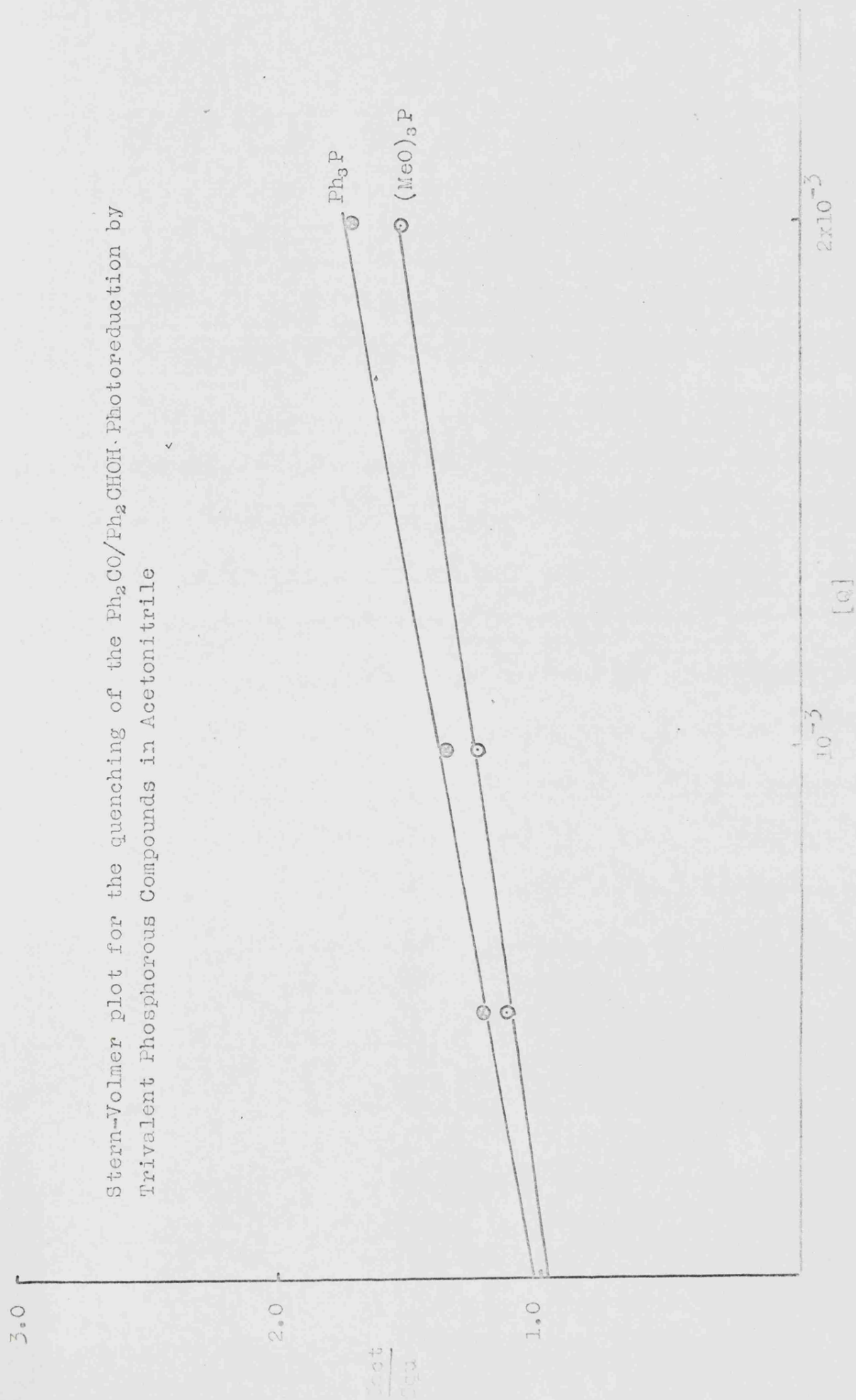
These results show that both trivalent phosphorus compounds quench excited benzophenone the efficiency of triphenylphosphine being about equal to that of triphenylamine, but change of solvent has little effect. This last result contrasts strongly with quenching by triphenylamine. The ionisation potential of triphenylphosphine is 7.36eV compared with 6.86eV for triphenylamine<sup>9,1</sup> so that any complex formed in the phosphorus case may be less able to dissociate into radical ions, or the ability of the solvent to stabilise the triphenylphosphine radical cation may be less than the triphenylamine radical cation thus accounting for the different solvent effect.

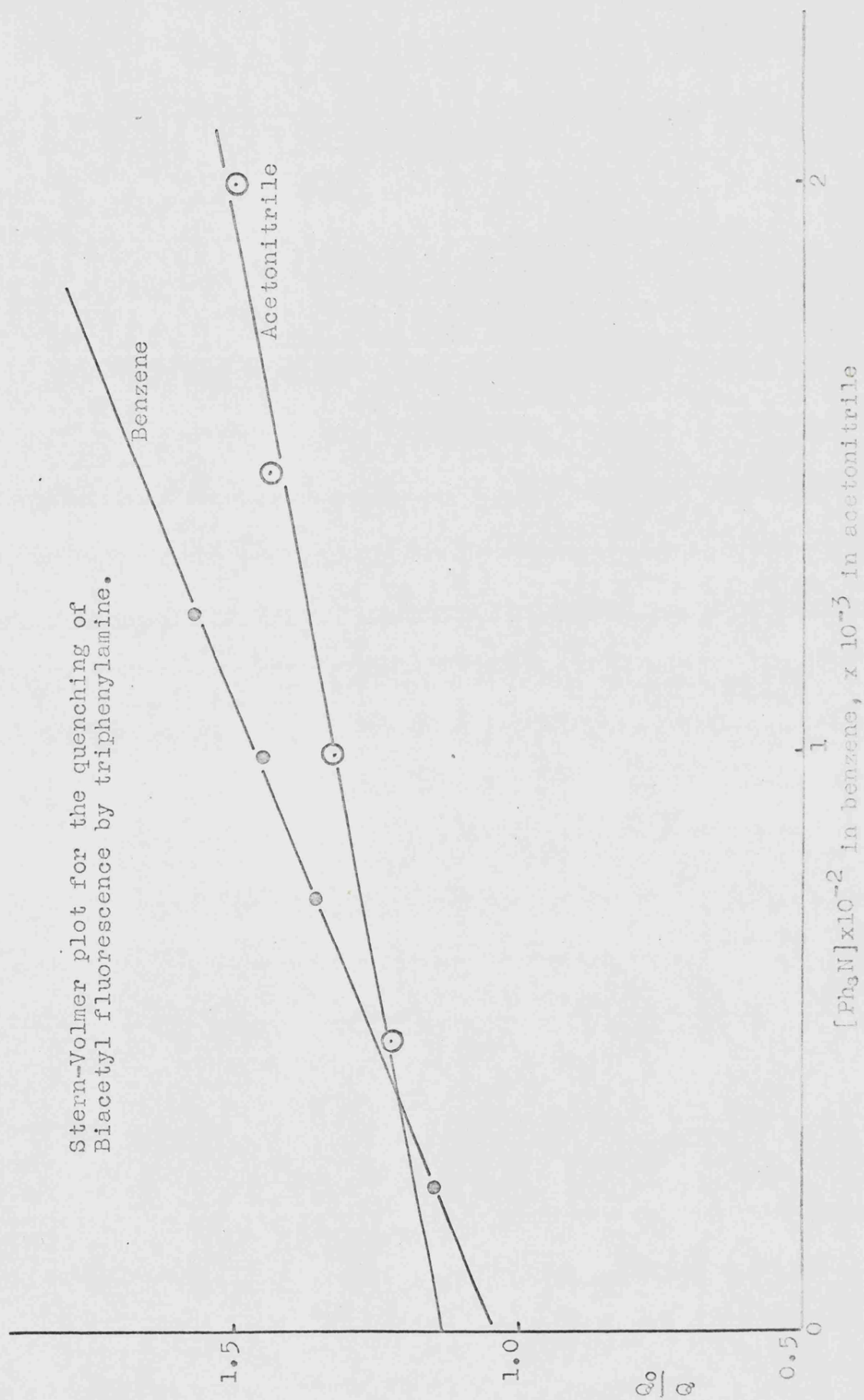
The effect of various compounds on the  $n \rightarrow \pi^*$  singlet excited state was investigated by studying the quenching of the fluorescence of biacetyl and fluorenone, and on the  $\pi \rightarrow \pi^*$  singlet excited state using anthracene. Solutions were made up using nitrogen bubbled solvents and the fluorescence spectra were obtained in the presence of varying concentrations of quencher. Most quenchers

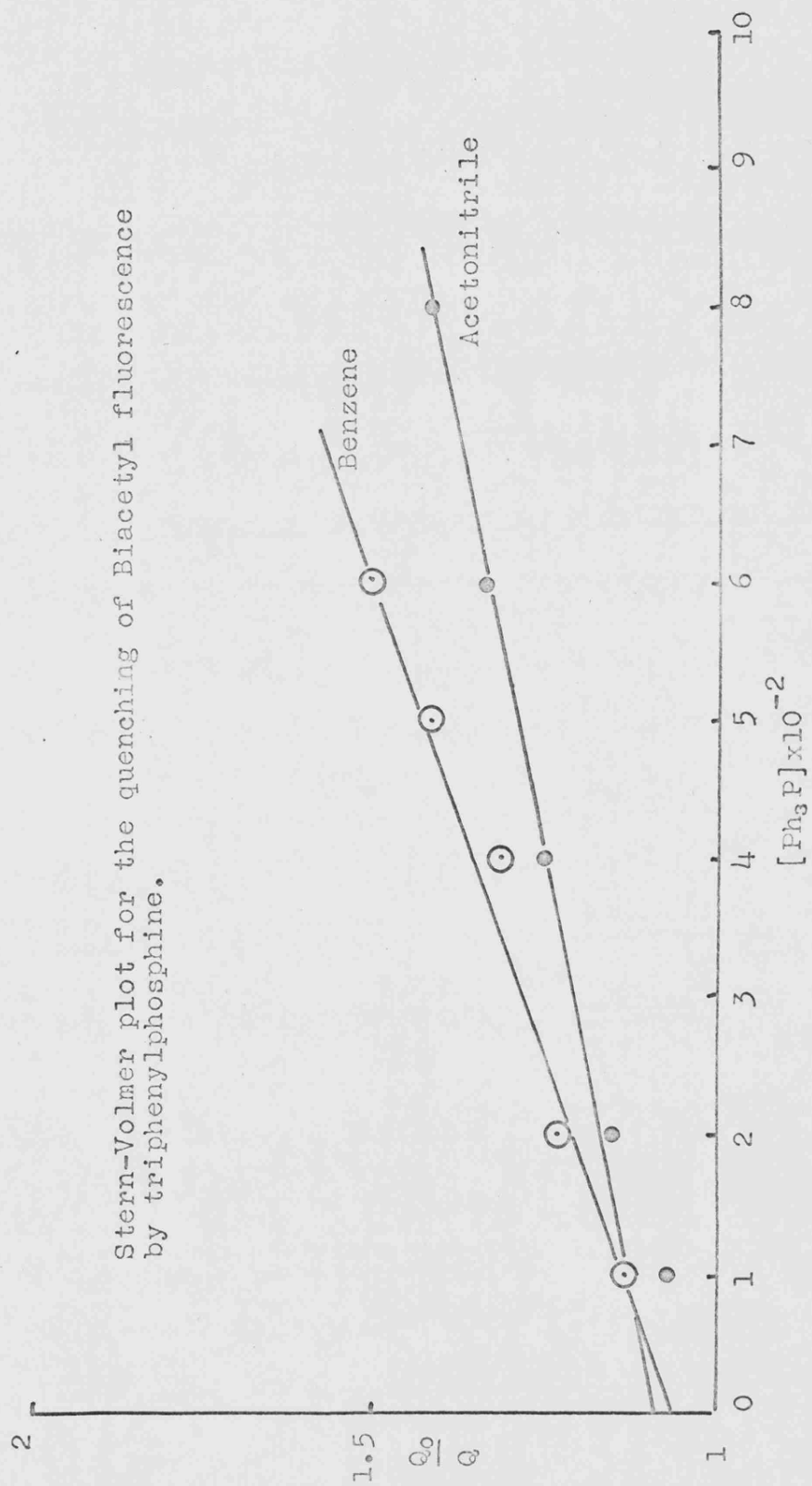




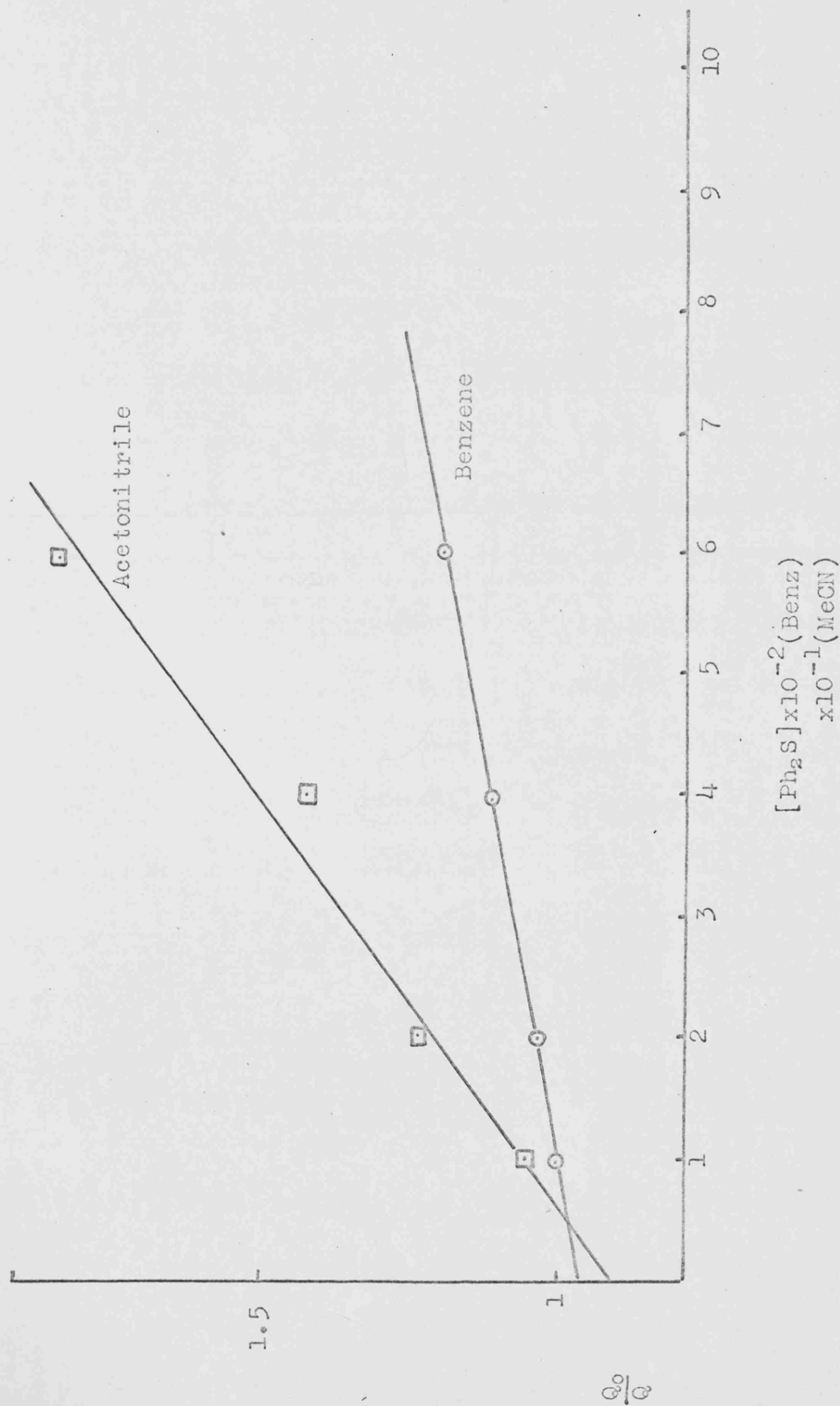
Stern-Volmer plot for the quenching of the  $\text{Ph}_2\text{CO}/\text{Ph}_2\text{CHOH}$  Photoreduction by  
Trivalent Phosphorous Compounds in Acetonitrile

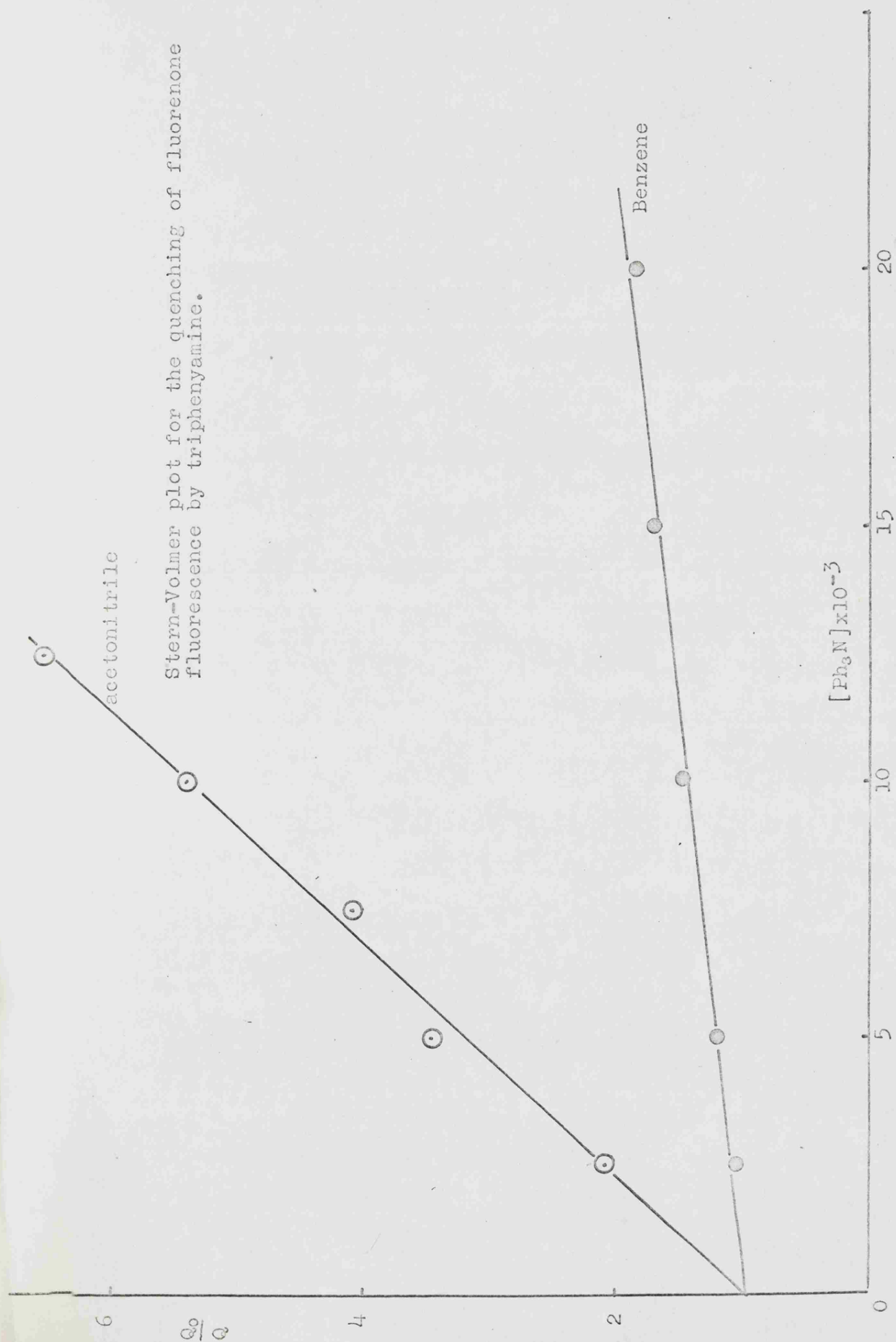


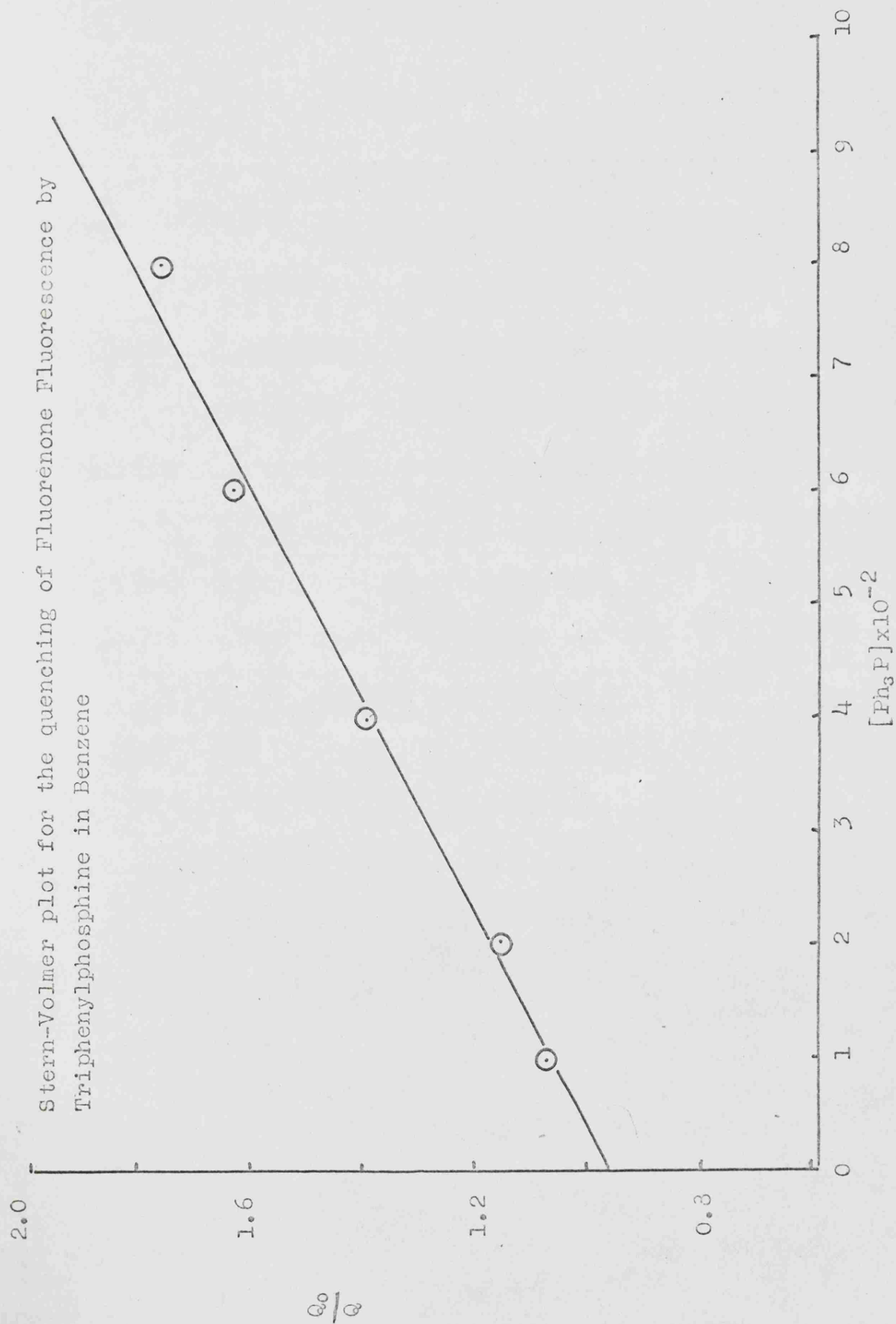


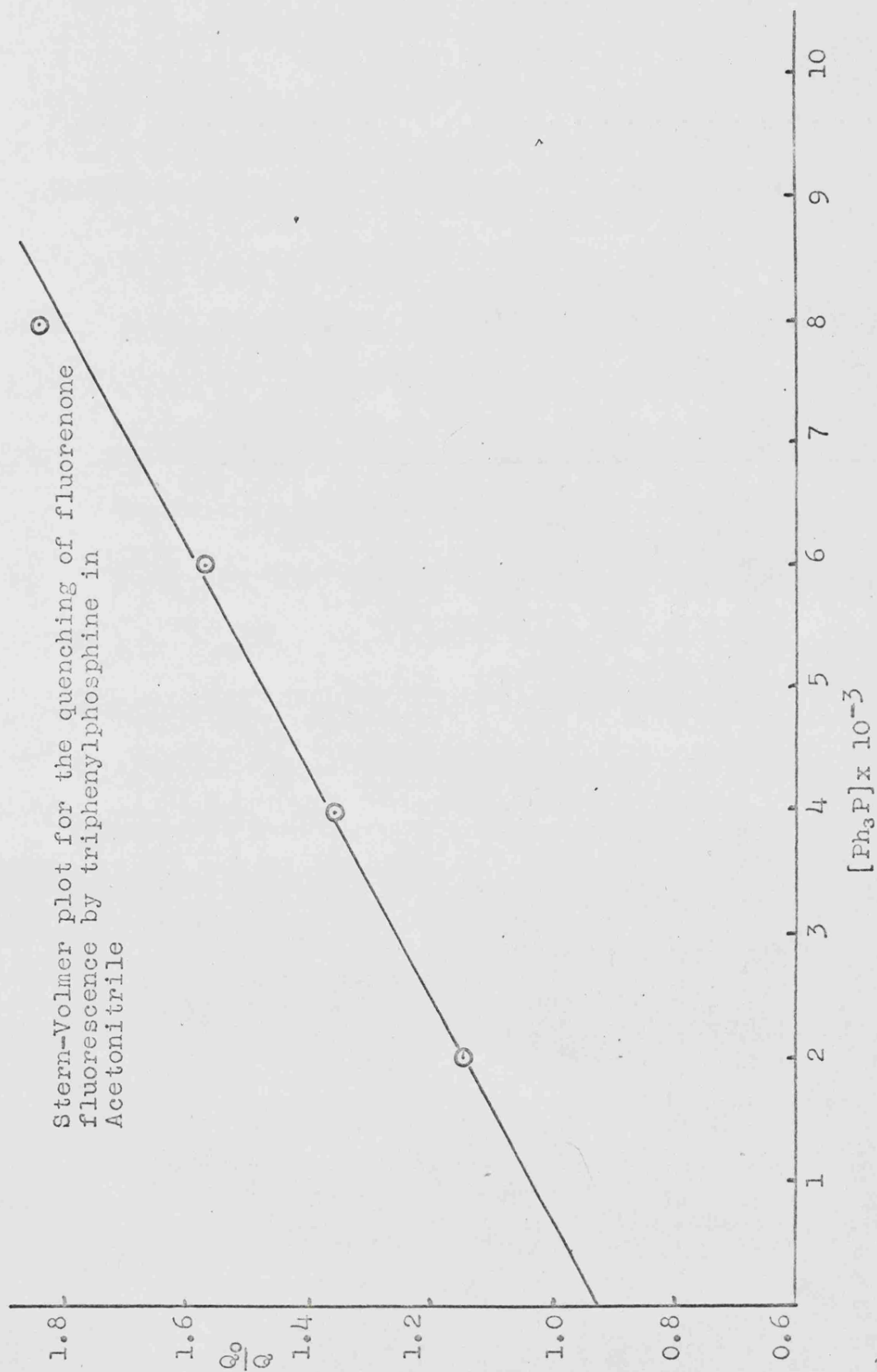


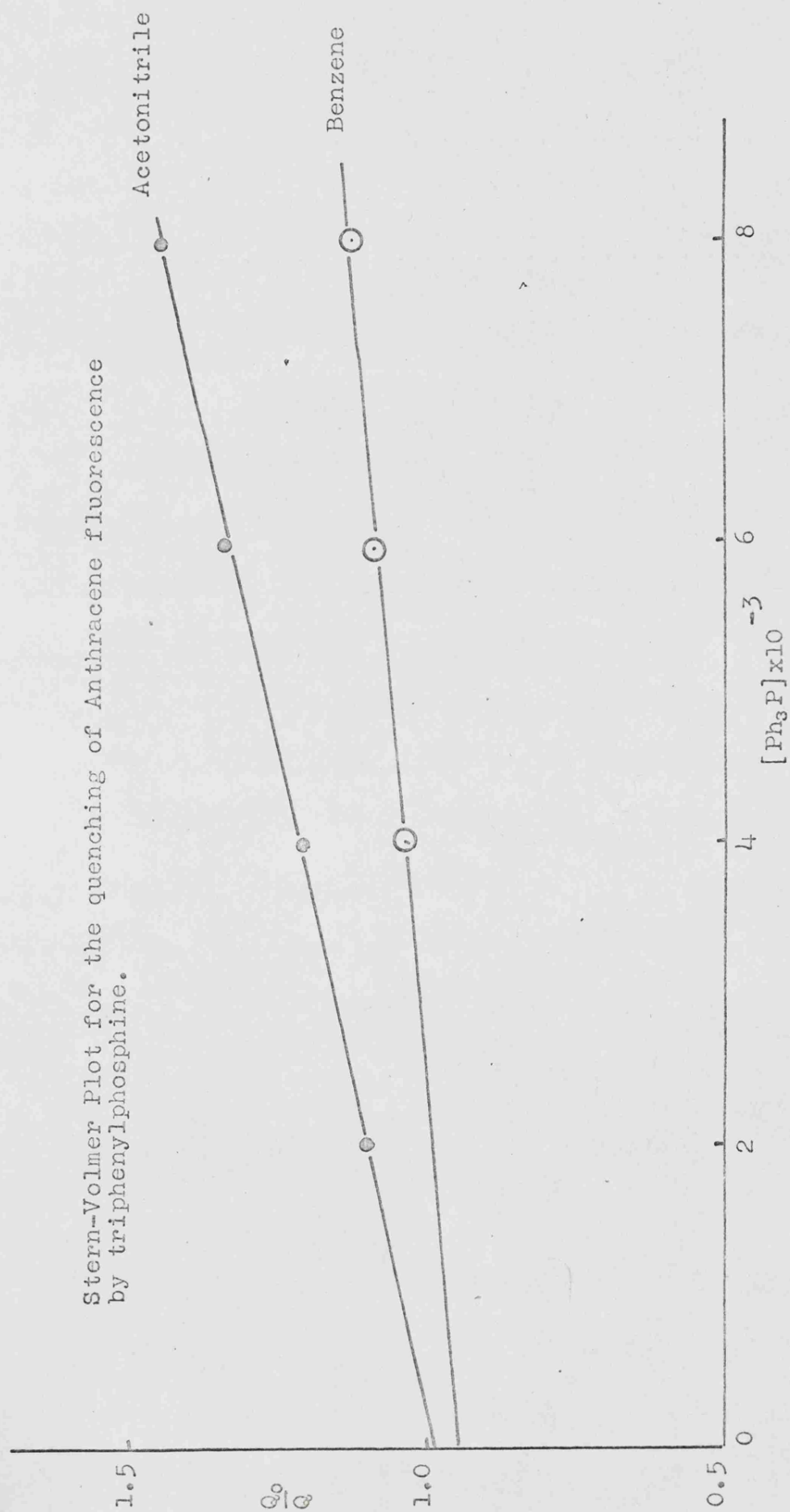
Stern-Volmer Plot for the quenching of Biacetyl fluorescence by Phenyl Sulphide



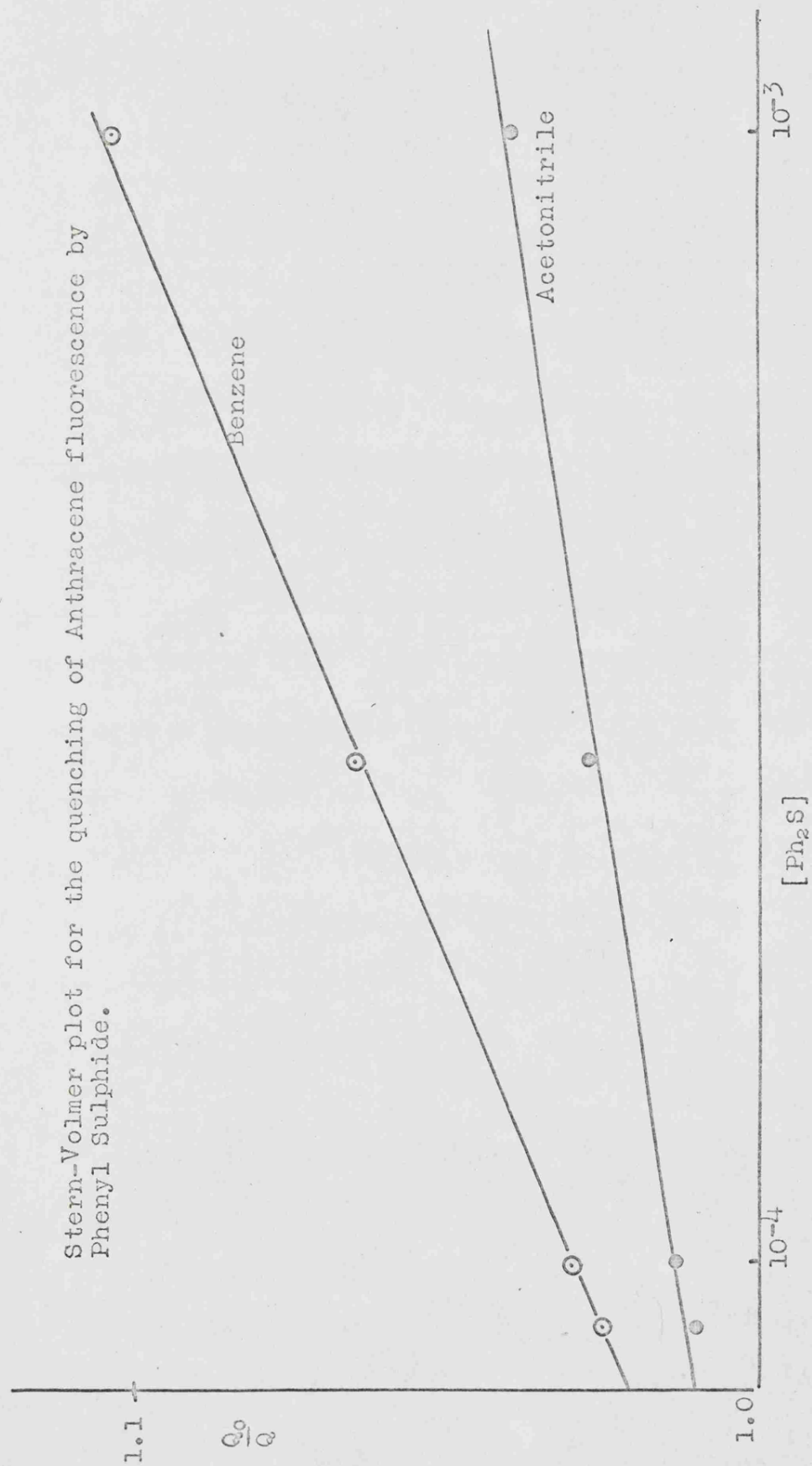












obey the Stern-Volmer equation:

$$\frac{Q_0}{Q} = 1 + K_q C$$

where:  $Q_0$  = efficiency of fluorescence without quencher.

$Q$  = efficiency of fluorescence with quencher

concentration  $c$  moles  $l^{-1}$ .

$$K_q = \frac{k_q}{k_d} \text{ and is the Stern-Volmer quenching constant}$$

( $k_q$  = bimolecular quenching rate constant and

$k_d$  = sum of unimolecular decay rate constants.

From this relationship, a plot of  $\frac{Q_0}{Q}$  versus quencher

concentration  $C$  should give a straight line of slope  $K_q$ .

The values obtained for  $K_q$  with a number of quenchers and fluorescers are shown in the following table.

Fluorescer and $\lambda_{\max}$ of fluorescence	Quencher	Solvent	$K_q (M^{-1})$
Biacetyl (382nm)	$Ph_3N$	Benzene	41
		Acetonitrile	202
	$Ph_3P$	Benzene	7
		Acetonitrile	4
	$Ph_2S$	Benzene	3.8
		Acetonitrile	1.5
Fluorenone (491nm in benzene, 515nm in MeCN)	$Ph_3N$	Benzene	45
		Acetonitrile	440
	$Ph_3P$	Benzene	11
		Acetonitrile	110

Anthracene (411nm in benzene, 407nm in MeCN)	$\text{Ph}_3\text{P}$	Benzene	21.5
		Acetonitrile	58
	$\text{Ph}_2\text{S}$	Benzene	83
		Acetonitrile	31
	$\text{PhCH}_2\text{SMe}$	Benzene	0
		Acetonitrile	0
	nBuSMe	Benzene	0
		Acetonitrile	0

The relative quantum yields of fluorescence of anthracene in benzene and acetonitrile were determined by the method of Parker<sup>6</sup> using a solution of quinine sulphate in 0.1N sulphuric acid as a standard. The concentration of the standard solution was such that its absorbance was the same as a  $10^{-5}\text{M}$  anthracene solution in benzene or acetonitrile, the concentration used for the quenching experiments. Since the conditions were identical in each measurement, the ratio of the areas under the fluorescence curves was the ratio of the quantum yields. Taking the quantum yield of fluorescence of quinine sulphate in 0.1N sulphuric acid as 0.55<sup>6</sup> the results were;

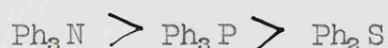
$$\phi_{\text{Benzene}} = 0.25$$

$$\phi_{\text{acetonitrile}} = 0.28$$

Parker quotes a value of 0.24 for the absolute quantum yield of fluorescence of anthracene in benzene based on the same standard.

Inspection of the results shows that the efficiency of quenching of the  $n\rightarrow\pi^*$  singlet state of biacetyl is in the order

one would expect if the non-bonding electrons were involved since it parallels the order of ease of removal of an electron i.e.



Only in the case of triphenylamine was there any enhancement upon change of solvent. In contrast, quenching of fluorenone fluorescence by both triphenylamine and triphenylphosphine showed evidence of radical ion formation in acetonitrile. This is probably due to the far greater stability of the fluorenone radical anion. Studies on the quenching of anthracene fluorescence yielded rather confusing results. Quenching by triphenylamine could not be studied due to it absorbing in the region required for excitation of the anthracene. The increase in efficiency of quenching by triphenylphosphine upon change of solvent suggested that radical ion formation may be taking place but flash photolysis of a solution of triphenylphosphine and anthracene in acetonitrile showed the formation of only triplet anthracene. Surprisingly, phenyl sulphide showed a higher quenching efficiency than triphenylphosphine despite the fact that it probably has a higher ionisation potential. Benzylmethyl sulphide and n-butylmethylsulphides had no quenching action on anthracene fluorescence, probably due to their high ionisation potential. Such a finding contrasts with that of Cohen and Guttenplan<sup>9,2</sup> who found that the efficiency with which sulphides quenched triplet benzophenone was



Such an order is not in accordance with the expected order based on the ionisation potentials of the above sulphides. The efficiency of quenching in the systems studied with the exception of anthracene, is related to the ionisation potential of the quencher, although radical ion formation only occurs when the electron donor has a low ionisation potential and solvation of the highly polar ions is efficient enough to stabilise them. In other cases, quenching occurs by the formation of an excited charge transfer complex.

Photoreduction of Fluorenone and Benzophenone by Amines in  
Alcoholic or Aqueous Media.

Introduction

Fluorenone is not photoreduced by alcohols or alkanes because the lowest triplet state is of the  $\pi \rightarrow \pi^*$  type which is not efficient as a hydrogen abstractor as previously mentioned. Fluorenone is photoreduced by amines<sup>3,4</sup> and the quantum yield of fluorenone disappearance for a selection of amines is shown in the following table.

Amine	$\phi$
2-BuNH <sub>2</sub>	0.04
0.1M 2-BuNH <sub>2</sub> in cyclohexane	0.02
2-BuNHMe	0.05
0.08M 2-BuNHMe in cyclohexane	0.13
Et <sub>3</sub> N	0.094
0.198M Et <sub>3</sub> N in cyclohexane	0.92

Dilution of triethylamine with cyclohexane to 0.2M increased the quantum yield ten-fold. Further dilution caused it to decrease slightly. This increase on dilution has been attributed to quenching of fluorenone singlets by triethylamine at concentrations  $> 0.2M$ , probably in a diffusion controlled manner<sup>3,4</sup>. In more dilute cyclohexane solution, photoreduction takes place from the lowest triplet level since quenching by trans-stilbene is observed  $\frac{k_q}{k_r} = 140$ , and it was suggested that if the first stage of

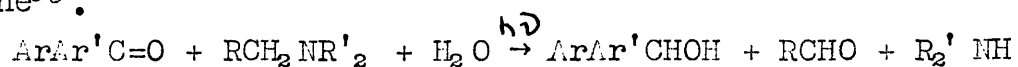
the reaction consists of an electron transfer from the amine to the excited fluorenone, the singlet ion-pair can back donate giving ground state reactants and resulting in quenching. In the triplet state, this would be a spin forbidden process and a slower hydrogen abstraction to form the radicals could then compete with quenching. It was also suggested that as the polarity of the medium increases, the  $\pi \rightarrow \pi^*$  levels drop and the  $n \rightarrow \pi^*$  level rises in energy<sup>95</sup> leading to the following dispositions.

<u>Non Polar</u>		<u>Polar</u>	
<u>Singlet</u>	<u>Triplet</u>	<u>Singlet</u>	<u>Triplet</u>
$\pi \rightarrow \pi^*$ _____		$\pi \rightarrow \pi^*$ _____	
	_____ $\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$ _____	
$n \rightarrow \pi^*$ _____			_____ $n \rightarrow \pi^*$
$\pi \rightarrow \pi^*$ _____			_____ $\pi \rightarrow \pi^*$
	_____ $n \rightarrow \pi^*$		
		$\pi \rightarrow \pi^*$ _____	
	_____ $\pi \rightarrow \pi^*$		
			_____ $\pi \rightarrow \pi^*$

Since intersystem crossing in aromatic ketones is more efficient when involving states of different electronic configuration<sup>12</sup> as the polarity of the solvent increases, the lowest triplet will have increasing  $\pi \rightarrow \pi^*$  character and photoreduction will be suppressed. This also accounts for the retardation of the photoreduction upon dilution

with acetonitrile and methanol. Cohen<sup>96</sup> has suggested that intersystem crossing is less efficient in polar solvents. Primary, secondary and tertiary amines containing  $\alpha$ -C-H bonds also photoreduce fluorenone in benzene and acetonitrile solutions producing fluoropinacol and 9-hydroxyfluorene, the latter probably occurring by thermal cleavage of the pinacol<sup>97</sup>. Studies on fluorescence quenching by amines showed that the quenching efficiency varied inversely with the ionisation potential of the amine and was greater in acetonitrile. This suggests that quenching occurs by an electron transfer process. Comparison of the rate of fluorescence quenching with the rate of photoreduction by triethylamine shows that the former is more efficient. Calculations show that only 32% of fluorescence quenching can be attributed to deactivation to the ground state so the other 68% must be due to singlet reaction or crossing to the triplet state induced by collision with the amine.

Photoreduction of 4-benzoylbenzoic acid by primary and tertiary amines in aqueous media gives the appropriate diarylcarbinol and products of oxidative cleavage of the amine<sup>98</sup>.



No difference in rate was observed when  $\text{D}_2\text{O}$  was used indicating that the N - H bond of the primary amine was not broken in a rate determining step. In benzene solution, reduction of 4-benzoylbenzoic acid was much less efficient due to the build up of a light absorbing transient. The aqueous medium is thought to enhance the previously mentioned electron transfer step, thus conferring increased reactivity over the use of benzene as



solvent. The formation of absorbing intermediates in the case of secondary and tertiary amines makes a kinetic study in benzene solution impossible except in the case of primary amines. This problem can be overcome by reducing 4-benzoylbenzoic acid in aqueous media where none of the classes of amines forms such an intermediate<sup>99</sup>. The results are given in the following table.

Ketone	Amine	$\frac{k_d}{k_{ir}} M$	$\frac{k_q}{k_{ir}}$	$k_{ir} M^{-1} sec^{-1}$	$k_d sec^{-1}$
BCO <sub>2</sub> H	2-BuNH <sub>2</sub>	0.103	44	$6.3 \times 10^7$	$6.4 \times 10^6$
BCO <sub>2</sub> H	2-BuNHMe	0.03	16	$1.6 \times 10^8$	$4.8 \times 10^6$
BCO <sub>2</sub> H	2-BuNMe <sub>2</sub>	0.011	2.7	$9.4 \times 10^8$	$10.2 \times 10^6$
BCO <sub>2</sub> H	Et <sub>3</sub> N	0.021	4.2	$6.0 \times 10^8$	$12.7 \times 10^6$
BCO <sub>2</sub> H	2-PrOH	1.65	1730	$1.7 \times 10^6$	$2.8 \times 10^6$
B	2-PrOH	0.102	2020	$1.4 \times 10^6$	$1.5 \times 10^5$

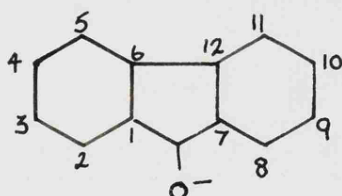
Photoreduction of 0.10M 4-benzoylbenzoate Anion, BCO<sub>2</sub><sup>⊖</sup> and Benzophenone, B in 0.12N NaOH in 1:1 Water-Pyridine.

Values of  $k_{ir}$  (the rate of interaction of the ketone triplet with the amine) rise in the order primary < secondary < tertiary and it is suggested that the interaction may be essentially diffusion controlled. This supports the theory of an initial charge transfer interaction since the order of reactivity is that of decreasing ionisation potentials of the amines. Values of  $\frac{k_q}{k_r}$

were obtained using naphthalene as a quencher.

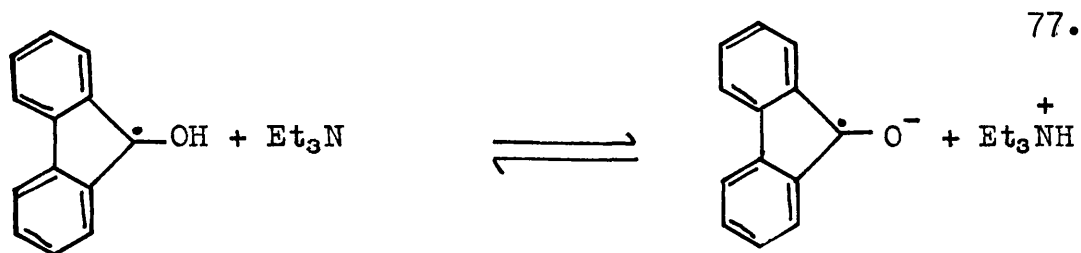
### Results and Discussion

As has previously been mentioned, photoreduction of fluorenone in benzene by triethylamine gave the 9-hydroxyfluorene radical which was characterised by its paramagnetic resonance spectrum. Change of solvent to ethanolic or aqueous triethylamine gave asymmetric spectra. Analysis of the spectrum obtained by photolysing fluorenone in ethanol containing 1.25 - 10% amine showed that both the 9-hydroxyfluorene radical and the fluorenone radical anion were being formed. Calculated values of the isotropic hyperfine coupling constants for the radical anion agreed well with these obtained by the photolysis of fluorenone in ethanol containing sodium ethoxide as the following table shows.

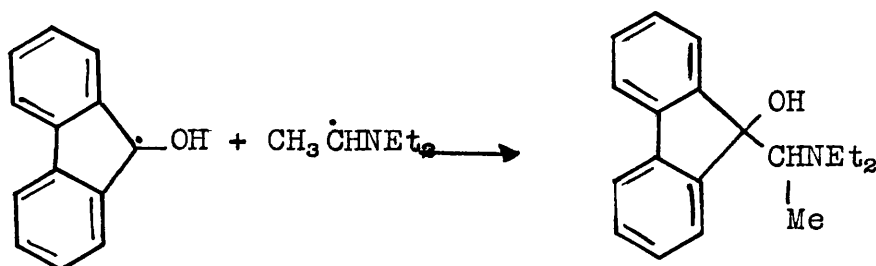


	$a_2 = a_8$	$a_3 = a_9$	$a_4 = a_{10}$	$a_5 = a_{11}$
Fluorenone /Et <sub>3</sub> N/EtOH	2.59G	0.40G	3.33G	0.73G
Fluorenone /NaOEt/EtOH <sup>100</sup>	2.61G	0.38G	3.34G	0.73G

Since triethylamine is a strong base,  $pK_b 3.24$ , it is possible that the 9-hydroxyfluorene radical is ionised in its presence, although it cannot be ruled out that the radical anion may be produced directly by electron transfer from the amine to the excited ketone.



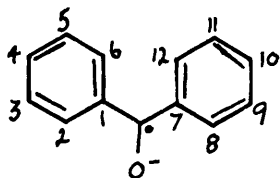
In general, reactions which involve the formation of ketyl radicals give pinacol and those which involve the formation of ketyl radical anions give secondary alcohols. The photoreduction of fluorenone was performed under a variety of conditions and the products of the reaction are summarised in the following table. The mixed product refers to 9-hydroxy-9- (NN-diethyl-1-methylethylamino) -fluorene formed by cross-coupling of the 9-hydroxyfluorene and NN-diethylamino-1-ethyl-radicals.



Reducing Medium.	Fluorenol.	Pinacol.	Mixed.
Et <sub>3</sub> N/EtOH (1:1)	31%	28%	10%
Et <sub>3</sub> N/H <sub>2</sub> O (1:1)	29%		21%
Et <sub>3</sub> N/EtOH/H <sub>2</sub> O (7:2:7:)	31%		
Et <sub>3</sub> N/iPrOH	14%	5%	17%

Photoreduction of benzophenone in aqueous isobutylamine and ethanolic t-butylamine also gave the benzophenone ketyl

radical anion probably by a similar mechanism to that occurring in the fluorenone case. The anion was characterised by its electron paramagnetic resonance spectrum, the proton coupling constants being given in the following table.



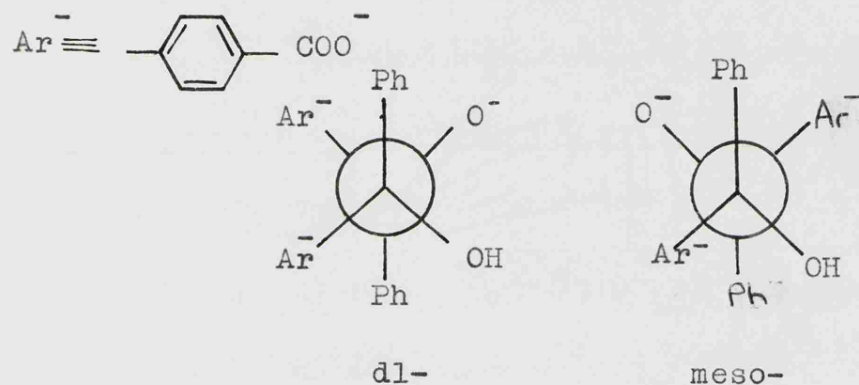
	$a_2 = a_6 = a_8 = a_{12}$	$a_3 = a_5 = a_9 = a_{11}$	$a_4 = a_{10}$
$\text{Ph}_2\text{CO}/\text{isoBuNH}_2/\text{H}_2\text{O}$	2.81G	1.02G	3.50G
$\text{Ph}_2\text{CO}/\text{tBuNH}_2/\text{EtOH}$	2.82G	1.02G	3.45G
$\text{Ph}_2\text{CO}/\text{NaOEt}/\text{EtOH}^{100}$	2.80G	1.03G	3.46G

In an analogous manner to the fluorenone case and the observations of Cohen<sup>98</sup>, the photoreduction of benzophenone under these conditions should give rise to benzhydrol. The experiments were repeated on a preparative scale and the results are summarised in the following table together with those for the photoreduction p-phenylbenzophenone and  $\beta$ -acetylnaphthalene under similar conditions.

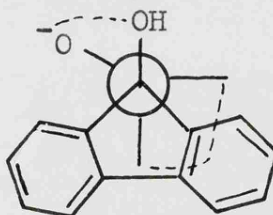
Ketone	Reducing Medium	Hydrol	Pinsol
Benzophenone	$\text{Et}_3\text{N}/\text{EtOH}$ (1:1)	8%	61%
	$\text{nBuNH}_2/\text{H}_2\text{O}$ (1:1)		50%
	$\text{secBuNH}_2/\text{H}_2\text{O}$ (2:3)		73%
p-Phenylbenzophenone	$\text{Et}_3\text{N}/\text{EtOH}$ (1:1)		30%
	$\text{Et}_3\text{N}/\text{H}_2\text{O}$ (1:1)		31%
$\beta$ -Acetylnaphthalene	$\text{Et}_3\text{N}/\text{EtOH}$ (1:1)		38%



In the cases under consideration here, the benzophenone pinacol anion can be stabilised by hydrogen bonding as in the dl-form shown above so equilibrium will lie on the side of pinacol formation. In basic solution 4-benzoylbenzoic acid will be present as the anion so path one would lead to a pinacol anion in which the meso form would have adjacent negative charges and the dl-form would require the overlap of the aryl groups, if hydrogen bond formation was present. Thus both isomers are unstable and path 2 is more likely to be followed producing secondary alcohol.



The production of the fluorenone pinacol monoanion is hindered since hydrogen bond formation would entail eclipsing of the bulky fluorenyl residues to a certain degree.



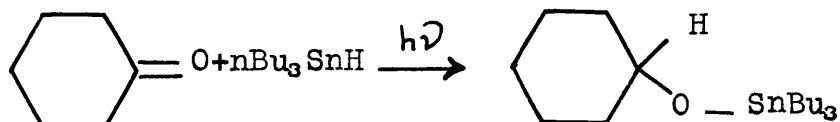
This, and the fact that the fluorenone radical anion is very stable<sup>75</sup> favour the following of pathway 2 and formation of secondary alcohol.



Photoreduction by Tin Alkyls.

Aromatic carbonyl compounds whose lowest triplet state is of the  $\pi \rightarrow \pi^*$  type and which are not photoreduced by alcohols can be photoreduced if tri-n-butylstannane is used as the hydrogen donor. It was shown by Hammond and Leermakers<sup>31</sup> that photoreduction of 1-naphthaldehyde and 2-acetylnaphthalene by tri-n-butylstannane probably occurred by way of the triplet state producing 1-naphthylcarbinol and the pinacol in the case of 1-naphthaldehyde and methyl-2-naphthylcarbinol from the 2-acetylnaphthalene. The tributyl tin radicals were assumed to couple. The greater reactivity of the tin hydride as a hydrogen donor compared with isopropanol was attributed to the weak tin-hydrogen bond and the possible formation of a charge transfer complex. This was envisaged as partial transfer of the excited  $\pi^*$  electron from the carbonyl group to the tin atom. That triplet ketone was involved in the photoreduction of 2-acetylnaphthalene by tri-n-butylstannane was shown by Bryce and Wells<sup>102</sup> who obtained its absorption spectrum ( $\lambda_{\text{max}}$  430 nm) and studied the kinetics of its decay. Quenching of the reaction by 1-naphthol was attributed to triplet-triplet energy transfer. Wagner<sup>44</sup> has used the stannane to demonstrate that the lowest triplet state of acetone is much more efficient at abstracting hydrogen than the lowest excited singlet state. Fluorenone is also photoreduced by tri-n-butylstannane to fluoropinacol<sup>97</sup>, reaction occurring mainly from the triplet state since 1.0M stannane was only a weak quencher of fluorenone fluorescence at which concentration the quantum yield of photoreduction was 0.71. The addition of

tri-n-butylstannane to the carbonyl group upon irradiation of a 2:1 mixture of ketone and stannane has also been reported.<sup>103</sup>



In all cases studied, the corresponding alcohol was also formed by reduction of the ketone. Photoreduction of nitrobenzene and 1-nitronaphthalene also occurs upon irradiation with the stannane in benzene solution<sup>104</sup>. In the former case, hydrogen abstraction occurs from a short lived  $n \rightarrow \pi^*$  triplet state giving phenylhydroxylamine as the initial product. This undergoes a dark oxidation to nitrosobenzene which is converted into azoxybenzene. Photoreduction of 1-nitronaphthalene parallels that of 1-naphthaldehyde, occurring via a  $\pi \rightarrow \pi^*$  triplet and producing 1-naphthylamine.

Thermal reduction of carbonyl compounds by tin alkyls has been demonstrated<sup>105</sup>. Benzaldehyde is reduced to benzyl alcohol by reaction at 140°C for 15 hours.  $\alpha$ - $\beta$  Unsaturated ketones were reduced selectively to the  $\alpha$ - $\beta$  unsaturated alcohols.



### Results and Discussion.

The photoreduction of benzophenone, xanthone and fluorenone by tetra-*n*-butylstannane and tri-*n*-butylstannane was studied and the products are shown in the following table.

	$n\text{Bu}_4\text{Sn}$	$n\text{Bu}_3\text{SnH}$
Benzophenone	75% pinacol	85% pinacol
Xanthone	45% pinacol	45% mixture of pinacol and hydrol
Fluorenone	No reduction	56% pinacol

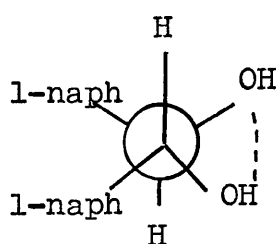
The relative efficiencies of tetra-*n*-butylstannane and tri-*n*-butylstannane compared with benzhydrol as sources of hydrogen for the photoreduction of benzophenone were ascertained by comparing the quantum yields of benzophenone disappearance in a similar manner to that employed when comparing the efficiencies of the amines earlier. The results obtained by comparing the slopes of the graphs shown overleaf show that the relative efficiencies are:

$$\begin{array}{ccccc} n\text{Bu}_4\text{Sn} & : & \text{Ph}_2\text{CHOH} & : & n\text{Bu}_3\text{SnH} \\ 0.41 & : & 1 & : & 2.1 \end{array}$$

The possibility of interaction between the tin atom and excited ketone was also investigated. In an analagous manner to the amine case, a tin alkyl which does not contain abstractable hydrogen, if added to the benzophenone-benzhydrol photoreduction should compete for excited carbonyl and quench the reaction if any complex formation occurs. Addition of 0.001M tetraphenylstannane had little effect

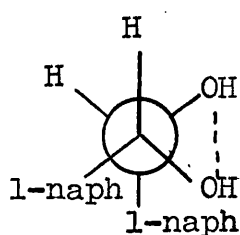
on the reaction rate. After one hour, 0.042 moles of benzophenone has been photolysed compared with 0.045 in the unquenched reaction. Comparison with triphenylamine at the same concentration showed that after one hour 0.031 moles of benzophenone had been consumed. This suggests that there is no interaction between the tin and the excited ketone and since both tetra-*n*-butyl and tri-*n*-butylstannane contain the same type of C-H bond the reactivity of the hydride as a hydrogen donor is due entirely to the weak tin-hydrogen bond.

The photoreduction of 1-naphthaldehyde by tri-*n*-butylstannane originally performed by Hammond<sup>31</sup> was repeated. Careful chromatography of the products obtained from photolysing 2:1 mixture of the stannane and 1-naphthaldehyde in benzene at 366 nm. gave two very similar compounds A and B in yields of 31% and 22%. Spectroscopic data showed that they were the *dl*- and *meso*- forms of the expected pinacol. Steric considerations predict that the *dl*- form will exhibit intramolecular hydrogen bonding since this will not entail eclipsing of the bulky 1-naphthyl groups as in I. For intramolecular hydrogen bonding to exist in the *meso*- form, the 1-naphthyl groups on adjacent carbon atoms will be in close proximity (II) so the isomer will exist in form III with no intramolecular hydrogen bonding.

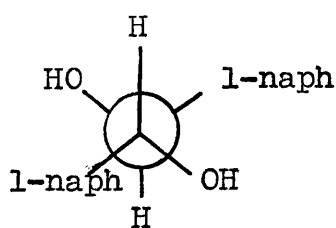


dl-

I

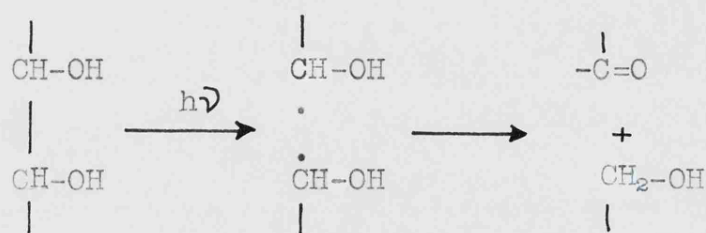


II



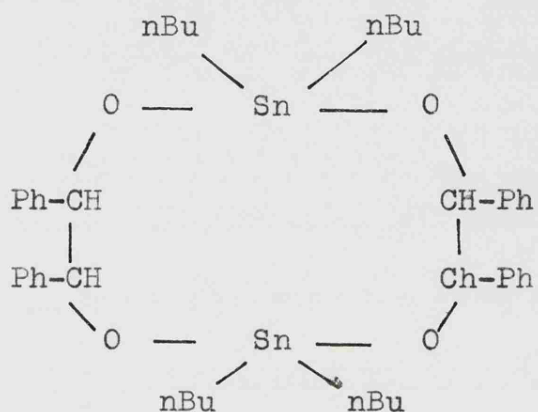
III

Inspection of the infra-red spectra show that A has a broad -OH stretching band centred at  $3460\text{ cm}^{-1}$  whilst B has a sharp peak at  $3540\text{ cm}^{-1}$ . The former is typical of hydrogen bonded hydroxyl groups therefore A is the dl- isomer and B is the meso form. Such an assignment is confirmed by examination of the proton magnetic resonance spectra, the resonance due to the hydroxyl proton of A occurring much further downfield ( $5.34\tau$ ) than that of B ( $7.0\tau$ ). Photolysis of a similar solution at 313 nm. was very slow, but on changing to a 100 watt mercury arc, 19% of the corresponding secondary alcohol, 1-naphthylcarbinol, and pinacol 13% of the dl- form and 31% of the meso- form were produced. The different products at higher energy could be due to the pinacol being formed as the initial photoproduct which is cleaved to give ketyl radicals. Disproportionation follows giving secondary alcohol and ketone.



Photoreduction of 2-acetylnaphthalene by tri-n-butylstannane at 366 nm. gave pinacol and 1-(2-naphthyl)-ethanol. This secondary alcohol must have come directly from the 2-acetylnaphthalene ketyl radical by abstraction of a second hydrogen since the pinacol does not absorb in the 366 nm. region. Contrary to the results of Calas<sup>103</sup> photoreduction of acetophenone by tri-n-butylstannane gave 1-phenylethanol and acetone was reduced to isopropanol. The great reactivity of the stannane as a hydrogen donor allows the initially

formed ketyl radical to abstract a second hydrogen as opposed to dimerising. Photoreduction of benzaldehyde gave no benzyl alcohol detectable by gas-liquid chromatography but instead a white crystalline solid was formed. The analytical and spectral datae are satisfied by the following structure:



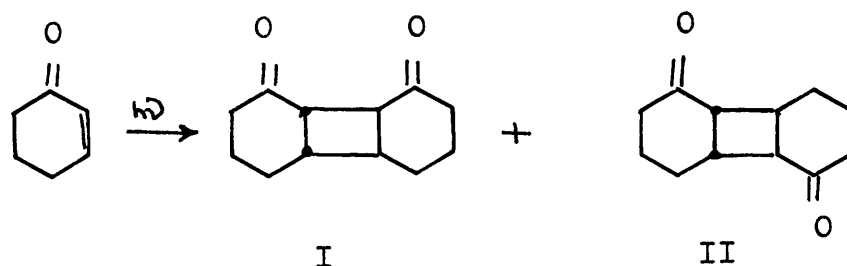
No satisfactory mechanism to account for the formation of the product could be formulated.

Photoreduction of  $\alpha$ - $\beta$  Unsaturated Ketones and Diketones.

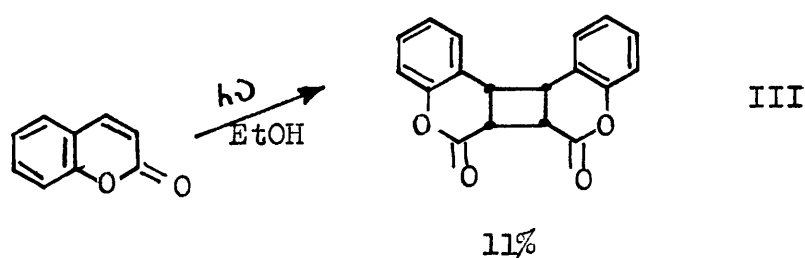
Introduction

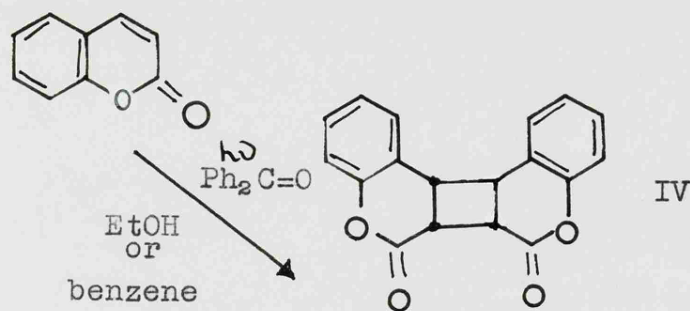
The photochemical dimerisation of  $\alpha$ - $\beta$ -unsaturated ketones and related compounds to give cyclobutane derivatives has been known a long time and the products obtained from such photodimerisations have been reviewed by Mustafa<sup>106</sup>.

Mechanistic studies on the photodimerisation of cyclopentenone<sup>107</sup> and cyclohexenone<sup>108</sup> showed that triplet enone attacks ground state enone forming a biradical and ring closure takes place to give mainly the trans head to head dimer (I) and the trans head to tail dimer (II).

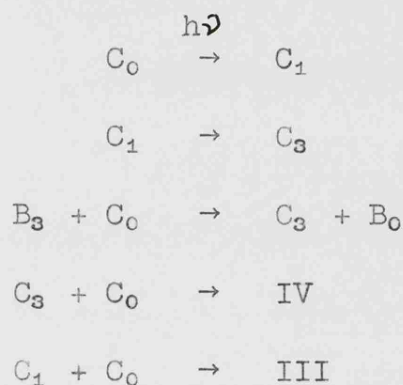


The photodimerisation of coumarin can proceed from either the singlet or the triplet state, the isomers formed depending on the multiplicity of the excited state involved. Direct photolysis in ethanol yields the head to head cis dimer (III)<sup>109</sup> but no reaction occurred in benzene<sup>110</sup>. Sensitisation of the reaction with benzophenone in both benzene and ethanolic solution produced predominantly the trans head to head dimer (IV)<sup>111</sup>.





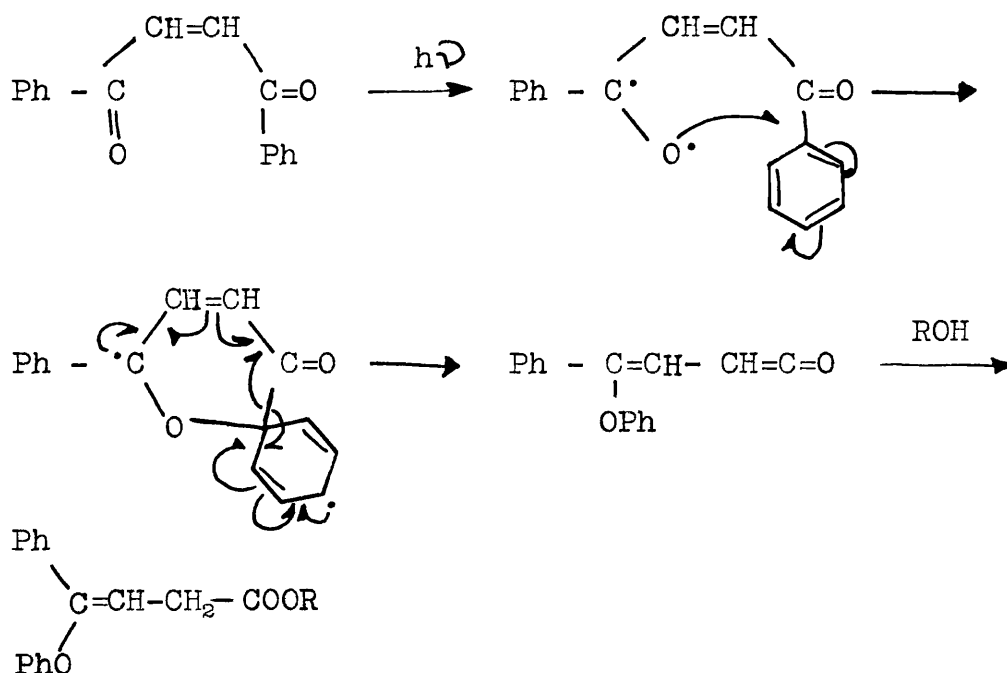
The following mechanism has been proposed<sup>111</sup>.



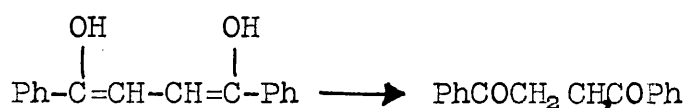
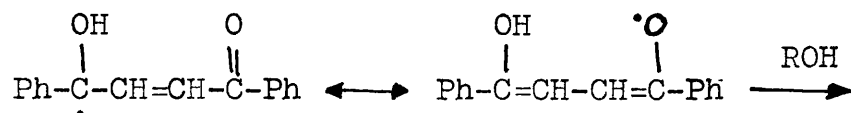
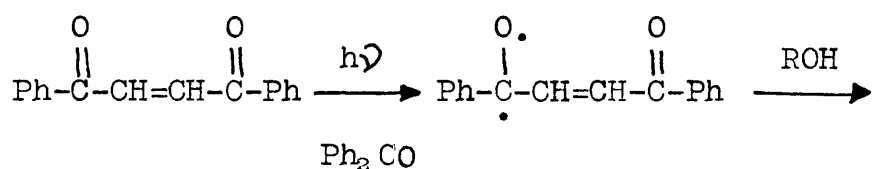
$C_{0 \rightarrow 3}$  refers to the various states of coumarin and  $B_0$  and  $B_3$  refer to ground and triplet state benzophenone. In non-polar solvents such as benzene,  $C_1$  is deactivated by self quenching. In polar solvents such as ethanol  $C_1$  reacts with  $C_0$  to produce the cis head to head dimer III. Energy transfer from triplet benzophenone takes place in both polar and non-polar solvents giving triplet coumarin and ultimately the trans head to head dimer IV. IV was also produced in the presence of benzophenone when >90% of the light was absorbed by the coumarin. This was believed to be due to the following process competing with deactivation. Singlet  $\rightarrow$  singlet energy transfer between  $C_1$  and  $B_1$  followed by intersystem crossing to give triplet benzophenone. Further energy transfer occurred giving triplet coumarin and ultimately IV. In dilute solution under

direct irradiation, coumarin singlets preferentially undergo intersystem crossing as opposed to the bimolecular dimerisation and IV is the product formed.

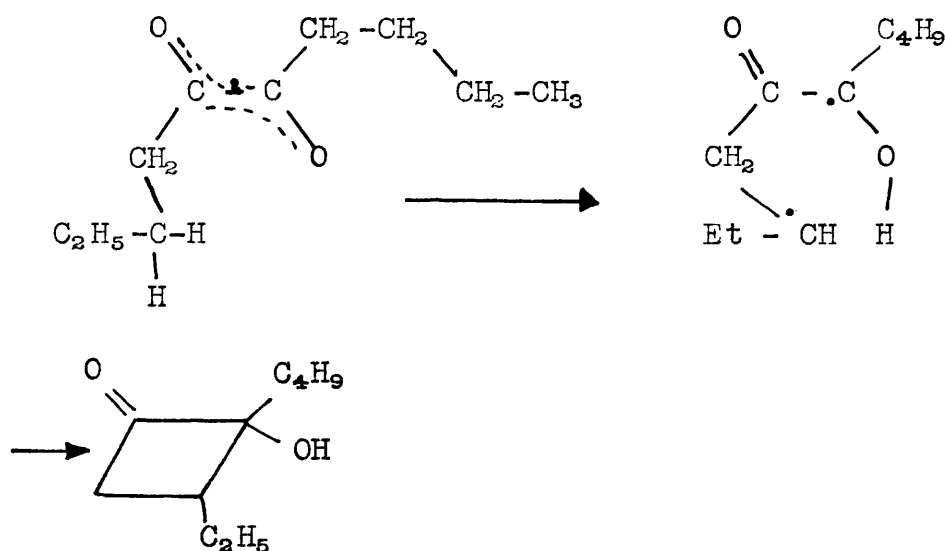
The photorearrangement of 1,2-dibenzoyl-ethylene has been extensively investigated<sup>112</sup>. The rearrangement involves a 1-5 phenyl migration from carbon to oxygen giving a ketene which reacts with the solvent. The reaction was shown to proceed at least 90% by way of the  $n \rightarrow \pi^*$  singlet state of dibenzoyl-ethylene by sensitisation and quenching experiments using acetophenone and naphthalene respectively. If trans-dibenzoyl-ethylene is irradiated, it is first converted into the cis isomer and the reaction proceeds as follows:



A similar rearrangement takes place with 1,2-dibenzoyl-styrene and -stilbene. Upon sensitisation with benzophenone, the reaction takes a different course<sup>113</sup> 1,2-dibenzoyl-ethane being the product.



Photolysis of alkyl-1,2-diketones in cyclohexane gives high yields of 2-hydroxycyclobutanones<sup>114</sup>. Quenching experiments suggest that the reactive species is the triplet state which then undergoes intramolecular hydrogen abstraction via a six-membered transition state followed by ring closure of the biradical intermediate.

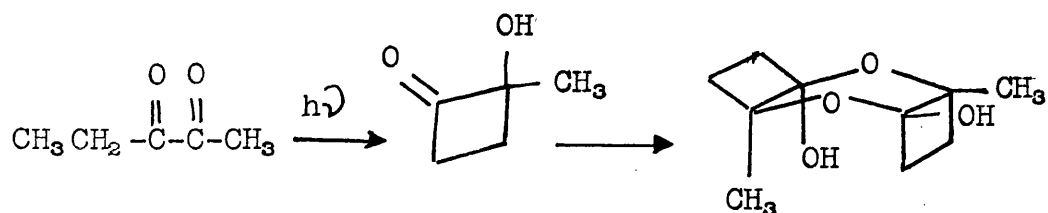


89%

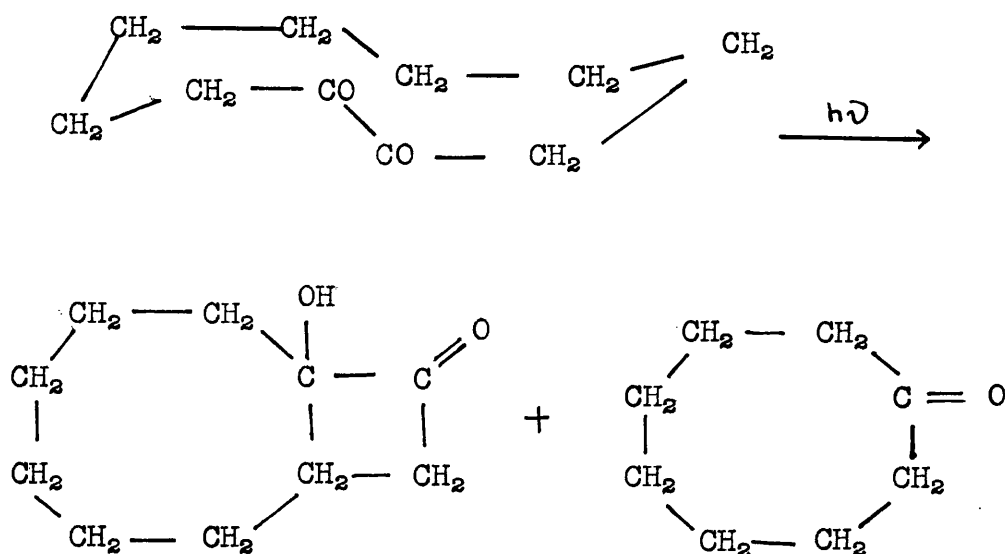
The simplest diketone that can undergo this photocyclization is 2,3-pentanedione<sup>115</sup>. Since abstraction involves a primary C-H bond, the reactivity is less than the previous



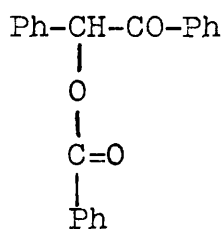
decadione, and the cyclobutane derivative formed dimerises on standing.



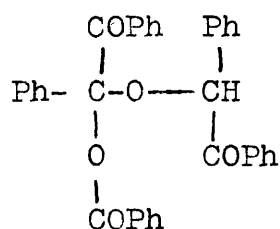
A similar reaction occurs with cyclic 1,2-diketones 1,2-cyclodecanedione in benzene on irradiation gives 1-hydroxybicyclo-[6.2.0]-decan-10-one which also undergoes photochemical cleavage eliminating ketene and forming cyclooctanone.



Irradiation of benzil in cyclohexane gives a mixture of products, the majority arising from the splitting of benzil into benzoyl radicals which can either react with the solvent or another molecule of benzil<sup>116</sup>. The proposed mechanism accounts in this way for the formation of benzaldehyde, phenylcyclohexylketone, benzoin benzoate (V) and desylbenzoyloxydesyl ether (VI)

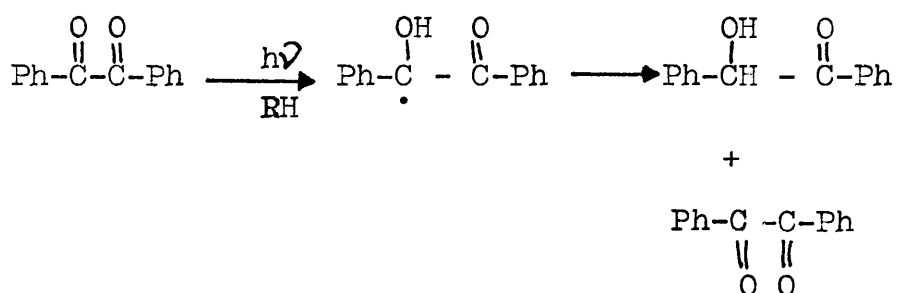


V



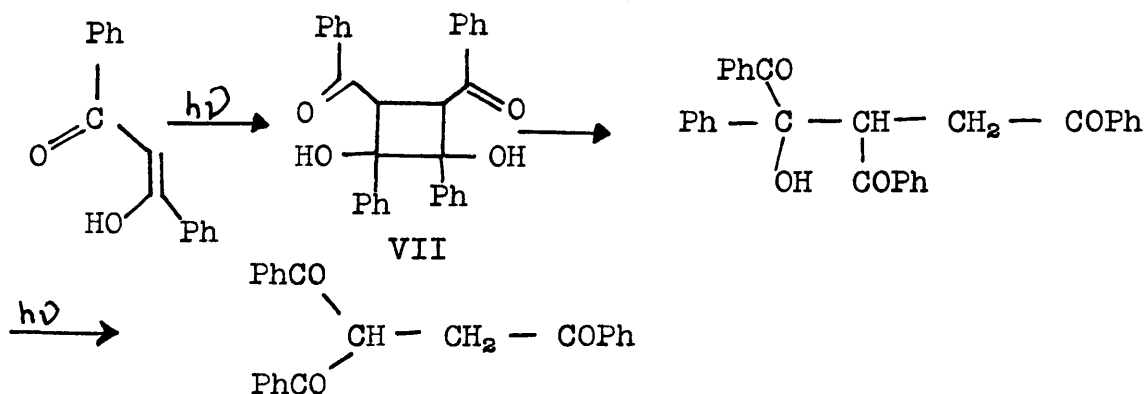
VI

Benzoin is also formed, probably by disproportionation of benzil ketyl radicals,

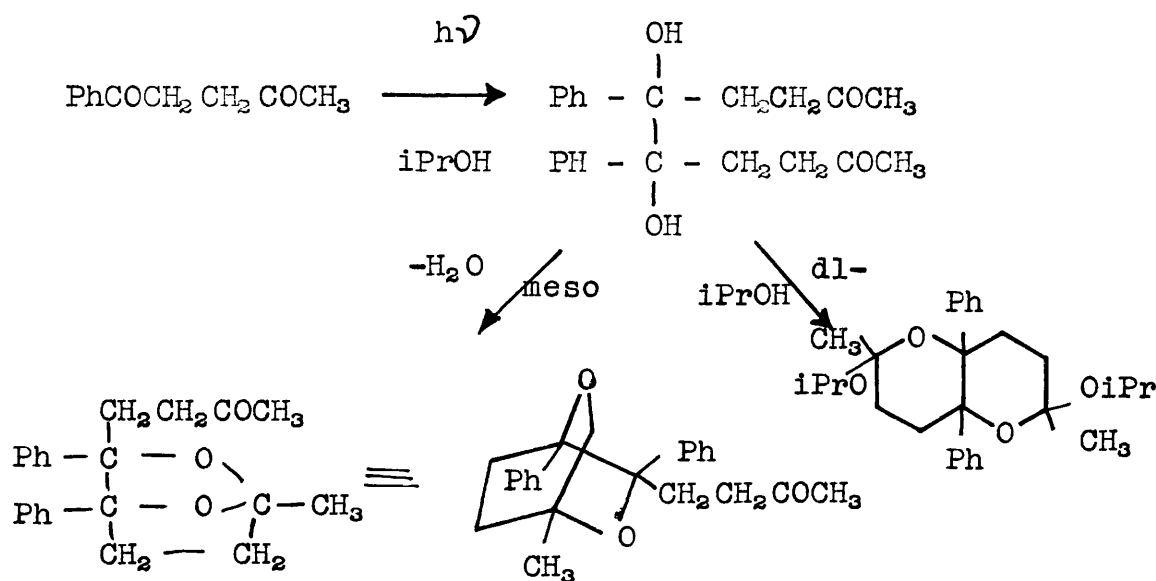


and also benzoic acid. This latter product could only be accounted for by the oxidation of an unstable product during the work up.

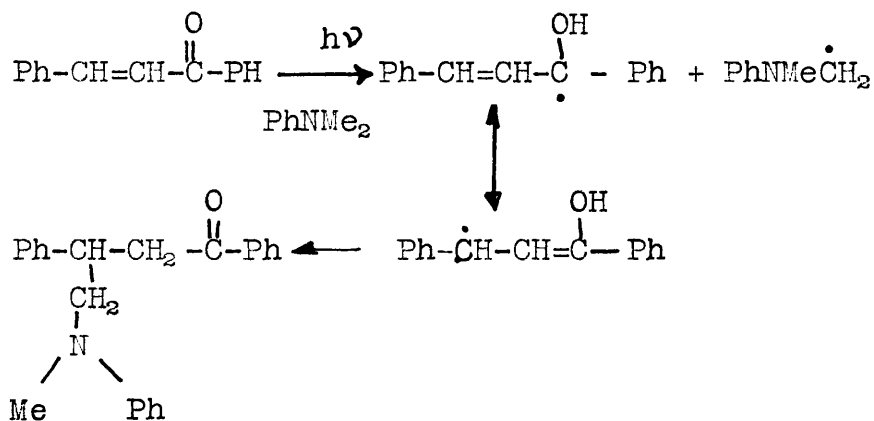
The photochemical conversion of dibenzoylmethane to tribenzoylthane has been investigated and shown to involve 2 photochemical and 1 thermal reactions<sup>117</sup>. The conversion proceeds via initial dimerisation of the enol form of dibenzoylmethane yielding the cyclobutane derivative VII. Dealdolisation of this accelerated by relief of steric strain due to the opening of the cyclobutane ring followed by a further photochemical step gives tribenzoylthane.



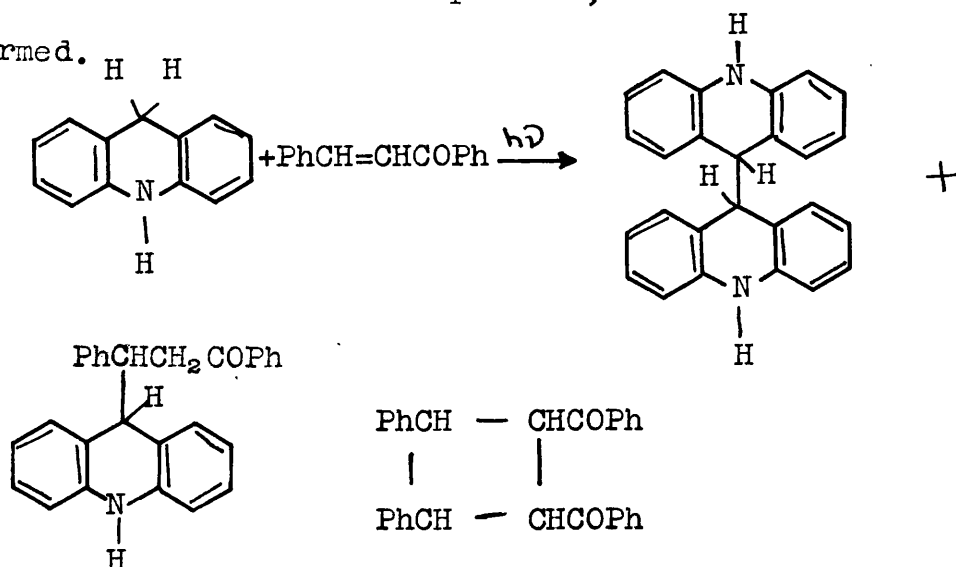
Little attention has been paid to the photochemistry of saturated 1,4-diketones. Acetylacetophenone does undergo photoreduction by isopropanol<sup>118</sup> forming a mixture of the dl- and meso-pinacols. These undergo further photochemical reactions, the meso- form losing a molecule of water to form the bicyclic compound VIII and the dl- isomer reacts with isopropanol forming the isopropylketal IX.



Initial attempts to photoreduce benzalacetophenone with NN-dimethylaniline in benzene gave N-phenyl-N-methyl-1-amino-2,4-diphenylbutan-4-one formed as follows.

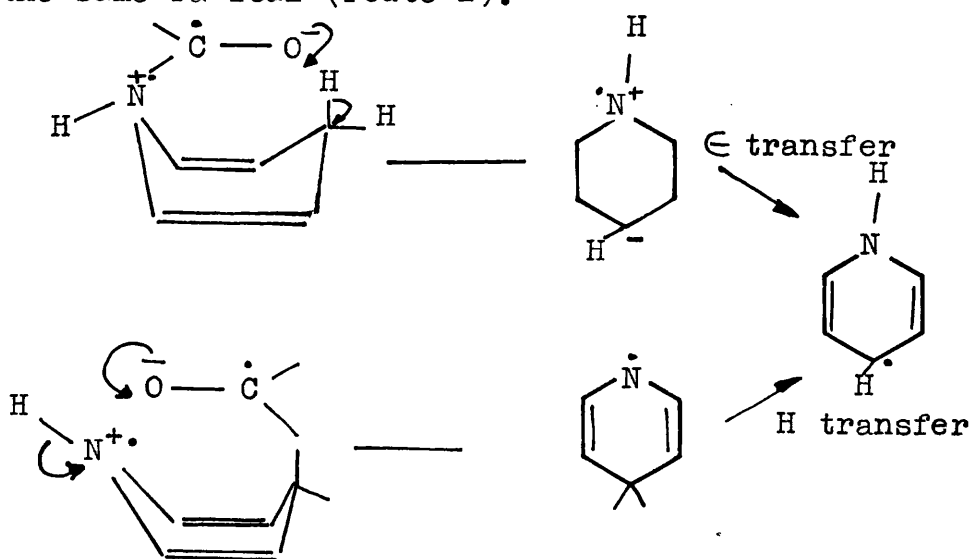


Such an addition reaction is in agreement with the results of Cookson<sup>119</sup> who photoreduced a number of enones and unsaturated esters with tertiary aliphatic amines. As well as the formation of  $\beta$ -aminoketones, hydrogenation of the double bond occurred in a number of cases. This latter reaction was thought to be of synthetic use so an attempt was made to find a suitable hydrogen donor. The choice of 9,10-dihydroacridine was made since abstraction of hydrogen from either the benzylic carbon or the nitrogen should give a radical which would readily lose another hydrogen atom thus forming an aromatic system and favouring hydrogenation of the double bond. Photolysis of 9,10-dihydroacridine and benzalacetophenone (2:1) in benzene gave 9,10,9',10'-tetrahydro-9,9'-biacridanyl and 1,3-diphenyl-1-(9-acridanyl)-propan-3-one. The head to head dimer of benzalacetophenone, truxinic ketone was also formed.



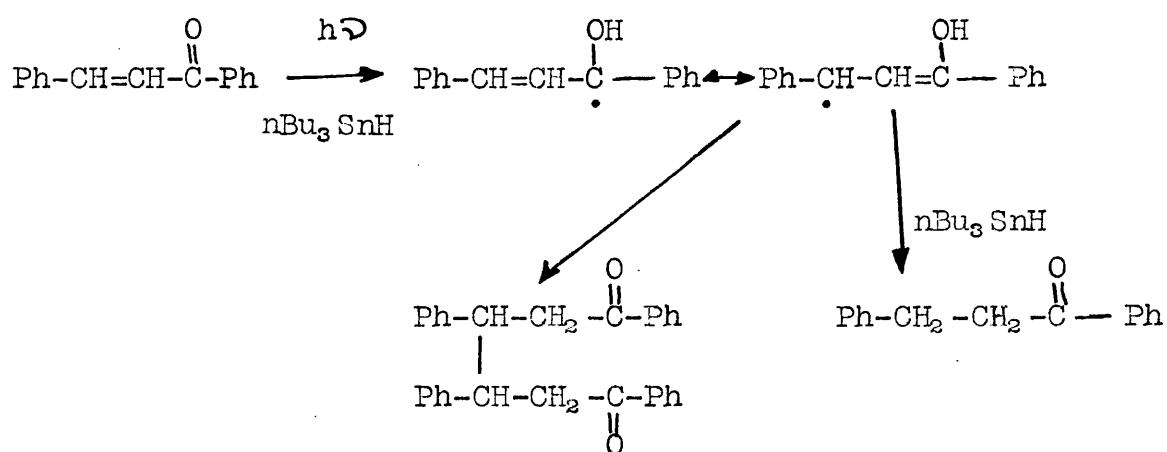
A similar photolysis of benzalacetone and dihydroacridine gave the acridine dimer and the corresponding 2-acridanyl ketone but although photolysis of mesityl oxide and dihydroacridine gave the acridine dimer, products from the mesityl oxide were not found. A gas-liquid chromatography

examination of the product mixture showed that isobutyl-methyl ketone was not produced. The surprising aspect of this reaction is that the products are apparently derived by abstraction of hydrogen from the benzylic C-H whereas the N-H bond is preferentially attacked by free radicals. Bridger and Russell found that the N-H bond in diphenylamine is 3.3 times more reactive towards phenyl radicals than the benzylic C-H bond of diphenylmethane<sup>120</sup>. Flash photolysis studies on the reaction of riboflavin and diphenylamine have shown that electron transfer occurs<sup>121</sup>, and since the ionisation potentials of diphenylamine and dihydroacridine are probably similar (ionisation potentials of diphenylamine and acridine are 7.4 and 7.78eV respectively)<sup>90</sup> photoreduction by dihydroacridine may involve initial complex or radical ion formation. Following this, hydrogen abstraction from the benzylic C-H bond followed by a 1-4 electron transfer would give the benzylic radical which accounts for the products formed. (route 1). It is also possible for hydrogen abstraction from the nitrogen to occur followed by a 1-4 hydrogen transfer which would give the same radical (route 2).



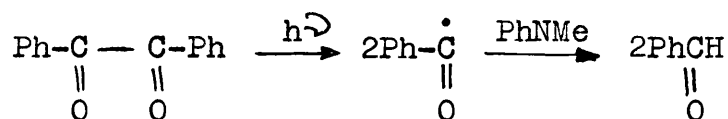
2-Cyano-2-propyl radicals have also been shown to attack dihydroacridan giving products derived from the benzylic radical <sup>122</sup>. Evidence showing that the latter process may occur was obtained when flash photolysis of a solution of benzophenone and diphenylamine in acetonitrile showed the formation of the diphenylamino radical. ( $\lambda_{\text{max}}^{740}$ )<sup>121</sup>

Since amines were not found to be suitable hydrogen donors for conversion to the saturated ketone, tri-n-butylstannane was considered as a possibility since as previously mentioned, the weak tin-hydrogen bond confers high reactivity on it as a hydrogen donor. Photolysis of tri-n-butylstannane and benzalacetophenone (2:1 in benzene) gave 1,3-diphenyl-propan-3-one and meso 1,3,4,6-tetraphenyl-hexan-1,4-dione. The latter product occurs from dimerisation of the initial formed radical which competes with a further hydrogen abstraction.

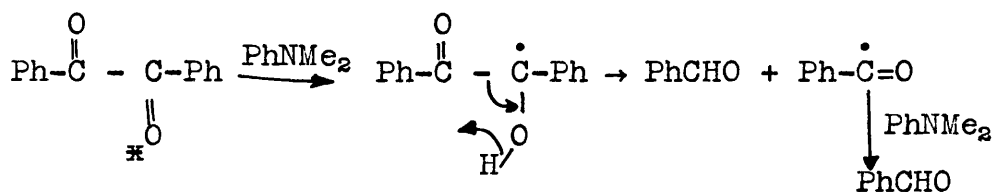


A similar photoreduction with  $\Delta^4$ -cholestene-3-one and tri-n-butylstannane gave cholestan-3-one i.e. rings A and B are transfused. These results contrast with those obtained by the thermal reduction of  $\alpha$ - $\beta$  unsaturated ketones by tin alkyls where selective reduction of the carbonyl group occurs.

Unfortunately, owing to lack of time, only a limited number of experiments on the photoreduction of diketones were performed. Photoreduction of 0.05M benzil by 0.01M NN-dimethylaniline in benzene gave a mixture of meso- and dl- 1,2-diphenyl-1,2-dihydroxyethane. The initial reaction is the formation of benzaldehyde either by dissociation of benzil into benzoyl radicals which abstract hydrogen from the amine



or by the following sequence:



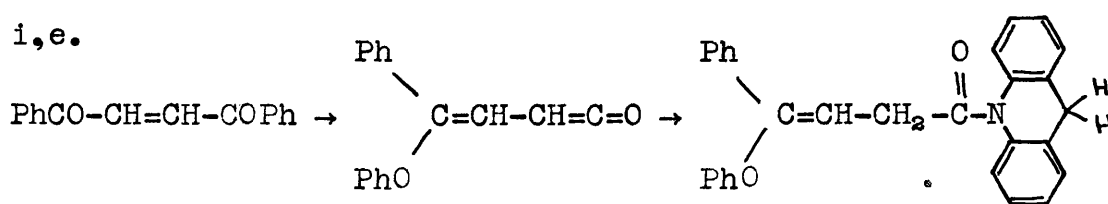
Photopinacolisation of benzaldehyde gives the product. That photoreduction of 0.05M benzil by 0.1M triethylamine in benzene at least partly follows the latter course was shown by the formation of benzoin. This could either be produced by the benzil monoketyl radical abstracting a further hydrogen from the amine or by disproportionation. The formation of benzaldehyde was followed by gas-liquid chromatography and reached maximum (24%) after 6 hours and then remained constant. Photoreduction of benzoin under similar conditions also gave rise to benzaldehyde, 14% maximum after 5 hours confirming that at least some of the benzaldehyde is formed by initial abstraction of hydrogen by excited benzil.

Photolysis of dibenzoylmethane and NN-dimethylaniline produced the pinacol, 1,3,4,6-tetraphenyl-3,4-dihydroxy-hexan-1,2-dione as the primary photoproduct in 12% yield. This also lost a molecule of water directly to give 8% of 1,3,4,6-tetraphenyl-3-hydroxy-hex-4-ene-1,6-dione. Also formed was a substance which was not identified.

Elementary analysis gave the empirical formula as  $C_{11}H_9O$  and mass spectrometry a molecular weight 433. Both carbonyl and hydroxyl stretching frequencies were absent in the infra-red and the nuclear magnetic resonance spectra showed only 2 types of protons.

Photolysis of 1,2-dibenzoyl ethylene and 9,10-dihydro-acridine would be expected to give 1-phenyl-1-phenoxy-4-(10-acridanyl)-but-1-ene-4-one(I) via an analogous phenyl carbon to oxygen rearrangement to that observed by Zimmerman et al<sup>1,2</sup>, and subsequent attack of the ketene upon the secondary amine.

i.e.



I

The product obtained from such a photolysis was not fully characterised. The infra-red spectrum agreed with the structure of I but mass spectrometry gave a value of 473 for the molecular weight, whilst I has a molecular weight of 417. Unfortunately a suitable solvent for a nuclear magnetic resonance spectrum could not be found.



## Experimental

### Instrumentation and General Details.

Melting points were determined on a Kofler Block using corrected thermometers.

Routine infra-red spectra were recorded on a Unicam SP 200 spectrophotometer, and spectra of new compounds on a Perkin Elmer 237 Grating Spectrophotometer.

Nuclear magnetic resonance spectra were obtained on Varian instruments models A60 and T60 in deuteriochloroform solution unless otherwise stated. Mass spectra were run on an A.E.I. M.S. 9 mass spectrometer and gas-liquid chromatography was carried out on a Perkin Elmer F11.

Ultra-violet spectra were recorded on a Unicam SP800 spectrophotometer. Elemental analyses were carried out by Rapid Elemental Analyses, Beaconsfield or Alfred Berhardt, West Germany.

All solvents used were purified by distillation under dry nitrogen before use. Benzene was 'Analar' grade, dried with sodium wire and alcohols were boiled under reflux with calcium hydride before distillation.

All liquid amines were redistilled under nitrogen before use.

Reagent grade benzophenone was used direct since recrystallisation from 60°-80° petrol made no difference to the melting point.

Unless otherwise stated, the lamp was a Hanovia 100 watt medium pressure mercury arc fitted with a pyrex sleeve. All photolyses were carried out with dry nitrogen bubbling through them.

Preparation of N-Methylcarbazole

Carbazole (15g. 0.09 moles), dimethyl sulphate (20g. 0.15 moles) and acetone (75ml.) were shaken with a solution of NaOH (15g.) in water (10ml.) for a few minutes. The mixture was poured into water and the precipitate filtered at the pump. This was recrystallised from ethanol to give white needles of N-methylcarbazole.

Yield. 14.5g. (89% theory)

m.p. 86.5 - 87.5°C (Lit. m.p. 87°C)<sup>123</sup>

Preparation of N-Benzylcarbazole

Carbazole (10g. 0.06 moles) was dissolved in 50 ml. of sodium dried xylene contained in a three-necked round-bottomed flask, fitted with a reflux condenser and dropping funnel. Sodamide powder (2.5g. 0.065 moles) was added and the mixture was heated under reflux under nitrogen and stirred with a magnetic stirrer overnight. A white precipitate of the sodium salt of carbazole was formed. Redistilled benzyl bromide (10g. 0.06 moles) was added dropwise over a period of 30 minutes and the mixture was heated under reflux for 4 hours. The precipitated sodium bromide was filtered off, the xylene was distilled off at low pressure and the brown solid remaining was recrystallised twice from ethanol to give N-benzylcarbazole as colourless needles.

Yield: 10.6g. (69% theory)

m.p. 118-119°C. (Lit. m.p. 112-3°C)<sup>124</sup>

### Preparation of N-Benzyl diphenylamine

Analar diphenylamine (10g. 0.06 moles) was dissolved in 50ml. sodium dried xylene contained in a three-necked flask as above and powdered sodamide, (2.5g. 0.065 moles) was added. The mixture was heated under reflux under nitrogen and stirred for 24 hours. A white precipitate of the sodium salt of diphenylamine was formed. The flask was cooled in an ice-bath and redistilled benzyl bromide (10g. 0.06 moles) was added dropwise to the stirred salt over a period of 30 minutes. The mixture was allowed to warm up to room temperature with stirring and was then heated under reflux overnight. The precipitate of sodium bromide was filtered off and the xylene was removed under vacuum. The remaining brown solid was recrystallised twice from ethanol to give N-benzyl diphenylamine as colourless needles.

Yield 8.3g. (55% theory)

m.p. 88-89°C. (Lit.m.p. 86°C)<sup>125</sup>

### Preparation of N-Methyl diphenylamine

The method of Gibson and Vining<sup>126</sup> involving methylation of diphenylamine with dimethylsulphate was attempted but yields obtained were low and difficulty in removing all the unchanged diphenylamine made the product impure. An improved synthesis was used which involved preparation of the sodium salt of diphenylamine from sodamide (2.5g. 0.065 moles) and diphenylamine (10g. 0.06 moles) as outlined above. To this was added methyl iodide (10g. 0.07 moles) dropwise over a period of 15 minutes. The mixture was stirred at room temperature for 2 hours and then heated at

120°C under reflux overnight. The precipitate of sodium iodide was filtered off, solvent was removed under vacuum and the residual liquid distilled under reduced pressure. N-methyldiphenylamine was collected as a colourless liquid.

Yield. 8.9g. (66% theory)

b.p. 134-138°C at 1.0 mm.Hg.

(Lit.b.p. 291-2°C at atmospheric pressure)

Preparation of Copper Catalyst for use in the Preparation of  
Tri-p-tolylamine<sup>127</sup>.

Copper sulphate pentahydrate (100g. 0.4 moles) was dissolved in 350 ml. of hot water and after cooling to room temperature zinc dust (35g. 0.53 atoms) was gradually added. The solution became decolourised. The precipitated copper was washed by decantation with water and then with 2N hydrochloric acid to remove any unchanged zinc. When the evolution of hydrogen has ceased, the copper was removed by filtration, washed with water and kept in a moist condition in a well stoppered bottle.

Preparation of Tri-p-tolylamine.

This was prepared by the method of Walter<sup>128</sup> but the method of working the reaction mixture up was modified. p-Toluidine (22.5g. 0.21 moles), p-iodotoluene (98.5g. 0.45 moles), dry powdered potassium carbonate (32.5g.) and copper powder (1.15g.) were mixed with 150ml. of nitrobenzene and heated under reflux for 48 hours. After steam distilling out the nitrobenzene, the black crystalline cake remaining in the aqueous layer was dissolved in 1 litre of benzene and absorbed onto basic alumina (Spence



type H). This was eluted with 500 ml. 40-60° petrol and after removal of the solvent, the brownish solid remaining was rechromatographed on alumina. Elution with 40-60° petrol gave tri-p-tolylamine which was recrystallised from glacial acetic acid to give colourless needles.

Yield. 11.5g. (14% theory)

m.p. 114-7°C (Lit.m.p. 110-117°C)<sup>128</sup>

Preparation of 2,4'-Dimethoxybenzophenone.

2-Hydroxy-4'-methoxybenzophenone (5g. 0.022 moles) was dissolved in an aqueous solution of potassium hydroxide (1.5g. in 10 ml. water) contained in a three-necked round-bottomed flask fitted with a stirrer, a condenser and a dropping funnel. The solution, which became yellow, was cooled in an ice bath and stirred whilst dimethyl sulphate (4.6g. 0.03 moles) was dropped in over a period of 30 minutes. The mixture was allowed to warm up to room temperature and then heated under reflux overnight. After cooling, it was extracted with ether (3 x 25 ml.), and the extract was washed with potassium hydroxide solution (2N) until the washings were no longer yellow, water (4 x 100ml.) and finally dried with anhydrous sodium sulphate. The ether was removed under vacuum and the remaining solid was recrystallised with difficulty from benzene/60-80 petrol giving 2,4'-dimethoxyophenone as colourless prisms.

Yield; 3.8g. (74% theory)

m.p. 82°C (Lit.m.p. 77-8°C)<sup>129</sup>

Preparation of p-Phenylbenzophenone<sup>130</sup>.

Anhydrous aluminium chloride (25.8g. 0.22 moles) was placed in a three-necked flask together with 75 ml. of sodium dried benzene. Biphenyl (31g. 0.2 moles) was added and the flask was equipped with a mechanical stirrer, condenser and dropping funnel fitted with calcium chloride drying tubes. Benzoyl chloride (31g. 0.22 moles) in 75 ml. dry benzene was dropped into the stirred mixture over a period of 45 minutes followed by heating under reflux for 4 hours. The benzene was removed under vacuum and the resulting solid was added to 500 ml. of ice/water and allowed to stand for 12 hours. The white precipitate was filtered off and recrystallised twice from ethanol giving p-phenylbenzophenone as white prisms.

Yield: 15.7g. (35%)

m.p. 103°C. (Lit.m.p. 106°C)<sup>130</sup>

Preparation of Ferric Acetylacetonate.<sup>131</sup>

Ferric ammonium sulphate (10g. 0.01 moles) was dissolved in 500 ml. water saturated with acetylacetone and ammonium was added dropwise until precipitation had ceased. The precipitate was filtered off and recrystallised from ethanol containing a few mls. of acetylacetone to prevent hydrolysis. Ferric acetylacetonate recrystallised as dark red prisms.

Yield: 5.1g. (73% theory)

m.p. 185°C.

Preparation of Ferric Dibenzoylmethanate<sup>20</sup>.

Ferric chloride hexahydrate (1.2 g., 0.004 moles) was dissolved in 150 ml. of a 1:1 mixture of ethanol /water containing excess sodium acetate. Dibenzoylmethane (3g. 0.013 moles) was dissolved in 100 ml. ethanol and slowly added to the stirred ferric chloride solution. Ferric dibenzoylmethanate was precipitated and the mixture was warmed on a steam bath for 10 minutes, allowed to cool and then extracted with benzene. The organic layer was washed with water and dried first with calcium chloride and then sodium sulphate, before removal of the solvent. The solid was recrystallised from benzene/40°-60° petrol to give ferric dibenzoylmethanate as very dark red prisms.

Yield: 1.6.g.(55% theory)

m.p. 275-6°C. (Lit. m.p. 275°C)<sup>20</sup>

Photolysis of N-Methylcarbazole and Benzophenone.

N-Methylcarbazole (3g. 0.016 moles) and benzophenone (3g. 0.016 moles) were dissolved in 150 ml. of benzene and photolysed for 16 hours. The benzene was removed under vacuum keeping the temperature as low as possible, and the resulting solid was triturated with 40-60° petrol and filtered. Fractional crystallisation of the insoluble portion from benzene gave;

a) Colourless prisms of 1,2-( 9-dicarbazoyl)-ethane

Yield; 0.25g. (8.5% theory)

m.p. 309-310°C.

I.R.  $\nu_{\max}$  1480, 745, 715cm<sup>-1</sup>.

N.M.R. (in d<sub>6</sub>DMSO) 6.4 $\tau$  4 hydrogen singlet

2.7 $\gamma$  12 hydrogen multiplet

2.0 $\gamma$  4 hydrogen multiplet

$m/e$  360, 180, 166, 152

Analysis; C.87.20, H.5.56, N.7.78% (Calculated for  
C<sub>26</sub>H<sub>20</sub>N<sub>2</sub> C.86.63, H.5.59, N. 7.77%)

b) Colourless prisms of benzpinacol.

Yield 0.8g.

m.p. and mmp. 203-4°C. (from benzene)

The petrol was removed from the soluble fraction and the resulting solid was chromatographed on Spence type 'H' alumina.

Elution with 10% benzene in 40-60° petrol gave unchanged N-methylcarbazole.

Yield; 0.2g.

m.p. and mmp 86-88°C (from ethanol)

Elution with 25% benzene in 40-60° petrol gave unchanged benzophenone.

Yield. 0.15g.

m.p. and mmp 43-50°C (from 60-80° petrol)

Elution with benzene gave benzpinacol.

Yield; 0.4g. (Total yield is 1.2g. 40%)

m.p. and mmp; 203-4°C (from benzene)

#### Preparation of 1,2-(9-Dicarbazoyl)-ethane.

N-Methylcarbazole (2g. 0.01 moles) and ditertiary butylperoxide (3.2g. 0.02 moles) were dissolved in chlorobenzene (50 ml.) and heated under reflux for 6 hours.



On cooling, crystals separated out which were filtered off and recrystallised from benzene.

Yield; 1.4g. (70% theory)

m.p. 312-3° C.

Analysis; C.87.12, H.5.48, N.7.72%

(calculated for  $C_{26}H_{20}N_2$  C.86.63, H.5.59, N.7.77%)

The infra-red and nuclear magnetic resonance spectra were identical to those of the 1,2-(9-dicarbazoyl)-ethane produced from the photolysis and a mixed melting point showed no depression.

#### Photolysis of N-Benzoyldiphenylamine and Benzophenone.

N-Benzoyldiphenylamine (3.8g. 0.015 moles) and benzophenone (1.35g. 0.0075 moles) were dissolved in 150 ml. of benzene and photolysed for 4 hours. The benzene was removed under vacuum keeping the temperature as low as possible and the resulting brownish solid was triturated with 40-60° petrol. Recrystallisation of the insoluble fraction from toluene gave colourless prisms of N,N,N',N',1,2-hexaphenylethylene-diamine.

Yield; 0.3g. (7.5% theory)

m.p. 293° C.

I.R.  $\nu_{\max}$  1600, 1510, 1270, 745, 705  $\text{cm}^{-1}$ .

Analysis; C.88.53, H.6.25, N. 5.37%

(Calculated for  $C_{38}H_{32}N_2$ : C.88.33, H.6.24, N. 5.42%)

The petrol was removed from the soluble fraction and the resulting brown oil was chromatographed on Spence type 'H' alumina.

Elution with 40-60° petrol gave unchanged N-benzylidiphenylamine.

Yield; 1.03 (37% recovery)

m.p. and mmp. 87-88°C (from ethanol)

Elution with 10% benzene in 40-60° petrol gave a white solid which was recrystallised from benzene/60-80° petrol to give colourless prisms of N,N,1,2,2,pentaphenyl-2-hydroxyethylamine.

Yield; 0.15g. (15% theory)

m.p. 162-163.5°C

I.R.  $\nu_{\max}$  3600, 1600, 1500, 1050, 700  $\text{cm}^{-1}$

N.M.R. 7.35 $\tau$  1 hydrogen singlet

3.75 $\tau$  1 hydrogen singlet

2.85 $\tau$  25 hydrogen multiplet.

Elution with benzene gave benzpinacol, recrystallised from ethanol/chloroform.

Yield; 0.4g. (36% theory)

m.p. and mmp 185-186°C.

#### Photolysis of N,N-Dimethylaniline and Xanthone.

N,N-Dimethylaniline (2.0g. 0.011 moles) and xanthone (1.5g. 0.008 moles) were dissolved in 150 ml. of benzene and photolysed for 6 hours. The solution was extracted with 2N hydrochloric acid (3 x 20 ml.) and the extract was neutralised with 2N sodium hydroxide. The neutral solution was extracted with ether (3 x 25 ml.) and the extract was washed with water and then dried with anhydrous sodium sulphate. Removal of the ether left 1.44g. of a brown liquid which was shown to be a mixture of unchanged N,N-dimethylaniline and N-methylaniline by comparison with

known infra red and nuclear magnetic resonance spectra. The benzene solution remaining from the initial acid extraction was washed with water and dried with anhydrous sodium sulphate before removal of the solvent under vacuum. The yellowish solid remaining was triturated with 40-60° petrol and filtered. The residue was recrystallised from toluene to give colourless needles of xanthopinacol.

Yield; 0.85g. (43% theory)

m.p. 185-6° C (Lit. mp. 185-7° C)<sup>80</sup>

I.R.  $\nu_{\max}$  3500, 1230, 1060, 890,  
760 cm<sup>-1</sup>.

#### Photolysis of N,N-Dimethylaniline and Fluorenone.

N,N-Dimethylaniline (6g. 0.05 moles) and fluorenone (2g. 0.01 moles) were dissolved in 150ml. of benzene and photolysed for 3 hours. The solution was extracted with 2N hydrochloric acid as described above yielding 3.4g. of a mixture of unchanged N,N-dimethylaniline and N-methylaniline. The benzene solution remaining was washed and dried as before and removal of the solvent gave a brown oil. Trituration of this with a mixture of benzene and 40-60° petrol gave a yellowish solid which was filtered off and recrystallised from ethanol to give colourless prisms of fluoropinacol.

Yield; 1.16g. (58% theory)

m.p. 190-1° C (Lit. mp. 190-2° C)<sup>80</sup>

The mother liquors from the trituration, on standing deposited a small amount of yellow crystals.

Yield. 47mg.

m.p. 262° C.

I.R.  $\nu_{\max}$  1700, 750, 730, 720  $\text{cm}^{-1}$

This is probably the pinacolone formed by the loss of a molecule of water and subsequent rearrangement of fluoro-pinacol. Reduction of fluorenone with zinc dust in the presence of acetyl chloride gives the same compound in addition to the acetylated pinacol<sup>132</sup>.

Photolysis of o-Aminobenzophenone and N,N-Dimethylaniline.

N,N-dimethylaniline (1.25g. 0.01 moles) and o-aminobenzophenone (1g. 0.005 moles) were dissolved in 150 ml. of benzene and photolysed for 7 hours. Acid extraction gave 0.95g. of a mixture of NN-dimethyl and N-methylanilines. The residue from the extraction after washing and drying gave unchanged o-aminobenzophenone upon recrystallisation from benzene/60-80° petrol.

Yield. 0.81g. (81% recovery)

m.p. and mmp 101-2° C.

Photolysis of 2,4'-dimethoxybenzophenone and N,N-dimethylaniline.

N,N-Dimethylaniline (1.8g. 0.015 moles) and 2,4'-dimethoxybenzophenone (1.8g. 0.008 moles) were dissolved in 150 ml. of benzene and photolysed for 1 hour. Extraction with 2N hydrochloric acid gave 0.4 g. of a mixture of NN-dimethyl- and N-methylanilines. After washing and drying the benzene solution as previously described, the solvent was removed under vacuum and the resulting yellow

oil was triturated with a mixture of benzene and 40-60° petrol. The resulting white solid was filtered off and recrystallised from a mixture of ethanol and chloroform. This gave colourless needles of 2,4',2'',4'''-tetramethoxybenzpinacol.

Yield; 0.71 g. (40% theory)

m.p. 186-7°C.

I.R.  $\nu_{\max}$  3450, 1270, 1040, 830  $\text{cm}^{-1}$ .

N.M.R. 6.7 $\tau$  3 hydrogen singlet

6.3 $\tau$  3 hydrogen singlet

4.8 $\tau$  1 hydrogen singlet

3.1 $\tau$  8 hydrogen multiplet.

#### Photolysis of NN-Dimethylaniline and p-Aminobenzophenone.

N,N-Dimethylaniline (1.8g. 0.015 moles) and p-amino-benzophenone (1.47g. 0.0075 moles) were dissolved in 150 ml of benzene and photolysed for 4 hours. The benzene was removed under vacuum and the resulting oil was dissolved in ether. 40-60° petrol was slowly added until precipitation had ceased. The brown oily solid was filtered off but all attempts to recrystallise it failed. The experiment was repeated and the solid was dissolved in methylene chloride and then reprecipitated with petrol. This procedure was repeated twice more to give a brown solid which was impure p,p'-diaminobenzpinacol.

Yield; 0.85g. (59% theory)

m.p. 163-171°C (Lit. m.p. 179-80°C)<sup>82</sup>

I.R.  $\nu_{\max}$  Complex of 5 peaks centred at 3450  $\text{cm}^{-1}$ . 1620, 1510, 1020, 770, 750  $\text{cm}^{-1}$

Photolysis of 2-Acetylnaphthalene and N,N-Dimethylaniline.

N,N-Dimethylaniline (1.8 g. 0.015 moles) and 2-acetylnaphthalene (1.3g. 0.0075 moles) were dissolved in 150 ml. of benzene and photolysed for 14 hours. N-Methylaniline and unchanged N,N-dimethylaniline were removed by washing with 2N hydrochloric acid and the benzene solution was washed and dried as previously detailed. Removal of the solvent gave a buff coloured solid which was recrystallised from benzene/60-80° petrol giving the pinacol as colourless prisms.

Yield; 0.47g. (36% theory)

m.p. 174-6°C

I.R.  $\nu_{\max}$  3560, 110, 780  $\text{cm}^{-1}$ .

N.M.R. 8.3 $\tau$  3 hydrogen singlet

7.65 $\tau$  1 hydrogen singlet

2.4 $\tau$  7 hydrogen multiplet

Photolysis of N,N-Dimethylaniline and Thioxanthone.

N,N-Dimethylaniline (1.8g. 0.015 moles) and thioxanthone (1.6g. 0.0075 moles) were dissolved in 150ml. of benzene and photolysed for 16 hours. Following the usual procedure for removal of excess N,N-dimethylaniline and solvent, the yellow solid remaining was recrystallised from benzene/60-80° petrol giving yellow needles of unchanged thioxanthone.

Yield; 0.95g. (61% recovery)

m.p. and mmp, 206-8°C.

Photolysis of N,N-Dimethylaniline and Acetophenone.

N,N-Dimethylaniline (1.8g. 0.015 moles) and acetophenone (0.9g. 0.0075 moles) were dissolved in 150 ml. of benzene and photolysed for 4 hours. The reaction mixture was worked up in the usual manner and yielded a white solid. This was recrystallised twice from 80-100° petrol in an attempt to raise the melting point to the value of 123°C as obtained by Weizmann et al<sup>133</sup>. It was finally concluded that the crystals obtained were a mixture of dl- and meso-isomers of the pinacol.

Yield: 0.3g. (33% theory)

m.p. 115-121°C.

I.R.  $\nu_{\max}$  3500, 1060, 700  $\text{cm}^{-1}$

Photolysis of N,N-Dimethylaniline and Cyclohexanone.

N,N-Dimethylaniline (1.8g. 0.015 moles) and cyclohexanone (0.75g. 0.0075 moles) were dissolved in 150 ml. of benzene and photolysed for 16 hours. A solution infra-red spectrum showed no decrease in the absorption due to the carbonyl group so it was concluded that photoreduction had not occurred.

Photolysis of N,N-Dimethylaniline and Isophorone.

A similar procedure to that employed in the cyclohexanone case showed that no photoreduction had occurred.

Photolysis of N,N-Dimethylaniline and p-Phenylbenzophenone.

N,N-Dimethylaniline (1.8g. 0.015 moles) and p-phenylbenzophenone (1.9g. 0.007 moles) were dissolved in 150 ml. of benzene and photolysed for 1 hour. The benzene was

removed under vacuum and the resulting brown oil was triturated with 40-60° petrol giving a brownish solid. This was filtered off and recrystallised from a mixture of chloroform and acetone to give p,p'-diphenylbenzpinacol as colourless needles.

Yield; 1.15g. (60% theory)

m.p. 198.5-199°C (Lit.m.p. 198°C)<sup>66</sup>.

I.R.  $\bar{\nu}_{\max}$  3550, 1160, 1020, 770, 700  $\text{cm}^{-1}$

#### Photolysis of Xanthone and Isopropanol.

Xanthone (1.47g. 0.0075 moles) was dissolved in 150 ml. of isopropanol and photolysed for 9 hours. The solvent was removed under vacuum and the resulting solid was recrystallised from toluene giving colourless needles of xanthopinacol.

Yield; 0.86 (59% theory)

m.p. and mmp. 185-6°C.

#### Determination of the Relative Reactivities of the Methyl and Benzyl C-H Bonds of Amines Towards Excited Carbonyl Groups.

The method used for determining the relative reactivities is illustrated for the photoreduction of benzophenone by N,N-dimethylaniline. The same procedure was employed for all the amine (or alcohol)-ketone systems studied. A standard reference curve was first drawn so that the amount of ketone photolysed could be computed at any time. Solutions containing known amounts of benzophenone and N,N-dimethylaniline were made up by dissolving the amounts of each component shown in the following table in 10 ml. of 'Analar' chloroform.



Molarity $\text{Ph}_2\text{C=O}$	0.05	0.04	0.03	0.02	0.01	0
No grams $\text{Ph}_2\text{C=O}$	0.09	0.078	0.0546	0.0364	0.0182	0
No grams $\text{PhNMe}_2$	0.121	0.139	0.157	0.176	0.194	0.212

Solution spectra of the carbonyl absorption band were then run on a Perkin-Elmer 137 Spectrophotometer and the peak height of the absorption band was plotted against the molarity of the benzophenone giving a standard reference curve. This curve (fig.1) is shown overleaf for the benzophenone/*N,N*-dimethylaniline system. For the reactivity determination, benzophenone (1.365g. 0.05M) and *N,N*-dimethylaniline (1.85g. 0.1M) were dissolved in 150 ml. of benzene and photolysed. At 15 minute intervals, 5ml. of the solution were withdrawn, the benzene was carefully removed by swirling in a warm water bath under vacuum and after cooling, the residues were dissolved in 5ml. of 'analar' chloroform. Solution spectra of the carbonyl absorption band were run and by comparing the intensity of the absorption with the reference curve, the amount of benzophenone remaining was found. The amount of benzophenone used was then plotted against time, a selection of these curves (fig.2) is shown on the second graph. From this graph, the value of  $\log_{10} \frac{[A_0]}{[A]}$  (where  $[A_0]$  is

the initial concentration of carbonyl compound and  $[A]$  is the concentration after time  $t$ ) was calculated, the values of this ratio for the different systems studied being shown in table 1. As previously detailed plots of  $\log_{10} \frac{[A_0]}{[A]}$

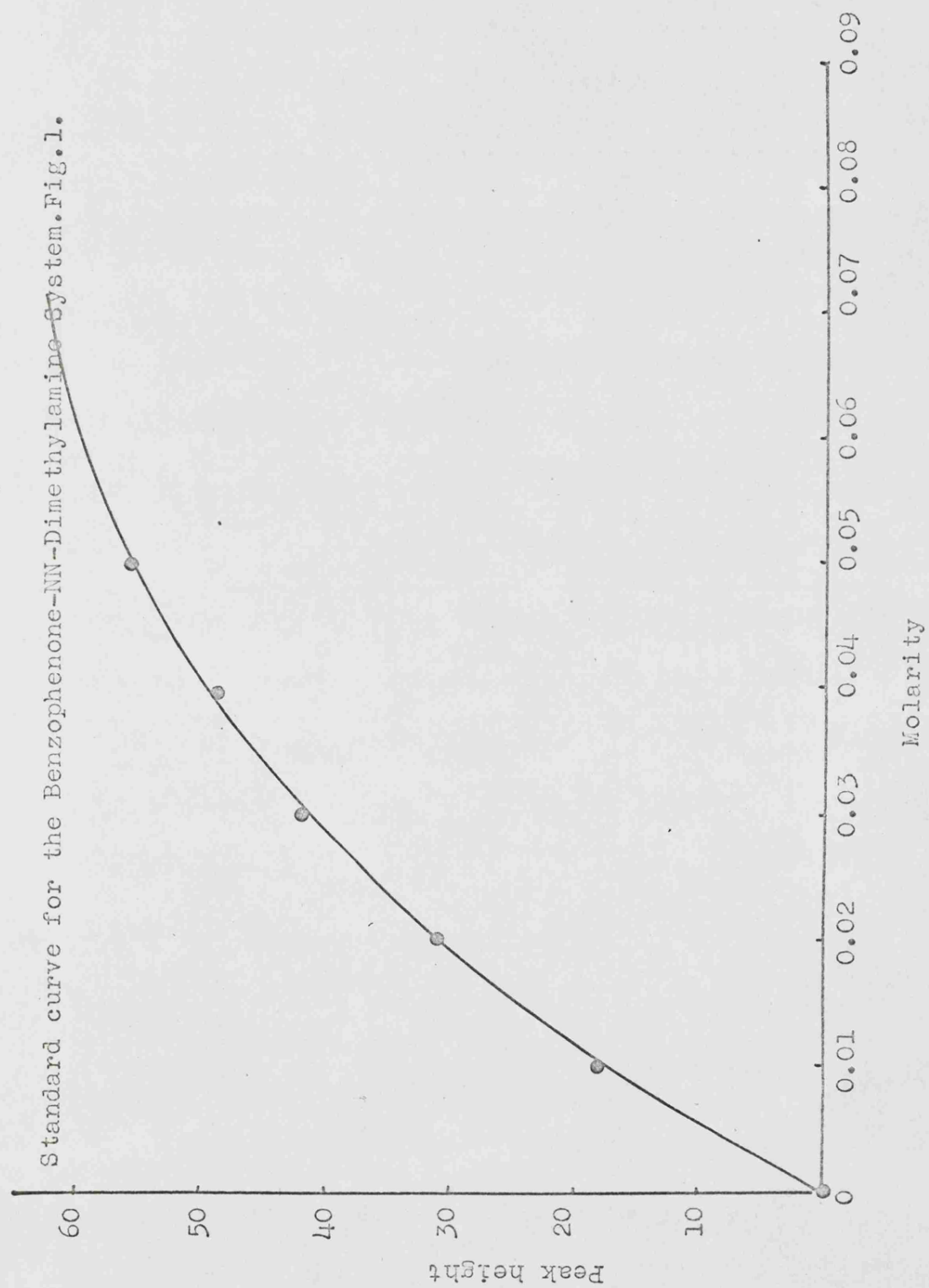


Fig.2. Rates of Photoreduction of Benzophenone by some Amines

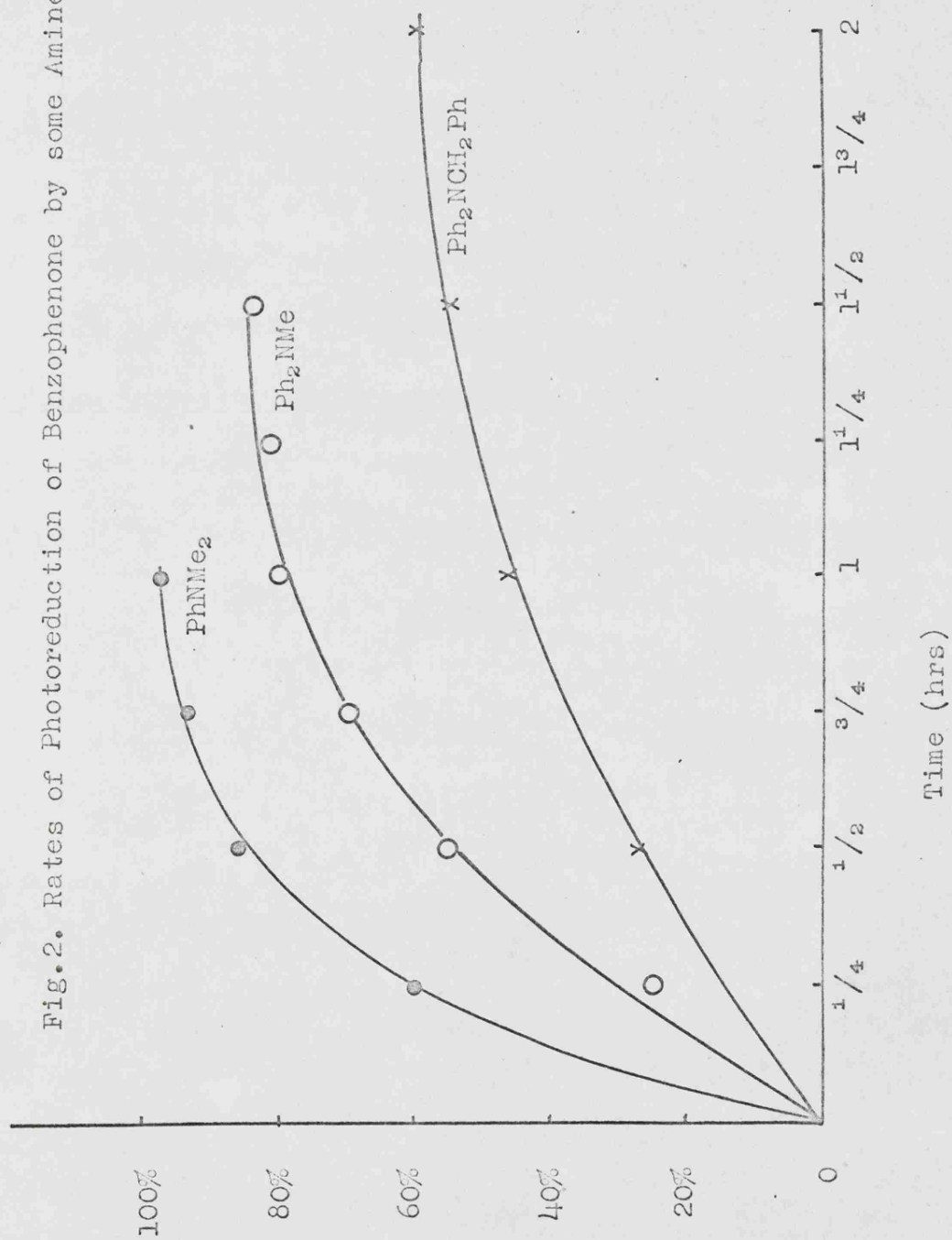


TABLE 1. $\text{Ph}_2\text{C=O/PhNMe}_2/\text{Benzene.}$ 

time (mins.)	A	$\frac{A_0}{A}$	$\log_{10} \frac{A_0}{A}$
7 $\frac{1}{2}$	0.0325	1.527	0.1837
15	0.020	2.50	0.3979
22 $\frac{1}{2}$	0.0125	4.00	0.6021
30	0.0075	6.67	0.8241
37 $\frac{1}{2}$	0.0045	11.10	1.0453

 $\text{Ph}_2\text{C=O/PhNMe}_2/\text{n-Heptane}$ 

7 $\frac{1}{2}$	0.044	1.136	0.0554
15	0.039	1.280	0.1072
22 $\frac{1}{2}$	0.034	1.47	0.1673
30	0.029	1.725	0.2367
37 $\frac{1}{2}$	0.025	2.00	0.3010

 $\text{Ph}_2\text{C=O/PhNMe}_2/\text{Acetonitrile}$ 

7 $\frac{1}{2}$	0.038	1.315	0.1189
15	0.028	1.785	0.2516
22 $\frac{1}{2}$	0.0205	2.44	0.3874
30	0.015	3.34	0.5237
37 $\frac{1}{2}$	0.0115	4.35	0.6385

TABLE 1 continued. $\text{Ph}_2\text{C=O}/\text{Ph}_2\text{CHOH}/\text{Benzene}$ 

time	A	$\frac{A_0}{A}$	$\log_{10} \frac{A_0}{A}$
$7 \frac{1}{2}$	0.036	1.39	0.1130
15	0.027	1.852	0.2676
$22 \frac{1}{2}$	0.019	2.637	0.4211
30	0.013	3.843	0.5846
$37 \frac{1}{2}$	0.01	5.00	0.6990

 $\text{Ph}_2\text{C=O}/i\text{PrOH}$ 

15	0.029	1.725	0.2367
30	0.0175	2.86	0.4564
45	0.0105	4.76	0.6776

 $\text{Ph}_2\text{C=O}/\text{Ph}_2\text{NMe}$ 

$7 \frac{1}{2}$	0.039	1.28	0.1072
15	0.033	1.52	0.1818
$22 \frac{1}{2}$	0.027	1.85	0.2672
30	0.0225	2.22	0.3464
$37 \frac{1}{2}$	0.0185	2.70	0.4314

 $\text{Ph}_2\text{C=O}/\text{N-methylcarbazole}$ 

$7 \frac{1}{2}$	0.045	1.11	0.0453
15	0.0405	1.235	0.0916
$22 \frac{1}{2}$	0.037	1.350	0.1303
30	0.0335	1.493	0.1741
$37 \frac{1}{2}$	0.030	1.665	0.2214

TABLE 1 continued $\text{Ph}_2\text{C=O/Ph}_2\text{NCH}_2\text{Ph}$ 

time	A	$\frac{A_0}{A}$	$\log_{10} \frac{A_0}{A}$
7 $\frac{1}{2}$	0.046	1.087	0.0363
15	0.042	1.190	0.0916
22 $\frac{1}{2}$	0.039	1.28	0.1303
30	0.036	1.39	0.1741
37 $\frac{1}{2}$	0.032	1.47	0.2214

 $\text{Ph}_2\text{C=O/N-benzylcarbazole}$ 

7 $\frac{1}{2}$	0.047	1.063	0.0265
15	0.045	1.11	0.0453
22 $\frac{1}{2}$	0.0425	1.177	0.0708
30	0.040	1.25	0.0969
37 $\frac{1}{2}$	0.038	1.315	0.1189

 $\text{Xanthone/PhNMe}_2$ 

7 $\frac{1}{2}$	0.0415	1.11	0.0453
15	0.0405	1.235	0.0916
22 $\frac{1}{2}$	0.0365	1.370	0.1367
30	0.033	1.515	0.1804
37 $\frac{1}{2}$	0.030	1.67	0.2227

TABLE 1 continuedXanthone/ $\text{Ph}_2\text{NMe}$ 

time	A	$\frac{A_0}{A}$	$\log_{10} \frac{A_0}{A}$
7 $\frac{1}{2}$	0.043	1.162	0.0653
15	0.0375	1.332	0.1245
22 $\frac{1}{2}$	0.0335	1.492	0.1738
30	0.033	1.515	0.1804
37 $\frac{1}{2}$	0.030	1.67	0.227

Xanthone/ $\text{Ph}_2\text{NCH}_2\text{Ph}$ 

7 $\frac{1}{2}$	0.048	1.040	0.0170
15	0.046	1.088	0.0367
22 $\frac{1}{2}$	0.0435	1.150	0.0607
30	0.0415	1.205	0.0809
37 $\frac{1}{2}$	0.040	1.250	0.0969

## Xanthone/N-Methylcarbazole

7 $\frac{1}{2}$	0.046	1.088	0.0367
15	0.0425	1.177	0.0708
22 $\frac{1}{2}$	0.040	1.250	0.0969
30	0.0375	1.335	0.1255
37 $\frac{1}{2}$	0.0355	1.408	0.1485

TABLE 1 continued

## Xanthone/N-Benzylcarbazole

time	A	$\frac{A_0}{A}$	$\log_{10} \frac{A_0}{A}$
7 $\frac{1}{2}$	0.0485	1.03	0.0128
15	0.047	1.063	0.0265
22 $\frac{1}{2}$	0.0455	1.098	0.0408
30	0.0445	1.122	0.0500
37 $\frac{1}{2}$	0.0435	1.15	0.0607

Fluorenone/PhNMe<sub>2</sub>

7 $\frac{1}{2}$	0.0385	1.30	0.1139
15	0.0285	1.755	0.2442
22 $\frac{1}{2}$	0.0205	2.44	0.3874
30	0.014	3.57	0.5527
37 $\frac{1}{2}$	0.0085	5.88	0.7694

Fluorenone/Ph<sub>2</sub>NMe

7 $\frac{1}{2}$	0.0445	1.122	0.050
15	0.040	1.25	0.0969
22 $\frac{1}{2}$	0.037	1.35	0.1303
30	0.0345	1.45	0.1614
37 $\frac{1}{2}$	0.032	1.563	0.1939



TABLE 1 continuedFluorenone/ $\text{Ph}_2\text{NCH}_2\text{Ph}$ 

time	A	$\frac{A_0}{A}$	$\log_{10} \frac{A_0}{A}$
$7 \frac{1}{2}$	0.0455	1.123	0.0503
15	0.0400	1.25	0.0969
$22 \frac{1}{2}$	0.035	1.43	0.1553
30	0.0305	1.64	0.2148
$37 \frac{1}{2}$	0.027	1.85	0.2672

## Fluorenone / N-methylcarbazole

Reaction too slow to be followed.

## Fluorenone / N-benzylcarbazole

$7 \frac{1}{2}$	0.0465	1.075	0.0315
15	0.043	1.162	0.0652
$22 \frac{1}{2}$	0.0395	1.267	0.1028
30	0.036	1.389	0.1428
$37 \frac{1}{2}$	0.0325	1.54	0.1875

## Xanthone/iPROH

15	0.0455	1.10	0.0414
30	0.042	1.19	0.0755
45	0.0395	1.267	0.1028
60	0.0367	1.36	0.1335

against time were drawn and the relative reactivities were worked out.

### Energy Transfer Studies.

#### Determination of $\phi_{\text{actinometer}}$ .<sup>15</sup>

The actinometer consisted of 0.1M benzhydrol and 0.05M benzophenone in benzene. Varying concentrations of benzhydrol were photolysed with 0.05M benzophenone, the progress of the reaction being noted by following the decrease in the carbonyl absorption band as before. Assuming that the same amount of light is absorbed by all the samples, the ratio of the concentrations of benzophenone photolysed in the actinometer and the samples will be in the ratio of their quantum yields. The results of such a series of photolyses are given in the following table.

M $\text{Ph}_2\text{CHOH}$	$\frac{1}{\text{Ph}_2\text{CHOH}}$	$\frac{\phi_{\text{act.}}}{\phi_{\text{sample}}}$
0.03	12.5	1.27
0.05	20	1.6
0.03	33	1.91
0.01	100	4.09

A plot of the reciprocal of the benzhydrol concentration against  $\frac{\phi_{\text{act}}}{\phi_{\text{sample}}}$ , shown on the graph overleaf (fig.3)

gave a straight line, intercept = 0.9. The value of  $\phi_{\text{actinometer}}$  is thus 0.9.

Figure 3. Determination of  $\phi_{\text{actinometer}}$ 

The photoreduction of 0.05M benzophenone by 0.1M N,N-dimethylaniline in benzene was carried out in the presence of varying amounts of quencher, the progress of the reaction being followed as before. Graphs plotting the amount of benzophenone used against time were drawn (e.g. fig.4) and the normal Stern-Volmer plots were drawn (see the eariler section of results and discussion, pages 42 - 3) of  $\frac{\phi_{act}}{\phi_{quench}}$  against concentration of quencher,

for the photoreduction after 15 and 45 minutes. The results are shown in the following tables and the Stern-Volmer plots are given on pages 42-3.

1. Quenching action of naphthalene on the photoreduction of benzophenone by N,N-dimethylaniline.

Naphthalene	$\frac{\phi_{act}}{\phi_{quench}}$	
	15 mins.	45 mins.
$10^{-4}M$	1.29	1.20
$10^{-3}M$	1.24	1.06
$5 \times 10^{-3}M$	1.44	1.24
$10^{-2}M$	1.64	1.45

15 minutes

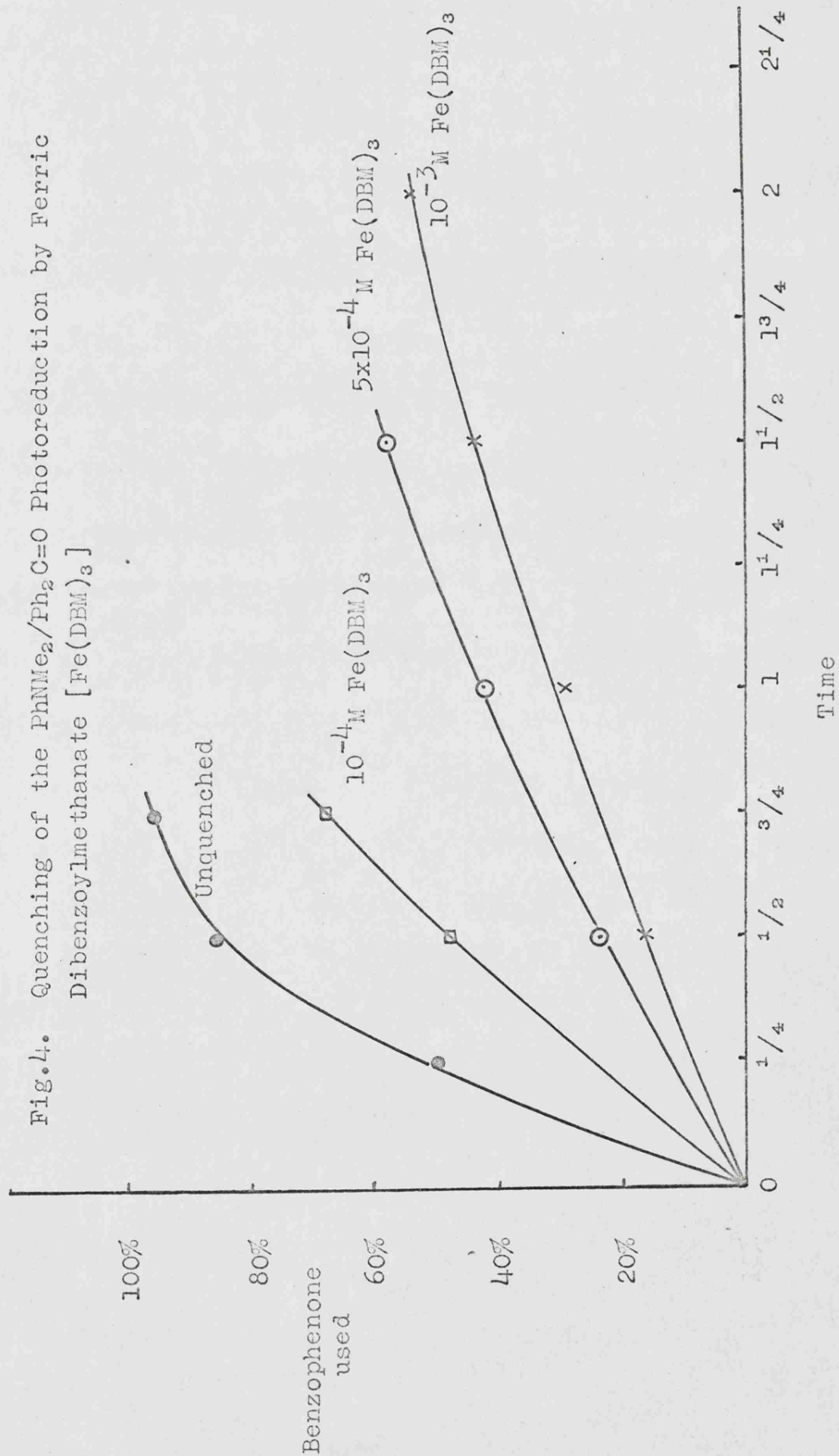
From the Stern-Volmer equation:

$$\frac{k_q}{k_r} = \frac{\text{slope} \times [\text{PhNMe}_2]}{\phi_{act} \times 1/a} = \frac{46 \times 0.1}{0.9 \times 1.8} = 4.35$$

45 minutes

$$\frac{k_q}{k_r} = \frac{42 \times 0.1}{0.9 \times 1.02} = 4.6$$

Fig. 4. Quenching of the  $\text{PhNMe}_2/\text{Ph}_2\text{C}=\text{O}$  Photoreduction by Ferric Dibenzoylemethane  $[\text{Fe}(\text{DBM})_3]$



The average value for  $\frac{k_q}{k_r} = 4.5$

2. Quenching action of naphthalene on the photoreduction of benzophenone by n-butylamine.

[Naphthalene]	$\frac{\phi_{act.}}{\phi_{quench.}}$	
	15 mins.	45 mins.
$10^{-3}M$	1.31	1.15
$3 \times 10^{-3}M$	2.06	1.84
$5 \times 10^{-3}M$	2.7	2.16

After 15 minutes:  $\frac{k_q}{k_r} = 41.5$

After 45 minutes:  $\frac{k_q}{k_r} = 24.0$

The average value for  $\frac{k_q}{k_r} = 32.8$

3. Quenching action of ferric acetylacetonate- $[Fe(acac)_3]$  on the photoreduction of benzophenone by  $N,N$ -dimethylaniline.

[ $Fe(acac)_3$ ]	$\frac{\phi_{act.}}{\phi_{quench}}$	
	15 mins.	45 mins.
$5 \times 10^{-4}$	1.53	1.28
$10^{-3}M$	1.64	1.42
$5 \times 10^{-3}M$	4.6	3.1
$7.5 \times 10^{-3}M$	5.1	3.4

After 15 minutes:  $\frac{k_q}{k_r} = 43.5$ . After 45 minutes  $\frac{k_q}{k_r} = 32$ .

The average value for  $\frac{k_q}{k_r} = 38$ .

4. Quenching action of ferric dibenzoylmethanate- $[\text{Fe}(\text{DBM})_3]$  on the photoreduction of benzophenone by N,N-dimethylaniline.

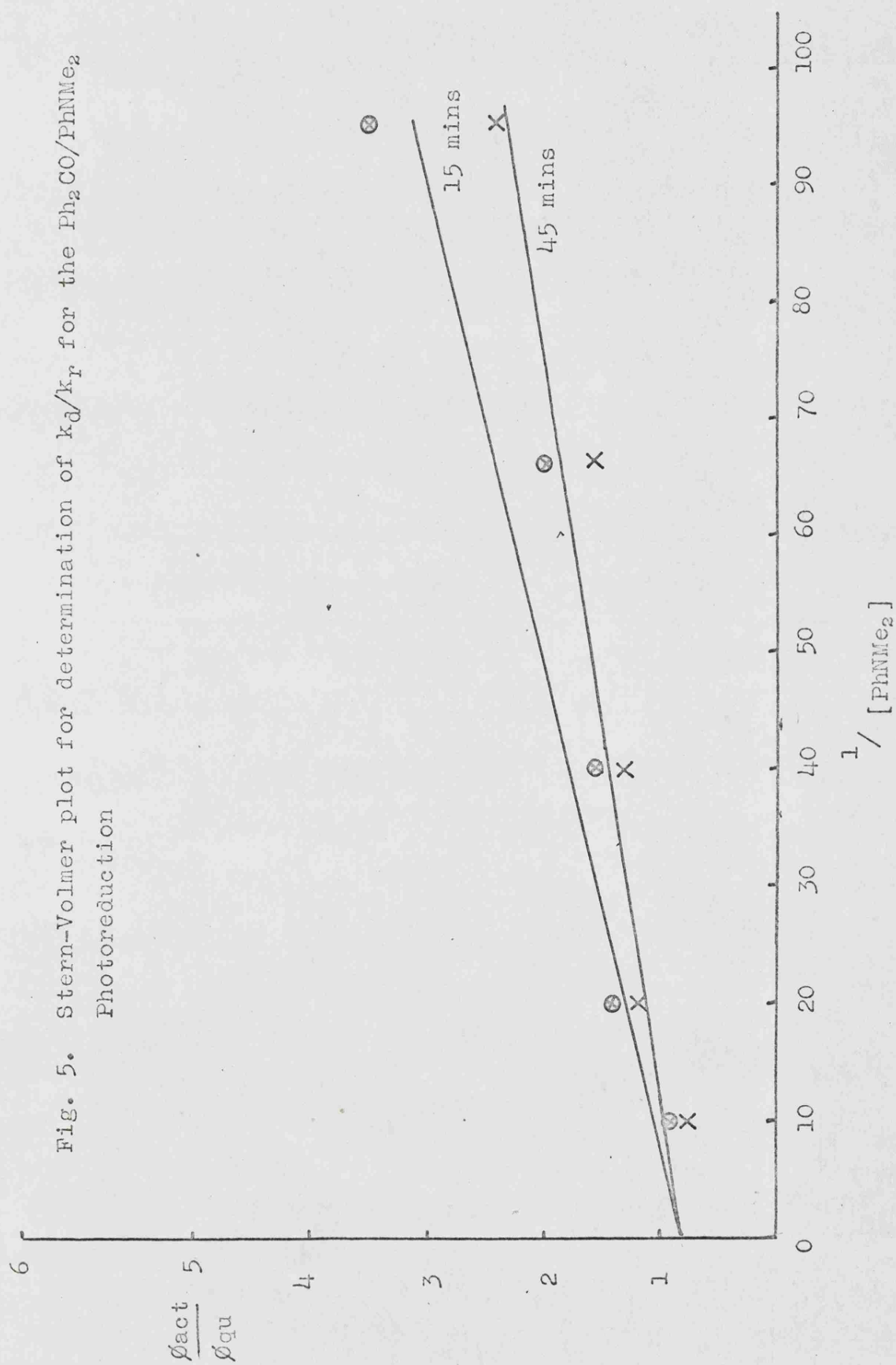
$[\text{Fe}(\text{DBM})_3]$	$\frac{\phi_{\text{act.}}}{\phi_{\text{quench.}}}$	
	15 mins.	45 mins.
$10^{-4}\text{M}$	1.84	1.32
$5 \times 10^{-4}\text{M}$	3.83	2.63
$10^{-3}\text{M}$	5.75	3.75

Determination of  $\frac{k_d}{k_r}$  for the photoreduction of benzophenone

by N,N-dimethylaniline.

The photoreduction of 0.05M benzophenone by varying concentrations of N,N-dimethylaniline in benzene was carried out following the progress of the reaction in the customary manner. A Stern-Volmer plot of  $\frac{\phi_{\text{act.}}}{\phi_{\text{sample}}}$

versus the reciprocal of N,N-dimethylaniline concentration was drawn (fig.5) from the results given in the following table.





[PhNMe <sub>2</sub> ]	$\frac{1}{[\text{PhNMe}_2]}$	$\frac{\phi_{\text{act.}}}{\phi_{\text{sample}}}$	
		15 mins.	45 mins.
0.1M	10	0.92	0.794
0.05M	20	1.395	1.22
0.025M	40	1.485	1.325
0.015M	66.6	1.97	1.58
0.01M	100	3.54	2.44

From the Stern-Volmer equation, in the absence of any quencher;

$$\frac{k_d}{k_r} = \frac{\text{slope} \times a}{\phi_{\text{act}}}$$

After 15 minutes:  $\frac{k_d}{k_r} = 0.0193$ . After 45 minutes

$\frac{k_d}{k_r} = 0.0294$ . The average value for  $\frac{k_d}{k_r} = 0.0243$ .

Quenching of the photoreduction of benzophenone by benzhydrol.

The quenching action of tertiary amines which do not contain abstractable hydrogen upon this system was studied in an analagous manner to the previous quenching investigations. The reaction being quenched was the photoreduction of 0.05M benzophenone by 0.1M benzhydrol. Stern-Volmer plots were drawn (pages 46 - 48) and the values of  $\frac{k_q}{k_r}$  were determined from the slope of the graphs.

1. Quenching by triphenylamine in benzene.

	$\frac{\phi_{\text{act.}}}{\phi_{\text{quench.}}}$	
[Ph <sub>3</sub> N]	15 mins.	45mins.
10 <sup>-3</sup> M	2.3	1.73
4 x 10 <sup>-3</sup> M	3.97	3.22
6 x 10 <sup>-3</sup> M	4.8	3.85
8 x 10 <sup>-3</sup> M	6.14	4.5
10 <sup>-2</sup> M	7.7	6.0

$$\frac{k_q}{k_r} \text{ after 15 minutes} = 43.5 \quad \frac{k_q}{k_r} \text{ after 45 minutes} = 44.5$$

$$\text{Average value for } \frac{k_q}{k_r} = 44$$

2. Quenching by triphenylamine in acetonitrile.

	$\frac{\phi_{\text{act.}}}{\phi_{\text{quench.}}}$	
[Ph <sub>3</sub> N]	15 mins.	45 mins.
10 <sup>-4</sup> M	3.84	2.64
5 x 10 <sup>-4</sup> M	7.68	5.0
10 <sup>-3</sup> M	15.3	10.5

$$\frac{k_q}{k_r} \text{ after 15 minutes} = 630 \quad \frac{k_q}{k_r} \text{ after 45 minutes} = 610$$

$$\text{Average value for } \frac{k_q}{k_r} = 620.$$

3. Quenching by tri-p-tolylamine (TPT) in benzene.

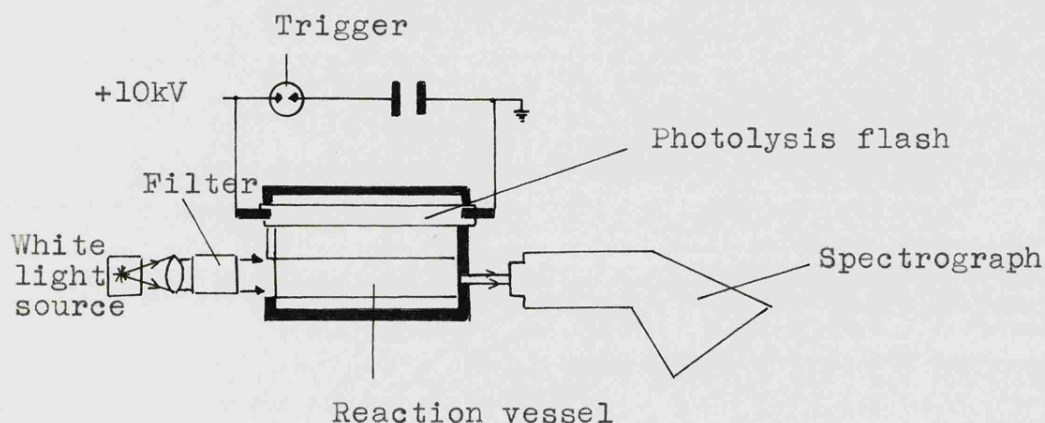
	$\frac{\phi_{\text{act}}}{\phi_{\text{quench}}}$	
[TPT]	15 mins.	45 mins.
$10^{-5}\text{M}$	1.48	1.32
$10^{-4}\text{M}$	2.19	1.77
$5 \times 10^{-4}\text{M}$	5.1	3.74

$$\frac{k_q}{k_r} \text{ after 15 minutes} = 560 \quad \frac{k_q}{k_r} \text{ after 45 minutes} = 492.$$

$$\text{Average value for } \frac{k_q}{k_r} = 525.$$

### Flash Photolysis of Amines and Benzophenone.

The flash photolysis unit was of conventional design, a diagram of such a unit being shown below<sup>135</sup>.



Xenon flash tubes having an output of 500 joules were used, the spectra being obtained on a Hilger spectrograph and recorded on either Ilford HP3 or Kodak IRER photographic plates. All solutions were  $10^{-2}$ M in amine and benzophenone and were contained in a quartz reaction vessel.

### Quenching of the Benzophenone/Benzhydrol Photoreduction by Trivalent Phosphorus Compounds.

The effect of trivalent phosphorus compounds on this photoreduction was investigated in a similar manner to that employed in the case of triphenylamine. Solutions containing 0.05M benzophenone, 0.1M benzhydrol and varying concentrations of triphenylphosphine or trimethylphosphite in benzene or acetonitrile were degassed by 4 freeze-thaw-freeze cycles on a vacuum line and irradiated simultaneously on a 'merry-go-round' apparatus in a

Rayonet photochemical reactor. The incident light was 360nm and the reactions were stopped after 12 minutes in benzene and 20 minutes in acetonitrile.  $\frac{k_q}{k_r}$  values

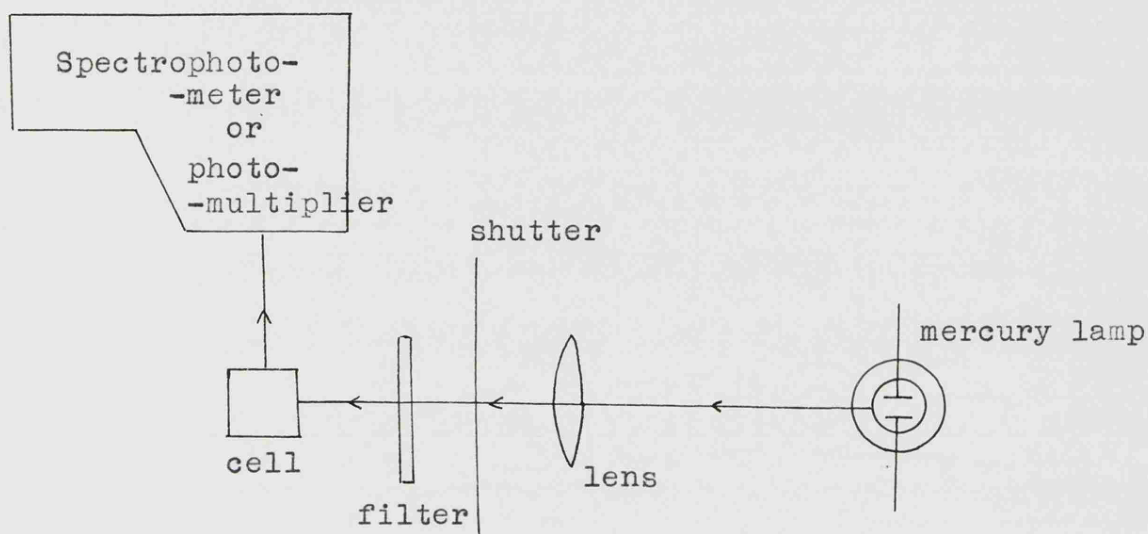
were determined from the slopes of the relevant Stern-Volmer plots shown on pages 58 - 59 drawn from the results which appear in Table II.

TABLE II

Quencher	Solvent	Conc.	$\frac{\phi_{act.}}{\phi_{quench.}}$
Triphenylphosphine	Benzene	$10^{-3}M$	1.24
		$2 \times 10^{-3}M$	1.66
		$5 \times 10^{-3}M$	2.74
Triphenylphosphine	Acetonitrile	$5 \times 10^{-4}M$	1.22
		$10^{-3}M$	1.36
		$2 \times 10^{-3}M$	1.72
Trimethylphosphite	Benzene	$10^{-3}M$	1.12
		$2 \times 10^{-3}M$	1.42
		$5 \times 10^{-3}M$	2.20
Trimethylphosphite	Acetonitrile	$5 \times 10^{-4}M$	1.12
		$10^{-3}M$	1.24
		$2 \times 10^{-3}M$	1.52

### Fluorescence Quenching Experiments.

Fluorescence quenching was investigated using a Baird Atomic Fluorispec SF 100E instrument. A simplified diagram showing the experimental arrangement for the measurement of relative fluorescence intensities follows.



Solutions of biacetyl ( $10^{-2}M$ ), fluorenone ( $2 \times 10^{-3}M$ ) and anthracene ( $10^{-5}M$ ) were made up in nitrogen bubbled solvents containing varying concentrations of quenchers and the fluorescence intensity was determined. The exciting wavelengths used were: biacetyl 420nm, fluorenone 400nm, anthracene 366nm. Stern-Volmer plots of  $\frac{Q_0}{Q}$  against quencher concentration were drawn (pages 60 - 67) and the values of the Stern-Volmer quenching constant,  $K_q$  were obtained from the slopes of the graphs.

Determination of the Relative Quantum Yields of Anthracene Fluorescence in Benzene and Acetonitrile.

This was done by comparing the fluorescent intensity of a  $10^{-5}$ M solution of anthracene in the two solvents with that of a standard solution of quinine sulphate in 0.1N sulphuric acid. The concentration of the standard solution was arranged so as to have the same absorbance as the test solution. Ultra-violet spectra of  $5 \times 10^{-4}$ M solutions of anthracene in benzene and acetonitrile and quinine in 0.1N sulphuric acid were run and the absorbances at 366nm were measured. From these, the concentration of the standard for each solvent was calculated. The results are shown in Table III.

	Absorbance	Conc. of Quinine Standard
Quinine in 0.1NH <sub>2</sub> SO <sub>4</sub>	1.64	-
Anthracene in benzene	0.92	$7.074 \times 10^{-6}$ M in 0.1NH <sub>2</sub> SO <sub>4</sub>
Anthracene in CH <sub>3</sub> CN	1.16	$5.611 \times 10^{-6}$ M in 0.1NH <sub>2</sub> SO <sub>4</sub>

Comparison the fluorescence intensity of a  $10^{-5}$ M solution of anthracene in benzene or acetonitrile with the relevant standard gave the relative quantum yield of fluorescence.

Flash Photolysis of Triphenylphosphine and Anthracene.

A solution of  $10^{-2}$ M triphenylphosphine and  $10^{-2}$ M anthracene in nitrogen bubbled acetonitrile, upon flash photolysis showed only the formation of one transient

$\lambda_{\max}$  415nm. Porter and Wilkinson have shown that

triplet anthracene has an absorption maxima at 423nm in hexane and 425nm in ethylene glycol<sup>18</sup>.

Photolysis of Fluorenone in Triethylamine/Ethanol.

Fluorenone (1.8g. 0.01moles) was dissolved in 200ml. of a 1:1 mixture of triethylamine and ethanol and photolysed for 15 hours. The solvent mixture was removed under vacuum and the resulting light yellow oil was chromatographed on Spence type 'H' alumina deactivated with 6% by weight of water.

Elution with benzene gave a white solid which was recrystallised from benzene/60°-80° petrol to give white prisms of 9-hydroxy-9(NN-diethyl-1-methylethylamino)-fluorene.

Yield: 0.2g. (10% theory)

m.p. 128-9°C

I.R.  $\nu_{\max}$  1210, 1060, 780, 740  $\text{cm}^{-1}$

N.M.R. 9.6 $\tau$  3 hydrogen doublet

8.8 $\tau$  6 hydrogen triplet

7.4 $\tau$  }  
6.75 $\tau$  } 5 hydrogens in 2 overlapping quartets.

4.2 $\tau$  1 hydrogen broad singlet

2.55 $\tau$  8 hydrogen multiplet

Analysis: C.81.11, H.8.36, N.5.04% (Calculated for  $\text{C}_{19}\text{H}_{23}\text{NO}$  C.81.10, H 8.24, N.4.98%)

$m/e$  281, 181, 164, 152, 100.

Elution with 10% ether in benzene gave 9-hydroxyfluorene, recrystallised with difficulty from a minimum amount of 60°-80° petrol.



Yield: 0.55g. (31% theory)

m.p. and mmp. 152-3°C.

Elution with ether gave fluoropinacol, recrystallised from ethanol.

Yield: 0.5g. (28% theory)

m.p. and mmp. 190-1°C.

The same procedure was followed for the photolysis of fluorenone in triethylamine/isopropanol mixture (1:1) and fluorenone in triethylamine/ethanol/water mixture (7:2:7). The products obtained were shown in the table on page 77.

#### Photolysis of Fluorenone in Triethylamine/Water.

75ml. of triethylamine and 75ml. of water were mixed and allowed to stand for 24 hours with occasional shaking to facilitate equilibration. Fluorenone (1.4g. 0.08 moles) was dissolved in the mixture which was photolysed for 24 hours. The solvents were removed under vacuum, benzene was added to the mixture and this was also removed under vacuum to azeotrope off as much of the water as possible. The resulting oil was chromatographed on Spence type 'H' alumina.

Elution with 40-60° petrol gave colourless crystals.

Yield: 0.08g.

m.p. 244-6°C.

I.R.  $\nu_{\max}$  750, 740  $\text{cm}^{-1}$ .

This is probably 9,9'-bifluorene which has been reported

as having a similar melting point<sup>134</sup>,

Elution with benzene gave 9-hydroxy-9-(NN-diethyl-1-methylethyl-amino)-fluorene.

Yield: 0.3g. (21% theory)

m.p. 128-9°C.

Elution with 10% ether in benzene gave 9-hydroxyfluorene.

Yield: 0.4g. (29% theory)

m.p. and mmp. 152-4°C.

#### Photolysis of Benzophenone in Triethylamine/Ethanol.

Benzophenone (1.8g. 0.01 moles) was dissolved in 200 ml, of a 1:1 mixture of triethylamine and ethanol and photolysed for 2 hours. The solvents were removed under vacuum and the white residual solid was fractionally crystallised from ethanol to give benzpinacol.

Yield: 1.1g. (61% theory)

m.p. and mmp. 185-6°C.

#### Photolysis of Benzophenone in n-Butylamine/Water.

Benzophenone (1.8g. 0.01 moles) was dissolved in 200ml. of a 1:1 mixture of n-butylamine and water which had been left to equilibrate for 24 hours. The mixture was photolysed for 3 hours and the white crystals which formed were filtered off and recrystallised from ethanol. This was benzpinacol. The solvents were removed under vacuum and as much as possible of the water was azeotroped off with benzene. The resulting white solid was fractionally recrystallised from ethanol to give benzpinacol.

Total Yield: 0.9g. (50% theory)

m.p. and mmp. 184-6°C

Photolysis of Benzophenone in sec-Butylamine/Water.

Benzophenone (3.65g. 0.045 moles) was dissolved in a mixture of 120 ml. of water and 80 ml. of sec-butylamine and photolysed for 12 hours. The precipitate which formed was filtered off and recrystallised from ethanol to give benzpinacol. The solvents were removed under vacuum, azeotroping off as much water as possible and the resulting solid was fractionally recrystallised from ethanol yielding:

1) Benzpinacol. Total Yield: 2.4g. (73% theory)

m.p. and mmp 185-6°C.

2) Benzhydrol. Yield: 0.3g. (8% theory)

m.p. and mmp 69°C.

Photolysis of p-Phenylbenzophenone in Triethylamine/Ethanol.

p-Phenylbenzophenone (2.6g. 0.01 moles) was dissolved in 200 ml. of a 1:1 mixture of triethylamine and ethanol and photolysed for 2 hours. The solvents were removed under vacuum and the resulting white solid was recrystallised from a mixture of acetone and chloroform to give p,p'-diphenylbenzpinacol.

Yield: 2.1g. (80% theory)

m.p. 197-9°C.

Photolysis of p-Phenylbenzophenone and Triethylamine/Water.

p-Phenylbenzophenone (1.3 g. 0.005 moles) was dissolved in 200ml. of a 1:1 mixture of triethylamine and water which had been previously left to equilibrate for 24 hours. The solution was photolysed for 9 hours and the precipitate which formed was filtered off and recrystallised from a mixture of acetone and chloroform to give p,p'-diphenylbenzopinacol.

Yield: 0.4 g. (31% theory)

m.p. 197-8°C.

Photolysis of 2-Acetylnaphthalene in Triethylamine/Ethanol.

2-Acetylnaphthalene (1.3g. 0.075 moles) was dissolved in 150 ml. of a 1:1 mixture of triethylamine and ethanol and photolysed for 24 hours. The solvents were removed under vacuum and the resulting oil was chromatographed on Spence type 'H' alumina. Only one fraction gave any solid product. Elution with 25% ether in benzene gave a white solid which was recrystallised from benzene/60-80° petrol to give the pinacol.

Yield: 0.5g. (38% theory)

m.p. 174-5°C.

Preparation of Phenyl p-Tolyl Ketone.

A 500ml. 3 necked flask was fitted with a condenser, a stirrer and a dropping funnel. Anhydrous aluminium chloride (10g. 0.075 moles) was suspended in 250ml.

of sodium dried toluene and benzoyl chloride (20g. 0.14 moles) was added dropwise to the stirred solution. After the initial reaction had subsided the mixture was boiled under reflux until the evolution of hydrogen chloride had ceased (4 hours). After cooling, 500ml. of water were added and the toluene layer was separated and washed with sodium carbonate solution and water before drying with anhydrous sodium sulphate. The toluene was removed under vacuum and the resulting oil was left to crystallise in a refrigerator overnight. The phenyl p-toly ketone was finally recrystallised from 60-80° petrol.

Yield: 25.2g. (89% theory)

m.p. 56°C (Lit.m.p. 59°C)<sup>136</sup>.

Conversion of Phenyl p-Toly Ketone to p-Benzoylbenzoic Acid.

Phenyl p-toly ketone (25g. 0.13 moles) was dissolved in 150 ml. of glacial acetic acid under reflux. Chromic oxide (35 g. 0.23 moles) was dissolved in a mixture of 80 ml. water, 130 ml. glacial acetic and 25 ml. concentrated sulphuric acid and added to the ketone solution dropwise to maintain a steady rate of reflux. After the addition the mixture was boiled under reflux for 15 minutes and then poured into 500 ml. of water. The precipitate was filtered off, washed with water until white and suspended in hot water. A 10% solution of potassium hydroxide was added to dissolve as much of the precipitate as possible and that remaining undissolved was filtered off.

The filtrate was acidified with concentrated hydrochloric acid and the precipitated p-benzoylbenzoic acid was recrystallised twice from ethanol.

Yield: 19.3g. (67% theory)

m.p. 198-9°C (Lit.m.p. 197-200°C)<sup>137</sup>.

Photolysis of p-Benzoylbenzoic Acid in Triethylamine/Water<sup>98</sup>.

p-Benzoylbenzoic acid (2.26 g. 0.01 moles) and triethylamine (2.0 g. 0.02 moles) were dissolved in 200 ml. of water and photolysed for 24 hours. The solution was made acid with 2N hydrochloric acid and extracted with ether (3 x 50 ml.). The ether extract was washed with water and dried with anhydrous sodium sulphate before removal of the ether. The remaining white solid was recrystallised twice from ethanol to give phenylp-carboxy-phenylmethanol as colourless prisms.

Yield: 1.4g. (62% theory)

m.p. 155-6°C (Lit. m.p. 164-5°C)<sup>98</sup>.

Preparation of Tri-n-butylstannane.

A 500ml. 3 necked flask was equipped with a nitrogen inlet, dropping funnel and reflux condenser and mounted on a magnetic stirrer. 150ml. of sodium dried ether was put into the flask and lithium aluminium hydride (1.8g. 0.05 moles) was carefully added. To the stirred suspension was added dropwise tri-n-butylchlorostannane (15g. 0.045 moles) and the reaction mixture was heated under reflux for 5 hours. After cooling, quinol

(0.5g. 0.045 moles), 12 ml. of water and 150 ml. of 20% sodium potassium tartrate solution were carefully added. The ether layer was separated, washed with water and dried with anhydrous sodium sulphate. The ether was removed under vacuum and the resulting liquid was distilled under reduced pressure of nitrogen, tri-n-butylstannane being collected between 98-102°C at 1.5 mm.Hg. (Lit. value 68-74°C at 0.3mm.Hg.). It was kept under nitrogen at -50°C.

Yield: 9.3g. (69% theory)

#### Photolysis of Benzophenone and Tetra-n-butylstannane.

Benzophenone (1.36g. 0.0075 moles) and tetra-n-butylstannane (5.2g. 0.015 moles) were dissolved in 150 ml. of benzene and photolysed for 3 hours. The benzene was removed under vacuum and the resulting oil was triturated with 40-60° petrol. The white solid thus produced was filtered off and recrystallised from ethanol to give colourless prisms of benzpinacol.

Yield: 1.02g. (75% theory)

m.p. and mmp. 185-6°C.

#### Photolysis of Benzophenone and Tri-n-butylstannane.

Benzophenone (1.36g. 0.0075 moles) and tri-n-butylstannane (4.35g. 0.015 moles) were dissolved in 150 ml. of benzene and photolysed for  $\frac{1}{2}$  hour. The reaction mixture was worked up in a similar manner to the previous experiment giving benzpinacol.

Yield: 1.15g. (85% theory)

m.p. and mmp 184-5°C.

Photolysis of Xanthone and Tetra-n-butylstannane.

Xanthone (1.47g. 0.0075 moles) and tetra-n-butylstannane (5.2g. 0.015 moles) were dissolved in 150 ml. of benzene and photolysed for 7 hours. Removal of solvent, trituration with 40-60° petrol and recrystallisation from toluene gave xanthopinacol.

Yield: 0.65g. (45% theory)

m.p. and mmp. 184-6°C.

Photolysis of Xanthone and Tri-n-butylstannane.

Xanthone (0.6g. 0.003 moles) and tri-n-butylstannane (1.8g. 0.006 moles) were dissolved in 60 ml. of benzene and photolysed for 7 hours. Removal of the benzene and trituration gave a white solid. Infra-red evidence suggested that this was a mixture of xanthopinacol and xanthyrol, by comparison with a spectrum of a known mixture.

Yield: 0.27g. (45% theory)

m.p. 103-9°C.

An attempt was made to separate the mixture by chromatography but the attempt failed.

Photolysis of Fluorenone and Tetra-n-butylstannane.

Fluorenone (1.35g. 0.0075 moles) and tetra-n-butylstannane (5.2g. 0.015 moles) were dissolved in benzene



and photolysed. Infra-red evidence after 8 hours photolysis showed that no photoreduction had taken place as signified by the intensity of the carbonyl absorption.

Photolysis of Fluorenone and Tri-n-butylstannane.

Fluorenone (1.35g. 0.0075 moles) and tri-n-butylstannane (4.35g. 0.015 moles) were dissolved in 150 ml. of benzene and photolysed for 6 hours. The reaction was worked up in the usual manner to give fluoropinacol recrystallised from ethanol.

Yield: 0.75g. (56% theory)

m.p. and mmp 190-1°C.

Determination of the Relative Reactivities of Tetra-n-butyl and Tri-n-butylstannane.

This was done using the same technique as that employed in the determination of the relative reactivities of the amines outlined earlier. A 0.05M solution of benzophenone and 0.1M stannane in benzene was photolysed and the progress of the reaction was monitored by following the disappearance of the carbonyl absorption in the infra-red. Plots of  $\log_{10} \frac{[A_0]}{[A]}$  were drawn as

before (fig. 6) and the slopes of the graphs gave the relative reactivities of the stannanes. Table IV shows the values obtained for  $\log_{10} \frac{[A_0]}{[A]}$ .

TABLE IV $\text{Ph}_2\text{C}=\text{O}/\text{n-Bu}_4\text{Sn}.$ 

time (mins.)	A	$\frac{[\text{A}_0]}{[\text{A}]}$	$\log_{10} \frac{[\text{A}_0]}{[\text{A}]}$
$7\frac{1}{2}$	0.043	1.163	0.0656
15	0.037	1.35	0.1303
$22\frac{1}{2}$	0.032	1.562	0.1937
30	0.028	1.785	0.2516
$37\frac{1}{2}$	0.025	2.00	0.3010
45	0.023	2.175	0.3375

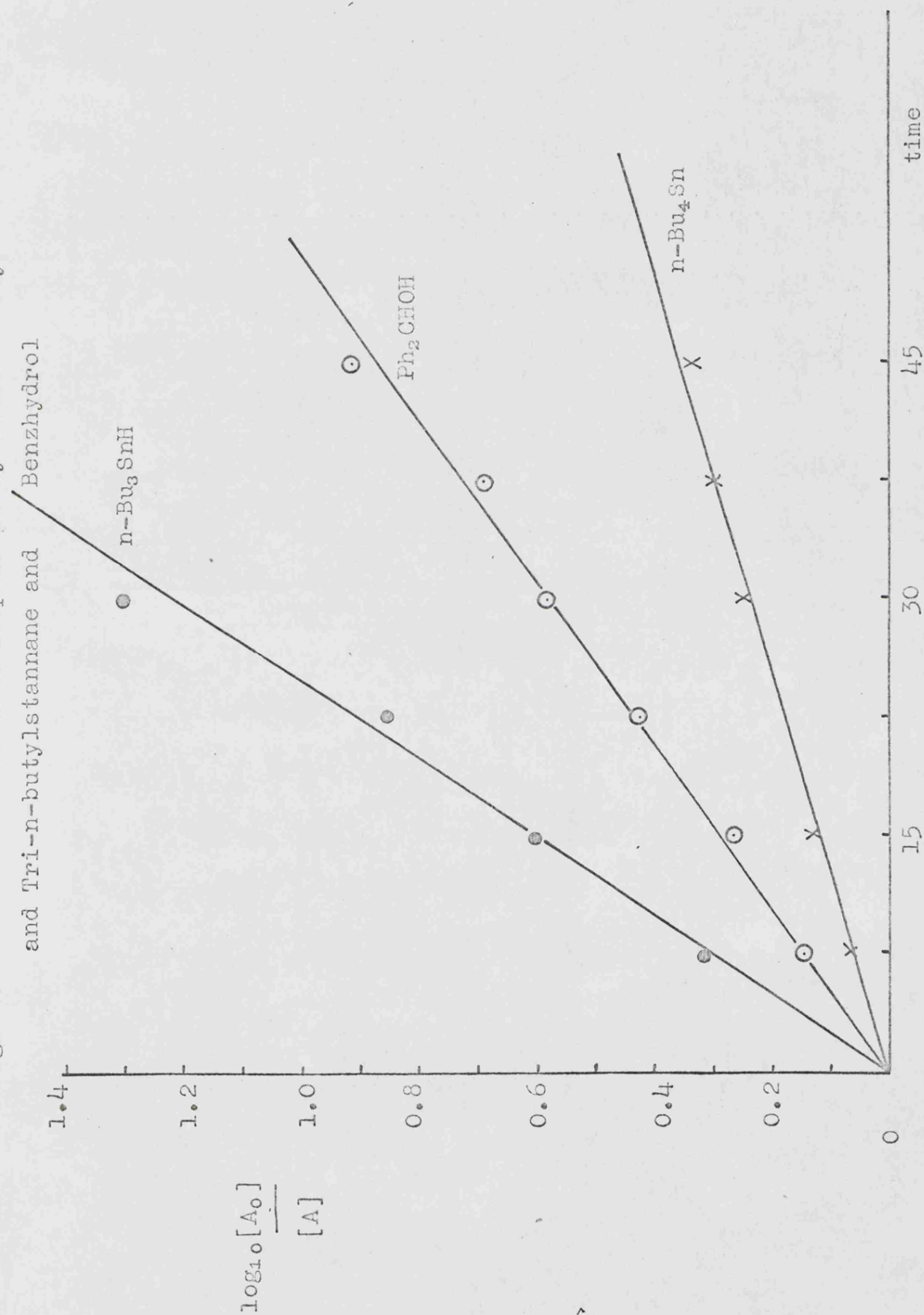
 $\text{n-Bu}_3\text{SnH}/\text{Ph}_2\text{C}=\text{O}$ 

$7\frac{1}{2}$	0.024	2.082	0.3185
15	0.0125	4.00	0.6021
$22\frac{1}{2}$	0.007	7.15	0.8543
30	0.0025	20.0	1.3010

 $\text{Ph}_2\text{CHOH}/\text{Ph}_2\text{C}=\text{O}$ 

$7\frac{1}{2}$	0.036	1.39	0.1430
15	0.027	1.852	0.2676
$22\frac{1}{2}$	0.0185	2.70	0.4314
30	0.013	3.843	0.5846
$37\frac{1}{2}$	0.01	5.00	0.6990
45	0.006	8.333	0.9208

Fig. 6. Photoreduction of Benzophenone by Tetra-*n*-butyl  
and Tri-*n*-butylstannane and Benzhydrol



Photoreduction of Benzophenone by Benzhydrol in the Presence of Tetra-phenylstannane.

A solution consisting of 0.05M benzophenone, 0.1M benzhydrol and 0.001M tetra-phenylstannane was photolysed, and the progress of it was recorded in the normal manner. Comparison with the progress of an unquenched reaction showed that the tetra-phenylstannane had little effect.

Photolysis of Tri-n-butylstannane and 1-Naphthaldehyde.

Tri-n-butylstannane (2.9g. 0.01 moles) and 1-naphthaldehyde (0.8g. 0.005 moles) were dissolved in 100 ml. of benzene and photolysed for 24 hours in a 'Rayonet' photochemical reactor with light of 360nm. The white precipitate which had formed was filtered off and the residual oil, after solvent removal was chromatographed on Spence type 'H' alumina.

Elution with 40-60° petrol gave unchanged tri-n-butylstannane.

Yield: 1.5g. (52% recovery)

Elution with 10% ether in benzene gave two fractions, both of which were recrystallised from benzene/60-80° petrol to give the two isomers of the pinacol as detailed earlier. The melting point of 1,2-di-(1-naphthyl)-ethane-1,2-diol given by Hammond is 185-6°C<sup>31</sup> which is slightly higher than either of those obtained for the different isomers. A mixed melting point showed considerable depression.

Fraction 1 is the dl- pinacol.

Yield: 0.25g. (31% theory)

m.p. 183-5°C.

I.R.  $\nu_{\max}$  3360, 1060, 770  $\text{cm}^{-1}$ .

N.M.R. 5.34 $\tau$  1 hydrogen broad singlet

5.63 $\tau$  1 hydrogen singlet

2.52 $\tau$  7 hydrogen multiplet

Fraction 2 is the meso- pinacol.

Yield: 0.17g. (22% theory)

m.p. 180°C.

I.R.  $\nu_{\max}$  3540, 1050, 1030, 810, 780  $\text{cm}^{-1}$ .

N.M.R. 7.0 $\tau$  1 hydrogen broad singlet

4.24 $\tau$  1 hydrogen singlet

2.5 $\tau$  7 hydrogen multiplet

The white precipitate originally filtered off was insoluble in all organic solvents and had a very high melting point. It was thought to be polydibutyltin oxide, originally identified by Trotter and Testa<sup>104</sup> since a nuclear magnetic resonance spectrum showed only aliphatic protons in the ratio methyl:methylene of 1:2.

Yield: 0.2g.

m.p. 350°C

I.R.  $\nu_{\max}$  1070, 665  $\text{cm}^{-1}$

N.M.R. (in  $\text{CF}_3\text{COOH}$ ) 9.0 $\tau$  1 proton

asymmetric triplet poorly resolved.

8.33 $\tau$  2 proton multiplet.

The photolysis was repeated using incident light at 313nm, but after 48 hours no photoreduction had taken place as shown by the intensity of the infra-red carbonyl absorption band so a 100 watt medium pressure mercury arc fitted with a pyrex sleeve was employed and the photolysis was continued for a further 18 hours. The precipitated polydibutyltin oxide was filtered off and the benzene was removed under vacuum. The residual oil was chromatographed as before.

Elution with 40-60° petrol gave unchanged tri-n-butylstannane.

Yield: 1.9g. (65% recovery)

Elution with benzene gave 1-naphthylcarbinol recrystallised from 60-80° petrol as colourless needles.

Yield: 0.15g. (19% theory)

m.p. 59-61°C (Lit.m.p. 60-61°C)<sup>31</sup>.

I.R.  $\nu_{\max}$  3320, 1160, 1000, 790cm<sup>-1</sup>

N.M.R. 7.85 $\tau$  1 hydrogen broad singlet

5.12 $\tau$  2 hydrogen singlet

2.32 $\tau$  7 hydrogen multiplet.

Elution with 5% ether in benzene gave the dl- isomer of 1,2-di-(1-naphthyl)-ethane-1,2-diol.

Yield: 0.1g. (12.5% theory)

m.p. 183-4°C.

Elution with 10% ether in benzene gave meso 1,2-di-(1-naphthyl)-ethane-1,2-diol.

Yield: 0.25g. (31% theory)

m.p. 180°C.

Photolysis of 2-Acetylnaphthalene and Tri-n-butylstannane.

2-Acetylnaphthalene (0.85g. 0.005 moles) and tri-n-butylstannane (2.9g. 0.01 moles) were dissolved in 100 ml. of benzene and photolysed for 24 hours using light at 360nm. The precipitate of polydibutyltin oxide was filtered off and after removal of the benzene, the residual oil was chromatographed on alumina.

Elution with petrol gave unchanged tri-n-butylstannane.

Yield: 1.3g. (45% recovery)

Elution with benzene gave methyl-(2-naphthyl)-carbinol recrystallised from 60-80° petrol as colourless needles.

Yield: 0.15g. (18% theory)

m.p. 69-70°C (Lit. m.p. 72-3°C)<sup>31</sup>

I.R.  $\nu_{\max}$  3320, 1160, 1080, 860, 830,  
750  $\text{cm}^{-1}$ .

N.M.R. 8.5 $\tau$  3 proton doublet

7.9 $\tau$  1 proton broad singlet

4.95 $\tau$  1 proton quartet

2.2 $\tau$  7 proton multiplet

Elution with 25% ether in benzene gave the pinacol, 1,2-di-(2-naphthyl)-butan-1,2-diol from benzene/60-80° petrol as colourless prisms.

Yield: 0.35g. (41% theory)

m.p. 174-5°C.

Photolysis of Acetone and Tri-n-butylstannane.

Acetone (0.3g. 0.005 moles) and tri-n-butylstannane (2.9g. 0.01 moles) were dissolved in 100 ml. of benzene

and photolysed in a 'Rayonet' photochemical reactor using light of 310 nm. for 36 hours. The white precipitate of polydibutyltin oxide was filtered off and the products of the reaction were investigated using gas-liquid chromatography. Use of a Waters Associates porapak 'Type Q' column at 170°C and an injection temperature of approximately 180° showed that a compound with the same retention time as isopropanol was formed.

Yield: 86.5%

After removal of benzene from the reaction mixture distillation of the residue at 4.5mm.Hg. gave unchanged tri-n-butylstannane.

Yield: 0.95% (33% recovery)

b.p. 121-6°C at 4.5 mm.Hg.

#### Photolysis of Acetophenone and Tri-n-butylstannane.

Acetophenone (0.6g. 0.005 moles) and tri-n-butylstannane (2.9g. 0.01 moles) were dissolved in 100 ml. of benzene and photolysed at 210 nm for 36 hours. The white precipitate of polydibutyltin oxide was filtered off and a gas-liquid chromatography examination done under similar conditions to the previous experiment showed the formation of a product having the same retention time as 1-phenylethanol.

Yield: 73%

After removal of benzene, distillation gave unchanged tri-n-butylstannane.



Yield: 1.1g. (38% recovery)

b.p. 115-8°C at 3mm.Hg.

Photolysis of Benzaldehyde and Tri-n-butylstannane.

Benzaldehyde (0.6g. 0.005 moles) and tri-n-butylstannane (2.9g. 0.01 moles) were dissolved in 100ml. of benzene and photolysed at 310nm. for 35 hours. A sample taken for gas-liquid chromatography performed under the same conditions that were used previously, showed that no benzyl alcohol was formed in this case. The benzene was removed from the reaction mixture under vacuum and the resulting liquid was left in a refrigerator overnight. Colourless crystals were deposited which were filtered off, washed with 60-80° petrol and recrystallised from ethanol/chloroform.

Yield: 0.3g.

m.p. 193-4°C.

I.R.  $\nu_{\max}$  1060, 1010, 720, 700cm<sup>-1</sup>.

N.M.R. 8.75 $\tau$  9 proton multiplet

5.15 $\tau$  1 proton multiplet

2.95 $\tau$  5 proton multiplet

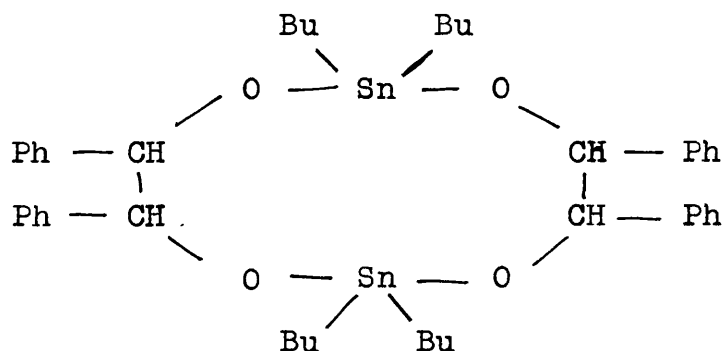
<sup>m</sup>/e >850 approx. 680 620 556. 515

383 342. (The counting in the upper limits is inaccurate).

Analysis. C.58.89, H.6.61, Sn 26.50% (Calculated for

C<sub>44</sub>H<sub>60</sub>O<sub>4</sub>Sn<sub>2</sub> C.59.46, H.6.75 Sn.26.58%)

The structure which best fits the above datae is the ring structure shown earlier.



The residues were distilled at 3mm.Hg. to give unchanged tri-n-butylstannane.

Yield: 2.3g. (79% recovery)

b.p. 101-4°C at 3mm.Hg.

#### Photolysis of Benzalacetophenone and NN-Dimethylaniline.

Benzalacetophenone (1.5g. 0.0075 moles) and NN-dimethylaniline (1.8g. 0.015 moles) were dissolved in benzene and photolysed for 17 hours. The reaction mixture was washed with 2N hydrochloric acid to remove unchanged amine and the benzene solution was washed with water and dried with anhydrous sodium sulphate. After removal of the benzene under vacuum, the resulting brown oil was chromatographed on Spence Type 'H' alumina.

Elution with 10% benzene in 40-60°C petrol gave unchanged benzalacetophenone as pale yellow crystals from a small amount of ethanol.

Yield: 0.6g. (40% recovery)

m.p. and mmp. 56-7°C

Elution with 25% benzene in petrol gave a white solid which was recrystallised from ethanol to give colourless needles of N-phenyl-N-methyl-2,4-diphenyl-1-amino-butan-4-one.

Yield: 0.34g. (14% theory)

m.p. 109-110°C.

I.R.  $\nu_{\max}$  1680, 1590, 1510, 740, 700cm<sup>-1</sup>.

N.M.R. 7.36 $\tau$  3 proton singlet

6.7 $\tau$  2 proton poorly resolved doublet

6.32 $\tau$  3 proton multiplet

2.67 $\tau$  15 proton broad multiplet

Analysis. C.83.79, H: 7.05, N.4.26% (Calculated for

C<sub>23</sub>H<sub>23</sub>NO: C.83.85, H.7.04, N.4.25%)

$m/e$  329, 210, 209, 106, 104.

#### Preparation of 9,10-Dihydroacridine.

This was prepared by the reduction of acridine by lithium aluminium hydride using the method of Bohlmann<sup>138</sup>. Colourless needles of 9,10-dihydroacridine were recrystallised from methanol.

Yield: 4.8g. (96% theory)

m.p. 170°C (Lit, m.p. 169°C)<sup>138</sup>.

#### Photolysis of Benzalacetophenone and 9,10-Dihydroacridine.

Benzalacetophenone (1.5g. 0.0075 moles) and 9,10-dihydroacridine (1.8g. 0.01 moles) were dissolved in 150ml. of benzene and photolysed for 17 hours. The white precipitate which formed was filtered off. Purification was found to be difficult since the precipitate was very insoluble and difficulty in finding a suitable solvent for recrystallisation hindered identification. On the basis of work by Kellman<sup>139</sup>, who found that photolysis of acridine gave 9,9',10,10',-tetrahydro-9,9'-

biacridine, the precipitate was recrystallised with difficulty from pyridine. It gave colourless prisms.

Yield: 0.8g. (45% theory)

m.p. 235-239°C.

I.R.  $\nu_{\max}$  3400, 1610, 1300, 760  $\text{cm}^{-1}$ .

The melting point was obtained using the method of Lehmstedt and Hundertmark<sup>140</sup>, by preheating the Kofler back to 230°C. and then raising the temperature slowly. The compound was shown to be identical to 9,9',10,10'-tetrahydro-9,9'-biacridine prepared by both a chemical and a photochemical method. After filtration, the benzene was removed under vacuum and the resulting oil was triturated with 40-60° petrol. The resulting white solid was recrystallised from ethanol chloroform giving colourless crystals of 1,3-diphenyl-1-(9-acridanyl)-propan-3-one.

Yield: 0.6g. (22% theory)

m.p. 181.5-182.5°C.

I.R.  $\nu_{\max}$  3400, 1680, 1600, 1290, 750, 700  $\text{cm}^{-1}$ .

N.M.R. (in  $d_6$ DMSO) 6.72 $\tau$  4 proton multiplet

5.85 $\tau$  1 proton broad

singlet

2.83 $\tau$  18 proton multiplet

Analysis. C.87.04, H.5.89, N.3.64% (Calculated for

$\text{C}_{28}\text{H}_{23}\text{NO}$ : C.86.34, H.5.95, N.3.60%)

The filtrate from the original trituration on standing deposited colourless platelets of truxinic ketone.

Yield: 0.15g. (10% theory)

m.p. 124-5°C. (Lit. m.p. 125°C)<sup>142</sup>

I.R.  $\nu_{\max}$  160, 1290, 1200, 780, 700  $\text{cm}^{-1}$ .

### Preparation of 9,9',10,10'-tetrahydro-9,9'-biacridine.

#### 1. Chemical Method.

9,9',10,10'-Tetrahydro-9,9'-biacridine was prepared by the method of Elliot and McGriff<sup>141</sup>. The crude material from the reaction mixture was extracted with pyridine for 3 days using a Soxhlet extractor and allowed to crystallise. The crystals were filtered off and recrystallised from pyridine.

Yield: 0.3g. (15% theory)

m.p. 242-4°C. (Lit.m.p. 247-8°C)<sup>141</sup>.

#### 2. Photochemical Method.

Acridine (1.3g. 0.0063 moles) and triethylamine (0.75g. 0.0075 moles) were dissolved in 150 ml. of benzene and photolysed for 17 hours. The white precipitate was filtered off and recrystallised from pyridine.

Yield: 0.4g. (31% theory)

m.p. 237-9°C.

All three samples of 9,9',10,10'-tetrahydro-9,9'-biacridine had identical infra-red spectra and the latter two did not depress the melting point of the compound obtained from the photolysis of benzalacetophenone and 9,10-dihydroacridine.

Photolysis of Benzalacetone and 9,10-Dihydroacridine.

Benzalacetone (1.1g. 0.0075 moles) and 9,10-dihydroacridine (1.8g. 0.01 moles) were dissolved in 150 ml. of benzene and photolysed for 16 hours. The white precipitate of 9,9',10,10'-tetrahydro-9,9'-biacridine was filtered off and recrystallised from pyridine.

Yield: 0.5g. (28% theory)

m.p. 236-9°C.

Removal of the benzene under vacuum gave a yellowish solid which was triturated with 40-60° petrol. The white solid remaining was filtered off and recrystallised ethanol to give unchanged 9,10-dihydroacridine.

Yield: 0.7g. (39% recovery)

m.p. and mmp. 169°C.

On standing the filtrate from the trituration in a refrigerator overnight it produced colourless crystals which were filtered off and recrystallised from ethanol. Colourless crystals of 1-phenyl-1-(9-acridanyl)-butan-3-one were formed.

Yield: 0.4g. (23% theory)

m.p. 178-9°C.

I.R.  $\nu_{\max}$  3350, 1700, 1600, 1290, 760,  
700  $\text{cm}^{-1}$ .

N.M.R. 8.1 $\tau$  3 proton singlet

7.25 $\tau$  2 proton doublet

5.84 $\tau$  2 proton multiplet

4.05 $\tau$  1 proton broad singlet

3.05 $\tau$  13 proton multiplet.

Analysis. C.83.59, H.6.27, N.4.31% (Calculated for  
 $C_{23}H_{21}NO$ : C. 84.37, H.6.47, N.4.28%)

Photolysis of Mesityl Oxide and 9,10-Dihydroacridine.

Mesityl oxide(0.75g. 0.0075 moles) and 9,10-dihydroacridine (1.8g. 0.015 moles) were dissolved in 150 ml. of benzene and photolysed for 13 hours. The precipitate of 9,9'-10,10'-tetrahydro-9,9'-biacridine was filtered off and recrystallised from pyridine.

Yield: 0.4g. (22% theory)

m.p. 234-9°C.

Removal of the benzene under vacuum and trituration with 40-60° petrol gave a white solid which was recrystallised from ethanol to give unchanged 9,10-dihydroacridine.

Yield: 1.0g. (56% recovery)

m.p. and mmp. 168-9°C.

A gas-liquid chromatography investigation upon the filtrate from the trituration using a Carbowax '1500' column at 60°C showed that no isopropylmethylketone was formed.

Photolysis of Benzalacetophenone and Tri-n-butylstannane.

Benzalacetophenone (1.0g. 0.005 moles) and tri-n-butylstannane (2.9g. 0.01 moles) were dissolved in 100 ml. of benzene and photolysed at 313nm in a 'Rayonet' photochemical reactor for 48 hours. The precipitate of polydibutyltin oxide was filtered off and the benzene was removed under vacuum. The resulting yellowish oil was chromatographed on Spence type 'H' alumina.

Elution with 40°-60° petrol gave unchanged tri-n-butylstannane.

Yield: 1.3g. (45% recovery)

Elution with 5% benzene in 40-60° petrol gave 1,3-diphenylpropan-1-one recrystallised from ethanol.

Yield: 0.48g. (48% theory)

m.p. 72°C (Lit. m.p. 72-3°C)<sup>143</sup>

I.R.  $\nu_{\max}$  1680, 1590, 1210, 750, 690 cm<sup>-1</sup>.

The semicarbazone derivative was prepared by warming an aqueous-ethanolic solution of the ketone, semicarbazide hydrochloride and excess sodium acetate on a steam bath and then cooling in ice. The semicarbazone was filtered off and recrystallised from ethanol.

m.p. 143-144°C. (Lit.m.p. 143°C)<sup>144</sup>.

Elution with benzene gave a solid which was recrystallised from ethanol giving colourless prisms of meso-1,3,4,6-tetraphenylhexan-1,6-dione.

Yield: 0.2g. (20% theory)

m.p. 267-8°C (Lit. m.p. 268-9°C)<sup>145</sup>

I.R.  $\nu_{\max}$  1675, 740, 695 cm<sup>-1</sup>.



Preparation of  $\Delta^4$ -Cholestene-3-one.

This was prepared from cholesterol by the method of Fieser<sup>146</sup>.

m.p. 81-82°C. (Lit.m.p. 81-82°C)<sup>146</sup>.

Photolysis of  $\Delta^4$ -Cholestene-3-one and Tri-n-butylstannane.

$\Delta^4$ -Cholestene-3-one (1.9g. 0.005 moles) and tri-n-butylstannane (2.9g. 0.01 moles) were dissolved in 100 ml. of benzene and photolysed for 24 hours at 313nm. The precipitated polydibutyltin oxide was filtered off and the residual oil after removal of benzene under vacuum was chromatographed on Spence type 'H' alumina.

Elution with 40-60° petrol gave unchanged tri-n-butylstannane.

Yield: 1.1g. (38% recovery)

Elution with 5% benzene in 40-60° petrol gave cholestan-3-one as colourless plates from ethanol.

Yield: 1.1g. (58% recovery)

m.p. 127-9°C. (Lit.m.p. 127-8°C)<sup>147</sup>.

Photolysis of Benzil and N,N-Dimethylaniline.

Benzil (1.6g. 0.0075 moles) and N,N-dimethylaniline (1.8g. 0.015 moles) were dissolved in 150 ml. of benzene and photolysed for 17 hours. The solution was washed with 2N hydrochloric acid to remove any unchanged amine and then with water before drying with anhydrous sodium sulphate. The benzene was removed under vacuum and the

resulting brown oil chromatographed on Spence Type 'H' alumina.

Elution with 10% benzene in 40-60° petrol gave unchanged benzil, recrystallised from 60-80° petrol.

Yield: 0.2g. (12.5% recovery)

m.p. and mmp. 94-6°C.

Elution with 25% benzene in 40-60° petrol gave a mixture of dl- and meso- 1,2-diphenyl-1,2-dihydroxyethane recrystallised twice from methanol.

Yield: 0.2g. (12.5% theory)

m.p. 125-136°C. (Lit. m.p. 114-125°C  
from benzene/petrol)<sup>148</sup>.

I.R.  $\checkmark_{\max}$  3400, 1280, 1040, 760, 700  $\text{cm}^{-1}$

N.M.R. 7.0 $\gamma$  1 hydrogen broad singlet

5.34 $\gamma$  1 hydrogen asymmetrical

doublet

2.9 $\gamma$  5 hydrogen multiplet

#### Photolysis of Benzaldehyde and Triethylamine.

Benzaldehyde (0.8g. 0.0075 moles) and triethylamine (1.5g. 0.015 moles) were dissolved in 150 ml. of benzene and photolysed for 3 hours. Benzene and excess triethylamine were removed under vacuum and the resulting brown oil was triturated with benzene/40-60° petrol. The brown solid produced was filtered off and recrystallised twice from 60-80° petrol to give slightly brownish crystals of the isomeric 1,2-diphenyl-1,2-dihydroxyethanes.

Yield: 0.4g. (50% theory)

m.p. 113-9°C.

The infra-red spectrum was identical with that of the compound produced by photolysis of benzil and NN-dimethylaniline but there was a slight depression  $\sim 3^{\circ}\text{C}$  when a mixed melting point was performed.

Photolysis of Benzil and Triethylamine.

Benzil (1.6g. 0.0075 moles) and triethylamine (1.5g. 0.015 moles) were dissolved in 150 ml. of benzene and photolysed for 18 hours, periodically removing a sample for gas-liquid chromatography. Use of a 'Carbowax 1500' column at 160°C showed that benzaldehyde was formed, the amounts produced at various times being:

1 hr.	8%	conversion
6 hrs.	24%	conversion
18 hrs.	22%	conversion

After removal of the benzene and any excess triethylamine under vacuum, chromatography on Spence Type 'H' alumina gave only a series of oils so the experiment was repeated at higher concentrations. Benzil (8.0g. 0.038 moles) and triethylamine (7.0g. 0.07 moles) were dissolved in 150 ml. of benzene and photolysed for 20 hours. After removal of benzene under vacuum the resulting oils were stood in a refrigerator overnight and partly crystallised. The mixture was triturated with 60-80° petrol and the crystals were filtered off and recrystallised from ethanol.

Colourless needles of benzoin were produced.

Yield: 2.1g.

m.p. and mmp. 136-7°C.

After removal of the petrol, the residual oil was distilled at 2.5mm.Hg. giving 2 fractions. The first fraction, (b.p. 205-220) upon trituration with 60-80° petrol gave a further 0.7g. of benzoin upon recrystallisation from ethanol.

Total Yield: 2.8g. (35% theory)

The second fraction (b.p. 235-260°C) was a dark brown oil from which no solid product could be isolated.

#### Photolysis of Benzoin and Triethylamine.

Benzoin (1.6g. 0.0075 moles) and triethylamine (1.5g. 0.015 moles) were dissolved in 150 ml. of benzene and photolysed for 15 hours. Samples withdrawn at various intervals for gas-liquid phase chromatography using a 'Carbowax 1500' column at 156°C showed the formation of benzaldehyde as follows:

2 hrs.	11% conversion
5 hrs.	14% conversion
15 hrs.	12.5% conversion

#### Photolysis of Dibenzoylmethane and NN-Dimethylaniline.

Dibenzoylmethane (3.4g. 0.015 moles) and NN-dimethylaniline (3.6g. 0.03 moles) were dissolved in 200 ml. of benzene and photolysed for 24 hours. A white precipitate was formed which was filtered off and recrystallised

from toluene giving colourless prisms of 1,3,4,6-tetra-phenyl-3,4-dihydroxy-hexan-1,2-dione.

Yield: 0.75g. (22% theory)

m.p. 241-4°C.

I.R.  $\nu_{\max}$  3500, 1660, 1210, 740, 690  $\text{cm}^{-1}$ .

Analysis C.79.84, H.5.83% (Calculated for  $\text{C}_{30}\text{H}_{26}\text{O}_4$ :

C.79.98, H.5.82%)

Excess amine was removed by extraction with 2N hydrochloric acid and after washing with water and drying with anhydrous sodium sulphate the benzene was removed under vacuum. This produced a yellow oil which was triturated with 60-80° petrol and the resulting solid was recrystallised from ethanol/chloroform. The colourless prisms were not identified.

Yield: 0.3g.

m.p. 240-2°C.

I.R.  $\nu_{\max}$  1290, 1040, 760, 700  $\text{cm}^{-1}$ .

N.M.R. 7.22 $\tau$  1 proton singlet

7.5 $\tau$  9 proton multiplet

Analysis. C.84.01, H.5.81% (Calculated for  $\text{C}_{11}\text{H}_9\text{O}$ :

C 84.05, H 5.77%)

$m/e$  432, 382, 343, 312, 296, 218.

The petrol from the trituration was removed under vacuum and the brownish oil was recrystallised from methanol. It produced unchanged dibenzoylmethane.

Yield: 1.3g. (38% recovery)

m.p. and mmp. 80-1°C.

On standing the mother liquors from the recrystallisation in a refrigerator overnight, colourless needles were deposited which were recrystallised from methanol giving 1,3,4,6-tetraphenyl-3-hydroxyhex-4-ene-1,6-dione.

Yield: 0.3g. (8% theory)

m.p. 158-161°C.

I.R.  $\gamma_{\max}$  34600, 1660, 1300, 760, 700  $\text{cm}^{-1}$ .

N.M.R. 7.2 $\tau$  2 proton singlet

6.17 $\tau$  1 proton singlet

5.95 $\tau$  1 proton singlet

4.6 $\tau$  1 proton singlet

7.5 $\tau$  10 proton multiplet

Analysis. C 82.71, H. 5.53 (Calculated for  $\text{C}_{30}\text{H}_{24}\text{O}_3$ :

C.83.31, H.5.59)

$m/e$  432, 414, 327, 314, 313.

#### Photolysis of Dibenzoylethylene and 9,10-Dihydroacridine.

Dibenzoylethylene (2.4g. 0.01 moles) and 9,10-dihydroacridine (18g. 0.01 moles) were dissolved in 200 ml. of benzene and photolysed for 24 hours. The white precipitate was filtered off and recrystallised from toluene. It was not positively identified owing to the limited amount of datae available.

Yield: 0.8g.

m.p. 255-8°C.

I.R.  $\gamma_{\max}$  1660, 1230, 940, 700  $\text{cm}^{-1}$ .

$m/e$  473, 369, 245, 236, 220, 178.

References

1. R. S. Mulliken, J. Chem. Phys., 3, 564, (1935).
2. E. J. Bowen, Quart. Rev., 4, 236, (1950).
3. H. Shaw and S. Toby, J. Chem. Ed., 43, 408, (1966).
4. J. W. Sidman, Chem. Rev., 58, 689, (1958)
5. R. Srinivansan, J. A. C. S., 84, 3432, (1962).
6. "'Photoluminescence of Solutions'", by C. A. Parker, Elsevier Publ. Co. (1968).
7. A. A. Lamola and G. S. Hammond, J. Chem. Phys., 43, 2129, (1965).
8. G. Porter and M. W. Windsor, Proc. Royal Soc. London, A245, 238, (1958).
9. D. S. McClure and P. L. Hanst, J. Chem. Phys., 23, 1772, (1955).
10. L.H. Piette, J. H. Sharp, T. Kuwana and J. N. Pitts Jr., J. Chem. Phys., 36, 3094, (1962).
11. G. Porter, Proc. Chem. Soc., 291, (1959).
12. S. K. Lower and M. A. El-Sayed, Chem. Rev., 66, 191, (1966).
13. M. A. El-Sayed, Accounts of Chem. Research, 1, 8, (1968).
14. G. Porter and F. Wilkinson, Trans. Farad. Soc., 57, 1686, (1961).
15. W. M. Moore and M. Ketchum, J. A. C. S., 84, 1368, (1962).
16. A. Terenin and E. Ermolaev, Trans. Farad. Soc., 52, 1042, (1956).
17. J. B. Farmer, C. L. Gardner and C. A. McDowell, J. Chem. Phys., 34, 1058, (1961).

18. G. Porter and F. Wilkinson, Proc. Royal Soc. London, A264, 1, (1961).
19. G. S. Hammond and R. P. Foss, J. Phys. Chem., 68, 3739, (1964).
20. R. P. Foss, D. O. Cowan and G. S. Hammond, J. Phys. Chem., 68, 3747, (1964).
21. M. L. Bhaunik and M. A. El-Sayed, J. Phys. Chem., 69, 275, (1965).
22. H. L. J. Bäckström and K. Sandros, Acta Chem. Scand., 16, 958, (1962).
23. G. S. Hammond and P. A. Leermakers, J. Phys. Chem., 66, 1148, (1962).
24. P. J. Wagner and I. Kochevar, J. A. C. S., 90, 2232, (1968).
25. G. S. Hammond, P. A. Leermakers and N. J. Turro, J. A. C. S., 83, 2396, (1961).
26. G. S. Hammond and J. Saltiel, J. A. C. S., 84, 4983, (1962).
27. G. S. Hammond, N. J. Turro and R. S. H. Liu, J. Org. Chem., 28, 3297, (1963).
28. G. S. Hammond and R. S. H. Liu, J. A. C. S., 85, 477, (1963).
29. H. E. Zimmerman, R. S. Givens and R. M. Pagni, J. A. C. S., 90, 6096, (1968).
30. A. Kuboyama, Bull. Chem. Soc. Jap., 37, 1540, (1964).
31. G. S. Hammond and P. A. Leermakers, J. A. C. S., 84, 207, (1962).
32. W. R. Ware and H. P. Richer, J. Chem. Phys., 48, 1595, (1968).



33. H. Leonhardt and A. Weller, Z. Phys. Chem. (Frankfurt) 29, 277, (1961), "'Luminescence of Organic and Inorganic Materials'". J. Wiley, New York (1962), P. 74.
34. N. Mataga and K. Ezumi, Bull. Chem. Soc. Jap., 40, 1355, (1967).
35. K. Kaneta and M. Koizuma, Bull. Chem. Soc. Jap., 40, 2254, (1967).
36. H. Yamashita, H. Kokubun and M. Koizuma, Bull. Chem. Soc. Jap., 41, 2312, (1968).
37. S. G. Cohen, S. Orman and D. A. Laufer, J. A. C. S., 84, 3907, (1962).
38. G. Giamician and P. Silber, Ber., 33, 2911, (1900).
39. W. E. Bachmann, Org. Syn. Coll. Vol. II, P. 71.
40. A. Schönberg and A. Mustafa, Chem. Rev., 40, 181, (1947).
41. C. Walling and M. J. Gibian, J. A. C. S., 81, 3361, (1965).
42. G. S. Hammond, W. P. Baker and W. M. Moore, J. A. C. S., 83, 2795, (1961).
43. S. G. Cohen and S. Aktipis, J. A. C. S., 88, 3587, (1966).
44. P. J. Wagner, J. A. C. S., 89, 2503, (1967).
45. A. Mustafa, Nature, 162, 856, (1948).
46. G. S. Hammond and W. M. Moore, J. A. C. S., 81, 6334, (1959).
47. H. L. J. Bäckström and K. Sandros, Acta. Chem. Scand., 14, 48, (1960).
48. W. M. Moore, G. S. Hammond and R. P. Foss, J. A. C. S., 83, 2789, (1961).

49. R. J. Becker, J. Mol. Spec., 3, 1, (1959).
50. H. L. J. Bäckström, Z. Physi. K. Chem., B25, 99, (1934).
51. P. J. Wagner, Mol. Photochem., 1, 71, (1969).
52. J. N. Pitts Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald and R. B. Martin, J. A. C. S., 81, 1068, (1959).
53. H. L. J. Backstrom, The Svedberg, 1884-1964, 60th. Birthday Memorial Vol., Uppsala University, (1944), P.45.
54. G. Porter and F. Wilkinson, Trans. Farad. Soc., 57, 1686, (1961).
55. G. O. Schenck, W. Meder and M. Pape, Proc.2nd. U.N. Int. Conf. Peaceful Uses Atomic Energy, 29, 352, (1958).
56. A. C. Testa, J. Phys. Chem., 67, 1341, (1963).
57. N. C. Yang and S. Murov, J. A. C. S., 88, 2852, (1966).
58. S. G. Cohen and J. I. Cohen, Israel J. Chem., 6, 757, (1968).
59. H. L. J. Bäckström, K. L. Appelgren and R. J. V. Nicklasson, Acta Chem. Scand., 19, 1555, (1965).
60. J. H. Sharp, T. Kuwana, A. Osborne and J. N. Pitts Jr., Chem. and Ind. (Lond.) 508, (1962).
61. G. O. Schenck, M. Cziesla, K. Eppinger, G. Matthias, and M. Pape, Tet. Letts., 193, (1967).
62. G. O. Schenck and G. Matthias, Tet. Letts., 699, (1967).
63. N. Filipescu and F. L. Minn, J. A. C. S., 90, 1544, (1968).

64. H. L. J. Bäckström and R. J. V. Niklasson, *Acta. Chem. Scand.*, 22, 2589, (1968).
65. R. Wilson, *Canad. J. Chem.*, 44, 551, (1966).  
*J. Chem. Soc.(B)*, 88, 1581, (1968).
66. W. E. Bachmann, *J. A. C. S.*, 55, 391, (1933).
67. S. G. Cohen and M. V. Sherman, *J. A. C. S.*, 85, 1642, (1963).
68. ''Molecular Photochemistry'' by N. J. Turro, P.144.
69. N. C. Yang and C. Rivas, *J. A. C. S.*, 83, 2213, (1961).
70. A. Beckett and G. Porter, *Trans. Farad. Soc.*, 59, 2051, (1963).
71. J. N. Pitts, Jr., H. W. Johnson and T. Kutawa, *J. Phys. Chem.*, 66, 2456, (1962).
72. G. Porter and P. Suppan, *Trans. Farad. Soc.*, 61, 1664, (1965).
73. S. G. Cohen and N. N. Siddique, *J. A. C. S.*, 86, 5047, (1964).
74. A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 67, (1944).
75. F. Younis, (Mrs.), Ph.D. Thesis, University of Leicester, 1969.
76. S. G. Cohen and R. J. Baumgarten, *J. A. C. S.*, 87, 2996, (1965).
77. S. G. Cohen and R. J. Baumgarten, *J. A. C. S.*, 89, 3471, (1967).
78. R. S. Davidson, *Chem. Comm.*, 575, (1966).
79. R. A. Claison and S. Searles Jr., *Chem. Comm.*, 289, (1966).

80. M. Gomberg and W. E. Bachman, J. A. C. S., 49, 236, (1927).
81. M. S. Newman, J. Org. Chem., 26, 582, (1961).
82. S. G. Cohen and J. I. Cohen, J. A. C. S., 89, 164, (1967).
83. P. J. Wagner and A. E. Kemppainen, J. A. C. S., 91, 3085, (1968).
84. R. A. Caldwell, Tet. Letts. 2121, (1969).
85. S. G. Cohen and H. M. Chao, J. A. C. S., 90, 165, (1968).
86. E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy and R. N. Adams, J. A. C. S., 88, 3498, (1966).
87. N. J. Turro and R. Engel, Mol. Photochem, 1, 143, (1969).
88. S. G. Cohen and J. I. Cohen, J. Phys. Chem., 72, 3782, (1968).
89. S. Granick and L. Michaelis, J. A. C. S., 62, 2241, (1940).
90. Bond Energies, Ionisation Potentials and Electron Affinities by V. I. Vedeneyev et al. Originally published by the Academy of Sciences, U. S. S. R., Moscow, 1962.
91. R. I. Vilisov and V. M. Saitsev, Dokl. Akad. Nauk. S. S. S. R. 154(4), 886, (1964). Chemical Abstracts, 60, 11870g (1964).
92. J. Guttenplan and S. G. Cohen, Chem. Comms., 247, (1967).
93. C. E. Griffen, W. G. Bentrude and G. M. Johnson, Tet. Letts., 969, (1969).

94. S. G. Cohen and J. B. Guttenplan, Tet. Letts, 5353, (1968).
95. L. A. Singer, Tet. Letts, 923, (1969).
96. J. B. Guttenplan and S. G. Cohen, Tet. Letts., 2125, (1969).
97. G. A. Davis, P. A. Carapelluci, K. Szoc and J. D. Gresser, J. A. C. S., 91, 2264, (1969).
98. S. G. Cohen, N. Stein and H. Chao, J. A. C. S., 90, 521, (1968).
99. S. G. Cohen and N. Stein, J. A. C. S., 91, 3690, (1969).
100. P. Ayscough and R. Wilson, J. Chem. Soc., 5412, (1963).
101. J. H. Stocker and D. H. Kern, J. Org. Chem., 33, 291, (1968).
102. W. A. Bryce and C. H. J. Wells, Canad. J. Chem., 41, 2722, (1963).
103. R. Calas, J. Valade and J.-C. Pommier, Compt. Rendus, 1450, (1962).
104. W. Trotter and A. C. Testa, J. A. C. S., 90, 7044, (1968).
105. H. G. Kuivila and O. F. Beumel Jr., J. A. C. S., 83, 1246, (1961).
106. A. Mustafa, Chem. Rev. , 51, 1, (1952).
107. P. E. Eaton and W. S. Hurt, J. A. C. S., 88, 5038, (1966).
108. E. Y. Y. Lam, D. Valentine and G. S. Hammond, J. A. C. S., 89, 3482, (1967).
109. F. A. L. Anet, Canad. J. Chem., 40, 1249, (1962).

- 110. G. O. Schenck, I. von. Wilucki and C. H. Krauch,  
Ber. 95, 1409, (1962).
- 111. G. S. Hammond, C. A. Stout and A. A. Lamola,  
J. A. C. S., 86, 3103, (1964).
- 112. H. E. Zimmermann, H. G. Durr, R. S. Givens and  
R. G. Lewis, J. A. C. S., 89, 1863, (1967).
- 113. G. W. Griffin and D. J. O'Connell, J. A. C. S.,  
84, 4148, (1962).
- 114. W. H. Urry and D. J. Trecker, J. A. C. S., 84,  
118, (1962).
- 115. W. H. Urry, D. J. Trecker and D. A. Winey, Tet.  
Letts, 609, (1962).
- 116. D. L. Bunbury and C. T. Wang, Canad. J. Chem., 46,  
1473, (1968).
- 117. G. Kornis and P. De Mayo, Canad. J. Chem., 42,  
2822, (1964).
- 118. T. Matsuura, Y. Kitaura and R. Nashima, Tetrahedron,  
24, 6601, (1968).
- 119. R. C. Cookson, J. Hudec and N. A. Mairza, Chem.  
Comm. 180, (1968).
- 120. R. F. Bridger and G. A. Russell, J. A. C. S.,  
85, 3754, (1963).
- 121. A. Terenin, V. Tachim and P. Shalchverdov,  
Photochem. and Photobiol., 4, 505, (1965).
- 122. R. A. Jackson and W. A. Waters, J. Chem. Soc.,  
4632, (1958).
- 123. T. S. Stevens and S. H. Tucker, J. Chem. Soc.,  
2145, (1923).
- 124. N. P. Buu-Hoi and R. Royer, J. Org. Chem.,  
16, 1198, (1961).

125. J. Forest, B. A. Liddell and S. H. Tucker,  
J. Chem. Soc., 454, (1946).
126. C. S. Gibson and D. C. Vining, J. Chem. Soc.,  
831, (1923).
127. R. Q. Brewster and T. Groening, Org. Syn.,  
Coll. Vol. II. P. 446.
128. R. I. Walter, J. A. C. S., 77, 5999, (1955).
129. M. H. Habacher, J. Org. Chem., 24, 1949, (1959).
130. L. M. Long and H. R. Henze, J. A. C. S., 63,  
1939, (1941).
131. G. S. Hammond, D. C. Nonhebel and C. H. S. Wu,  
Inorganic Chem., 2, 73, (1963).
132. H. Klinger and C. K. Lonnes, Ber., 29, 2152, (1896).
133. C. Weizmann, E. Bergmann and Y. Hirshberg, J. A. C. S.,  
60, 1530, (1938).
134. J. Stanvek, Chem. Listy, 44, 253, (1950), Chemical  
Abstracts, 45, 5136g, (1951).
135. N. K. Bridge and G. Porter, Proc. Royal Soc.  
London, A244, 276, (1958).
136. H. R. Snyder and C. T. Elston, J. A. C. S., 77,  
364, (1955).
137. E. Wertheim, J. A. C. S., 55, 2540, (1933).
138. F. Bohlmann, Ber., 85, 390, (1952).
139. A. Kellmann, J. Chim. Phys., 57, 1, (1960),  
Chemical Abstracts, 54, 12743g, (1960).
140. K. Lehmstedt and H. Hundertmark, Ber., 63,  
1229, (1930).
141. W. Elliot Jr., and R. B. McGriff, J. Org. Chem.,  
22, 514, (1957).

- 142. H. Stobbe and A. Hensel, Ber., 59, 2254, (1926).
- 143. R. Adams, J. W. Kern and R. L. Shriner, Org. Syn., Coll. Voll. I, P. 95.
- 144. S. Jacobson and B. Ghosh, J. Chem. Soc., 959, (1915).
- 145. L. R. Finch and D. E. White, J. Chem. Soc., 3367, (1950).
- 146. L. F. Fieser, J. A. C. S., 75, 5421, (1953).
- 147. F. Sondheimer and M. Nussim, J. Org. Chem., 26, 630, (1961).
- 148. D. Wittenberg, T. Wu and H. Gilman, J. org. Chem., 24, 1349, (1950).