PART I

THE CHEMISTRY OF LOW ENERGY π-π^* TRIPLET STATES. THE PHOTOREDUCTION OF 1-NAPHTHALDEHYDE AND 2-ACETONAPHTHONE

PART II

TRIPLET-TRIPLET ENERGY TRANSFER IN SOLUTION

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ABSTRACT

Part I

Photoreduction of 1-naphthaldehyde and 2-acetonaphthone has been accomplished by the use of tributylstannane as a hydrogen donor. Rate constants for hydrogen abstraction and thermal deactivation of the excited species have been estimated. The π-π^* triplet states of the two carbonyl compounds are responsible for the hydrogen abstraction reaction. The naphthoyl compounds do not undergo photoreduction by secondary alcohols. Their low reactivity is attributed to the fact that the π-π^* rather than the $\underline{n}$-π^* triplet is involved. Carbonyl compounds that are easily photoreduced have the $\underline{n}$-π^* configuration in their lowest triplets.

Part II

The phenomenon of energy transfer between triplet states of molecules in solution has been investigated. Two methods have been employed in this investigation. The first involves the photosensitized cis-trans isomerization of piperylene. Aromatic carbonyl compounds were used as sensitizers. The trans/cis ratio in the photostationary state was related to the energy of the lowest triplet state of the sensitizer.

The second method involved the study of the effects of quenchers on the quantum yield in the photoreduction of benzophenone by benzhydrol. Many of the quenchers were found to have about the same efficiency. It was concluded that the energy transfer (quenching) reaction is probably diffusion controlled.

PART I

THE CHEMISTRY OF LOW ENERGY π-π^* TRIPLET STATES. THE PHOTOREDUCTION OF 1-NAPHTHALDEHYDE AND 2-ACETONAPHTHONE

Introduction

The importance of the triplet state in solution photochemistry has become increasingly clear in the last few years. The classic paper by Lewis and Kasha (1) first established that triplet states of many aromatic compounds can be attained in a rigid glass at 77°K by direct irradiation. Since then many investigators have studied phosphorescence emission in glasses and observed in a number of cases that the quantum yields are high. Gilmore, Gibson and McClure (2) found that the quantum efficiency of benzophenone phosphorescence in the low-temperature glass is nearly unity.

Phosphorescence in solution is rarely observed, since the triplet, if formed, usually has easier, non-radiative pathways to the ground state.* Flash techniques, however, have permitted observation of triplet species in solution. An extremely intense flash of light is used to excite a very large number of molecules simultaneously into higher electronic singlet states. A significant number of these excited

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*There are some exceptions. Certain α-diketones phosphoresce strongly in solution.

molecules may decay by intersystem crossing to the metastable triplet. This transient triplet species is observed by simple spectrophotometric measurement of its T_1-T_2 absorption spectrum after the flash has subsided. Porter and Wright have studied naphthalene and anthracene in this manner, and have found triplet lifetimes of the order of 10^{-4} and 10^{-3} seconds respectively in hexane solution (3).

The demonstrated long triplet lifetimes both in the low-temperature rigid glass and in solution (as indicated above) portend that triplet states ought to be important photochemical intermediates.

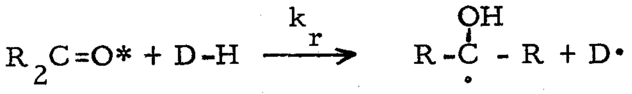
The photoreactions of many ketones and aldehydes with alcohols and alkyl benzenes are well known (4, 5). Mechanistic studies have been carried out by a number of workers (4, 6, 8), but only recently has the nature of the excited intermediates responsible for the photoreduction been elucidated (7, 9, 10). Bäckstrom (11) as early as 1934 proposed an excited "biradical" intermediate in photoreduction by primary alcohols. This was several years before the notion of triplet states was introduced by Lewis and Kasha.

Equations 1 through 8 summarize the mechanism believed to hold for reduction of a carbonyl compound by a hydrogen donor (D-H). Deactivation of the chemically active excited state both by first-order decay, reaction 2, and by energy transfer to a specific quencher, reaction 3, are included.

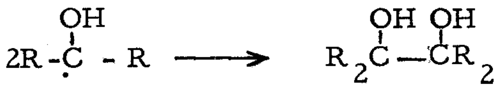
$$R_2C{=}O + h\nu \longrightarrow R_2C{=}O^* \qquad (1)$$

$$R_2C{=}O^* \xrightarrow{k_d} R_2C{=}O \qquad (2)$$

$$R_2C{=}O^* + Q \xrightarrow{k_q} R_2C{=}O + Q^* \qquad (3)$$

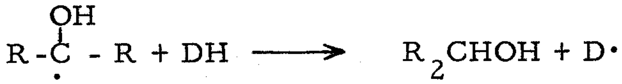


$$R_2C{=}O^* + D\text{-}H \xrightarrow{k_r} R\text{-}\overset{OH}{\underset{\bullet}{C}}\text{-}R + D\cdot \qquad (4)$$



$$2R\text{-}\overset{OH}{\underset{\bullet}{C}}\text{-}R \longrightarrow R_2\overset{OH}{C}\text{—}\overset{OH}{C}R_2 \qquad (5)$$

$$R\text{-}\overset{OH}{\underset{\bullet}{C}}\text{-}R + D\cdot \longrightarrow R_2\overset{OH}{C}\text{-}D \qquad (6)$$



$$R\text{-}\overset{OH}{\underset{\bullet}{C}}\text{-}R + DH \longrightarrow R_2CHOH + D\cdot \qquad (7)$$

$$2\,D\cdot \longrightarrow D\text{-}D \qquad (8)$$

Hammond and co-workers (7,9,10) showed that in the case of benzophenone, with benzhydrol or alkyl benzenes as hydrogen donors, the excited state responsible for hydrogen abstraction is a triplet. The variation of quantum yield with hydrogen donor and quencher concentrations follows the rate law of equation 9:

$$\frac{1}{\phi} = \frac{1}{\phi'} + \frac{k_d}{\phi'\,k_r\,[DH]} + \frac{k_q\,[Q]}{\phi'\,k_r\,[DH]} \qquad (9)$$

where ϕ is the quantum yield for the reduction of benzophenone. The quantum yield of triplets, ϕ', was equal to unity, in good agreement with the phosphorescence data of Gilmore, Gibson and McClure (2). The argument supporting a triplet intermediate is twofold. First, from the slope of a plot of $1/\phi$ vs. $1/[DH]$ in the absence of quenchers (where [DH] is benzhydrol concentration), k_d/k_r was found to be 0.050*. The largest value k_r could conceivably have is 10^9 liter $mole^{-1} sec^{-1}$, the diffusion controlled rate. This gives an upper limit of 5×10^7 sec^{-1} for k_d. However, k_r must be slower than diffusion controlled, because the hydrogen transfer reaction shows a deuterium isotope effect of 2.7. The calculated fluorescence rate constant for benzophenone is of the order of 5×10^6 sec^{-1} (12). Since benzophenone solutions have no detectable fluorescence, the actual rate of non-radiative quenching of the lowest singlet state must be at least 5×10^8 sec^{-1}. Thus it is clear that some state longer lived than the excited singlet must be involved. The second part of the argument supporting the triplet intermediate derives from the action of paramagnetic quenchers on the photoreduction reaction. Modest amounts of oxygen or ferric dipivaloylmethide were found to substantially reduce the quantum yield for photoreduction. Estimates of the absolute rates of the various processes were made on the assumption that quenching by ferric dipivaloylmethide is diffusion

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*From a re-evaluation of the data by Mr. R. P. Foss, k_d/k_r is now considered to be 0.033.

controlled. The value of k_r was estimated to be 5×10^6 liter mole^{-1} sec^{-1} and k_d was estimated to be 2.6×10^5 sec^{-1}. This latter value is in excellent agreement with that obtained by Bäckstrom and Sandros (13), who found $k_d = 5.3 \times 10^5$ in the same solvent (benzene). Their results were based on measurements of the quantum yields of phosphorescence of biacetyl sensitized by benzophenone. They also assumed that the rate of quenching (energy transfer from benzophenone to biacetyl) was diffusion controlled.

Part I of this thesis deals with the study of naphthalene ketones and aldehydes, specifically 2-acetonaphthone and 1-naphthaldehyde. It has been reported (14) that a number of naphthyl ketones are not photoreduced in the presence of secondary alcohols. It has been suggested (4) that the excited ketone abstracts hydrogen from the secondary alcohol, but that the hydrogen transfer is reversible so that no net reaction occurs. This explanation did not seem to be entirely satisfactory to us. It was thought that the low reactivity of these compounds might be associated with the nature and energy of their lowest triplet states. An attempt was made to find a hydrogen donor that could effect photoreduction of these compounds. Such a compound is tributylstannane which has been used in the following experiments.

Experimental

Materials.— 1-Naphthaldehyde (Eastman Kodak White Label) was vacuum distilled prior to preparations of 1.0-molar stock solutions in benzene. 2-Acetonaphthone (Eastman Kodak White Label) was recrystallized from ligroin, m.p. 55-56°. Tributylstannane was prepared from tributyltin chloride (Metal and Thermit Corp.) by reduction with lithium aluminum hydride (15), vacuum distilled and sealed in ampules for subsequent use. Ferric dipivaloylmethide was furnished by Dr. Karl Kopecky. Other chelates were prepared in these Laboratories; their syntheses will be reported elsewhere. Benzil (Eastman Kodak White Label) was used without further purification. Benzene (Mallinckrodt Analytical Reagent Grade) was used without further purification. Benzophenone (Matheson, Coleman and Bell, Reagent Grade) was used without further purification.

Apparatus.— The light source, optical system, reaction cells, etc., have been described previously.(10).

Filter System.— The filter system used in all runs consisted of a Corning 7-54 glass filter in series with an aqueous solution filter containing 145 g. of nickel sulfate hexahydrate and 41.5 g. of cobaltous sulfate heptahydrate per liter. This system passed 85% of the incident light at 3130 Å and 4% at 3660 Å. The incident light was totally absorbed by the reaction system in all runs.

Actinometry.— Uranyl oxalate actinometry was used throughout this study. An aqueous solution, 0.01 molar in uranyl acetate and 0.05 molar in oxalic acid, was irradiated for a period of one to two hours. The residual oxalic acid was then titrated with standard 0.100 normal permanganate.

Products of the Photoreaction between 1-Naphthaldehyde and Tributylstannane.— Solutions were prepared by mixing 5 to 15 ml. of a 1.0 M solution of 1-naphthaldehyde in benzene with 5 to 10 ml. of tributylstannane. The solution was diluted to 100 ml. with benzene, degassed and irradiated. Most of the benzene was stripped off, and the products were separated by chromatography on alumina. Two major products were always found; the first was a white solid , m.p. 60-61° after recrystallization from petroleum ether. The infrared spectrum of the solid was identical to that of 1-naphthylcarbinol, m.p. 60.5-61.5°, prepared by lithium aluminum hydride reduction of the aldehyde; mixed m.p., 60-61.5°. The second product was a high melting solid, m.p. 185-186°. A 12.4 mg. sample of the product was treated with lead tetraacetate in glacial acetic acid, and excess 2,4-dinitrophenylhydrazine in ethanol-phosphoric acid was added to the reaction mixture. An orange precipitate (34 mg.) was formed and recrystallized from ethyl acetate-chloroform, m.p. 262-269°. Authentic 1-naphthaldehyde-2,4-dinitrophenylhydrazone was prepared, m.p. 260°; mixed m.p. 262-270°.

Anal. Calc. for $C_{22}H_{18}O_2$: C, 84.20; H, 5.74. Found: C, 84.16; H, 5.88.

Irradiation of Acetonaphthone in the Presence of R-2-Octanol (16).— A solution of optically active 2-octanol (0.187 M) and 2-acetonaphthone (0.002 M) in benzene was irradiated for 24 hr. The observed rotation in a 20-cm. cell before irradiation was +0.37°; after irradiation the reading was +0.38°. Ultraviolet spectra taken before and after irradiation indicated no change in ketone concentration.

Products of the Photoreaction Between 2-Acetonaphthone and Tributylstannane.— A solution containing 15 ml. of 1.0 M 2-acetonaphthone, 5 ml. of tributylstannane and 52 ml. of benzene was irradiated with unfiltered light for 24 hr. The mixture was then chromatographed on alumina, and a substantial quantity of a white solid was obtained. The solid was recrystallized twice from petroleum ether, m.p. 73-74°. Authentic methyl-2-naphthylcarbinol, m.p. 74-76°, mixed m.p. 74-76°, was prepared by reduction of 2-acetonaphthone with lithium aluminum hydride. The infrared spectra of the two samples were identical. In a more quantitative experiment 0.59 g. of 2-acetonaphthone and 3.5 ml. of tributylstannane in benzene were degassed and photolyzed to completion. The product mixture was chromatographed on an alumina column 30 cm. x 1 cm. using 2 liters of ether as eluent. After elution with ether ceased to remove additional material, the column was flushed with methanol-chloroform. The ether fractions contained 0.56 g. of a white solid (crude) that was shown to be methyl-(2-naphthyl)-carbinol by infrared comparison with the authentic material. This accounts for 95% of the aromatic products. The methanol-chloroform fraction contained a trace of dark-colored oil. The oxidized product is presumed to be hexabutylditin.

Products of the Photoreaction of Benzophenone with Tributylstannane.— A heptane solution (70 ml.) containing 1.82 g. of benzophenone and 5 ml. of tributylstannane was degassed and irradiated for 6 hours with unfiltered light. White crystals (1.71 g.) of benzpinacol separated out, m.p. 175-177° (dec.); yield, 94%.

Quantitative Runs.— Benzene solutions, usually containing 0.02 or 0.05 M aldehyde or ketone and from 0.075 to 3.24 M tributylstannane, were prepared. Seventy milliliters of such a solution was placed in the reaction cell, which was degassed and sealed off. The cell was then placed in the optical system for a measured length of time, after which it was opened. The residual aldehyde or ketone was determined spectrophotometrically by measurement of absorbence at the long wavelength maximum after appropriate dilution. Parallel measurement was always made using samples that had been withdrawn from the original solution and not irradiated. In some runs quenchers (oil-soluble metal chelates or benzil) were added in low concentrations.

Results

1-Naphthaldehyde.— The absorption spectrum of 1-naphthaldehyde in the near ultraviolet shows two π-π^* maxima at 2120 Å (ϵ = 32,000) and at 3120 Å (ϵ = 6,500). The low intensity n - π^* absorption is presumably buried under the 3120 Å band. The compound was found not to undergo photoreactions with benzhydrol and other secondary alcohols. However, when irradiated with 3130 Å light in the presence of tributylstannane, a much better hydrogen donor, the aldehyde is reduced to yield the corresponding carbinol, 1-naphthylcarbinol, and the glycol, 1,2-di-(1-naphthyl)-ethane-1,2-diol, in a molar ratio of about 2:1. The tributyltin radicals presumably couple with themselves since no cross-coupled products were found.

Quantum yields for the disappearance of aldehyde were measured with varying concentrations of the stannane and, with the concentration of hydrogen donor fixed, as a function of the concentration of ferric dipivaloylmethide, a powerful quencher. The data are presented in Table I. Plots shown in Figures 1 and 2 indicate that the data fit equation 9. The intercept of the plot of $1/\phi$ against stannane concentration is unity within the limits of experimental error. From the slope of the line a value of 0.66 moles $\ell.^{-1}$ is calculated for k_d/k_r. The slope of the line drawn in Figure 2 gives a value of 1.8×10^3 for k_q/k_r. If it is assumed that k_q is 2×10^9 $\ell.$ mole^{-1} sec^{-1} (the diffusion-controlled rate), the values for the other rate constants can be estimated. The

TABLE I

PHOTOREDUCTION OF 1-NAPHTHALDEHYDE BY TRIBUTYLSTANNANE IN BENZENE SOLUTION

[Aldehyde]	[Stannane]	[Quencher]	Intensity[a] $\times 10^{-17}$	ϕ
0.050	0.185		1.52	.17
0.020	0.185		1.28	.18
0.050	0.185		0.90	.17
0.050	0.185	1.02×10^{-3} Fe(DPM)$_3$	1.63	.064
0.050	0.185	0.79×10^{-3} Fe(DPM)$_3$	1.16	.078
0.050	0.185	0.50×10^{-3} Fe(DPM)$_3$	1.22	.088
0.050	0.185	0.27×10^{-3} Fe(DPM)$_3$	1.20	.11
0.050	0.370		1.62	.31
0.050	0.075		1.56	.10
0.050	0.555		1.43	.36
0.050	0.113		1.34	.16
0.020	0.113		1.26	.16
0.050	0.094		1.25	.12
0.040	3.24		0.96	.85
0.050	0.185	1.03×10^{-3} La(DPM)$_3$	3.60	.130
0.050	0.185	1.00×10^{-3} Er(DPM)$_3$	3.80	.116

[a] Light intensity, quanta per second.

Figure 1

Photoreduction of 1-Naphthaldehyde with Tri-n-butylstannane.

◔ , average of three determinations

◴ , average of two determinations

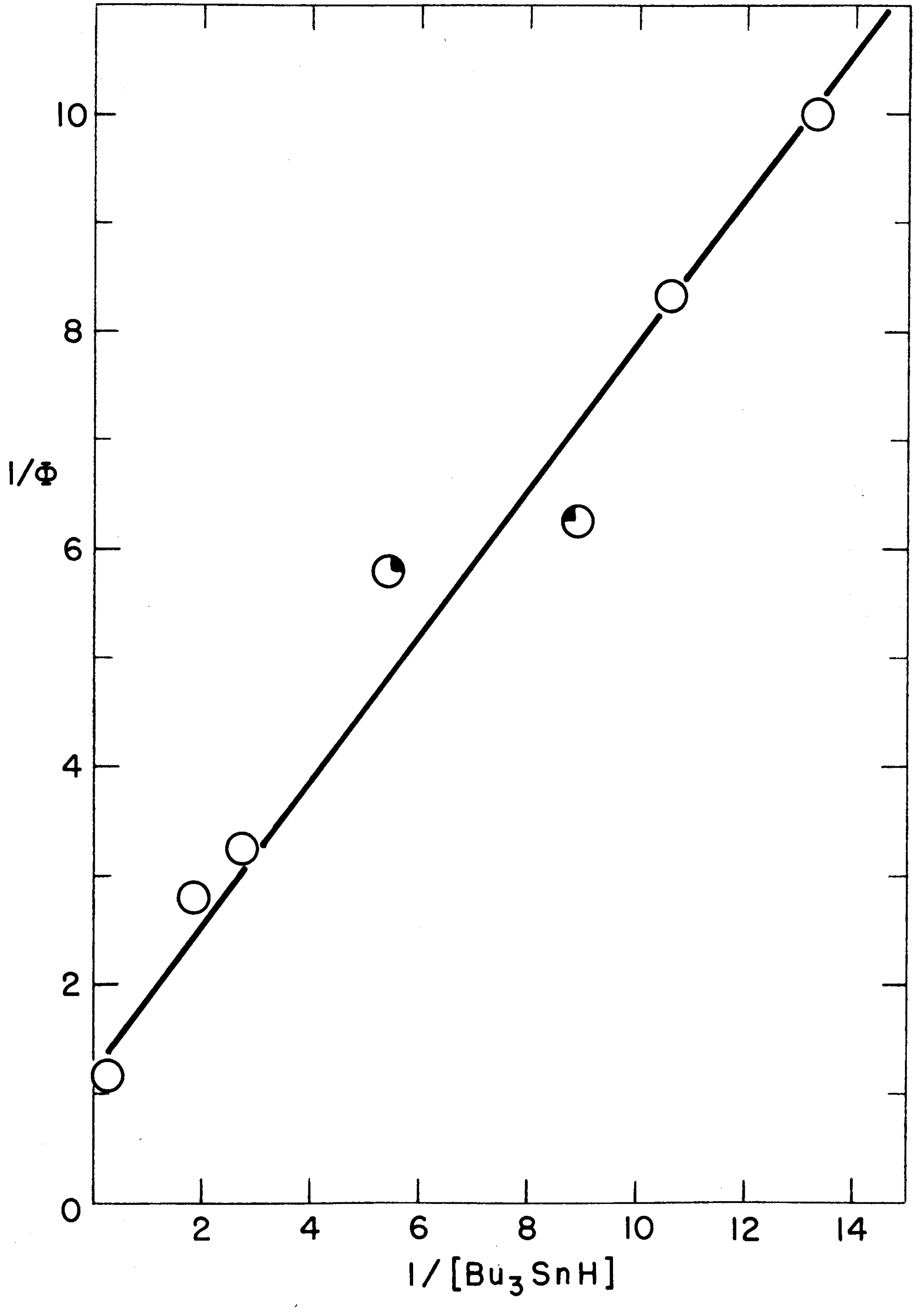
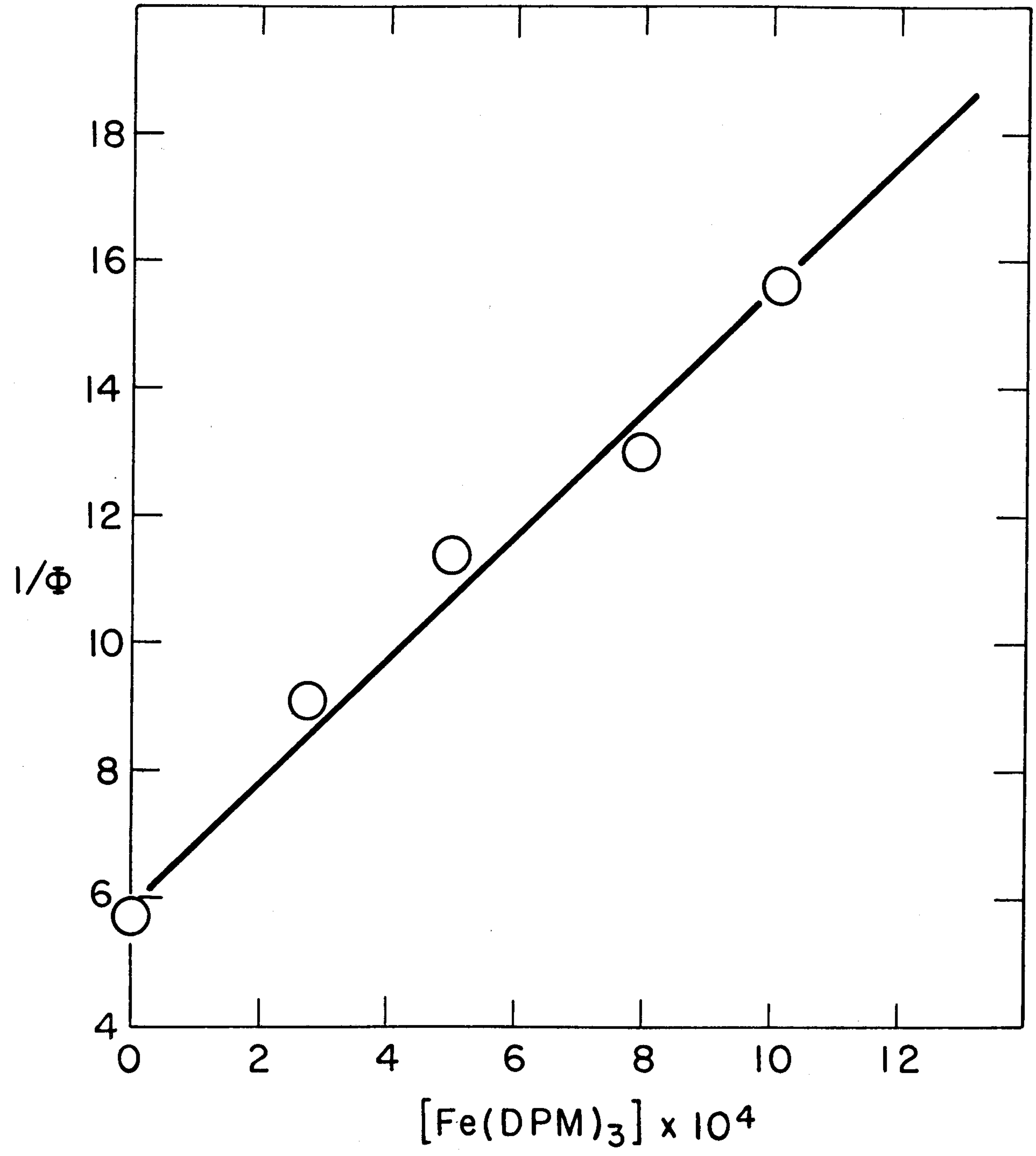

1/Φ
0
2
4
6
8
10
2
4
6
8
10
12
14
1/[Bu_3SnH]

Figure 2

Quenching of the Photoreduction of 1-Naphthaldehyde by Ferric Dipivaloylmethide.


18
16
14
12
10
8
6
4
1/Φ
0
2
4
6
8
10
12
[Fe(DPM)3] x 10⁴

results are listed in Table III. Erbium and lanthanum dipivaloylmethides showed quenching action, although they were less effective than the iron chelate [k_q/k_r = 500 for $Er(DPM)_3$ and 330 for $La(DPM)_3$].

2-Acetonaphthone.— This ketone possesses three $\pi - \pi^*$ maxima in its near ultraviolet absorption spectrum at 3350 Å (ϵ= 2,000), 2,800 Å (ϵ= 10,000) and at 2450 Å (ϵ = 70,000). The ketone must also possess a low intensity $n - \pi^*$ absorption, but this would surely be hidden under the 3350 Å band. In agreement with previous reports (14), we found that 2-acetonaphthone is not photoreduced in the presence of secondary alcohols. Furthermore, irradiation of a solution of the ketone in active 2-octanol did not lead to racemization of the alcohol. However, as in the case of 1-naphthaldehyde, the ketone is photoreduced when irradiated with light 3130 Å in the presence of tributylstannane. The product is the corresponding alcohol, methyl-2-naphthylcarbinol.

Quantum yields for the photoreduction (disappearance of ketone) have been measured as functions of the concentrations of hydrogen donor and quencher [$Fe(DPM)_3$]. The effects of other quenchers have been observed. Results of the quantitative experiments appear in Table II.

The data are again treated according to equation 9. Figure 3 gives a plot of $1/\phi$ vs. reciprocal hydrogen donor concentration . A linear function is obtained with an intercept at the ordinate of 1.65, indicating that the quantum yield for triplet formation is about 0.6. The slope is 0.28, from which k_d/k_r is calculated to be 0.17. Figure 4

TABLE II

PHOTOREDUCTION OF 2-ACETONAPHTHONE BY TRIBUTYLSTANNANE IN BENZENE SOLUTION

[Ketone]	[Stannane]	[Quencher]	ϕ
0.060	2.95		0.63
0.050	0.185		0.29
0.050	0.185		0.26
0.050	0.185		0.30
0.050	0.113		0.24
0.050	0.075		0.19
0.050	0.185	2.5×10^{-4} Fe(DPM)$_3$	0.18
0.050	0.185	4.8×10^{-4} Fe(DPM)$_3$	0.110
0.050	0.185	7.0×10^{-4} Fe(DPM)$_3$	0.103
0.050	0.185	5×10^{-3} Benzil	0.03
0.050	0.185	1.0×10^{-3} Benzil	0.13
0.050	0.185	5.5×10^{-4} Zn(DPM)$_2$	0.27
0.050	0.185	5.0×10^{-4} Cr(DPM)$_3$	0.24
0.050	0.185	4.9×10^{-4} Gd(DPM)$_3$	0.25
0.050	0.185	5.0×10^{-4} Er(DPM)$_3$	0.23
0.050	0.185	5.0×10^{-4} Er(DPM)$_3$	0.22

shows a plot of reciprocal quantum yield as a function of ferric dipivaloylmethide concentration. From the slope of 8800, k_q/k_r is found to be 10^3. If the quenching reaction is again assumed to be diffusion-controlled the absolute rate constants tabulated in Table III can be estimated.

TABLE III

RATE CONSTANTS FOR REACTIONS INVOLVED IN PHOTOREDUCTION BY TRIBUTYLSTANNANE

	Carbonyl Compound	
	1-Naphthaldehyde	2-Acetonaphthone
k_q(calc.)	2×10^9 ℓ. $\text{mole}^{-1}\text{sec}^{-1}$	2×10^9 ℓ. $\text{mole}^{-1}\text{sec}^{-1}$
k_r	1.1×10^6 ℓ. $\text{mole}^{-1}\text{sec}^{-1}$	2.0×10^6 ℓ. $\text{mole}^{-1}\text{sec}^{-1}$
k_d	7.3×10^5 sec^{-1}	3.4×10^5 sec^{-1}

The quenching effect of benzil is rather striking. In this case the quenching mechanism must involve the formation of the triplet state of benzil by energy transfer from the triplet state of the ketone. In the run with a moderately high concentration of benzil (5×10^{-3} M), the characteristic green phosphorescence of benzil was observed even though the light was entirely absorbed by the acetonaphthone. Although no exact value can be calculated since the benzil itself is partly consumed in the reaction (probably by photoreduction), the quenching efficiency

Figure 3

Photoreduction of 2-Acetonaphthone by Tri-*n*-butylstannane.

◔ is average of three determinations

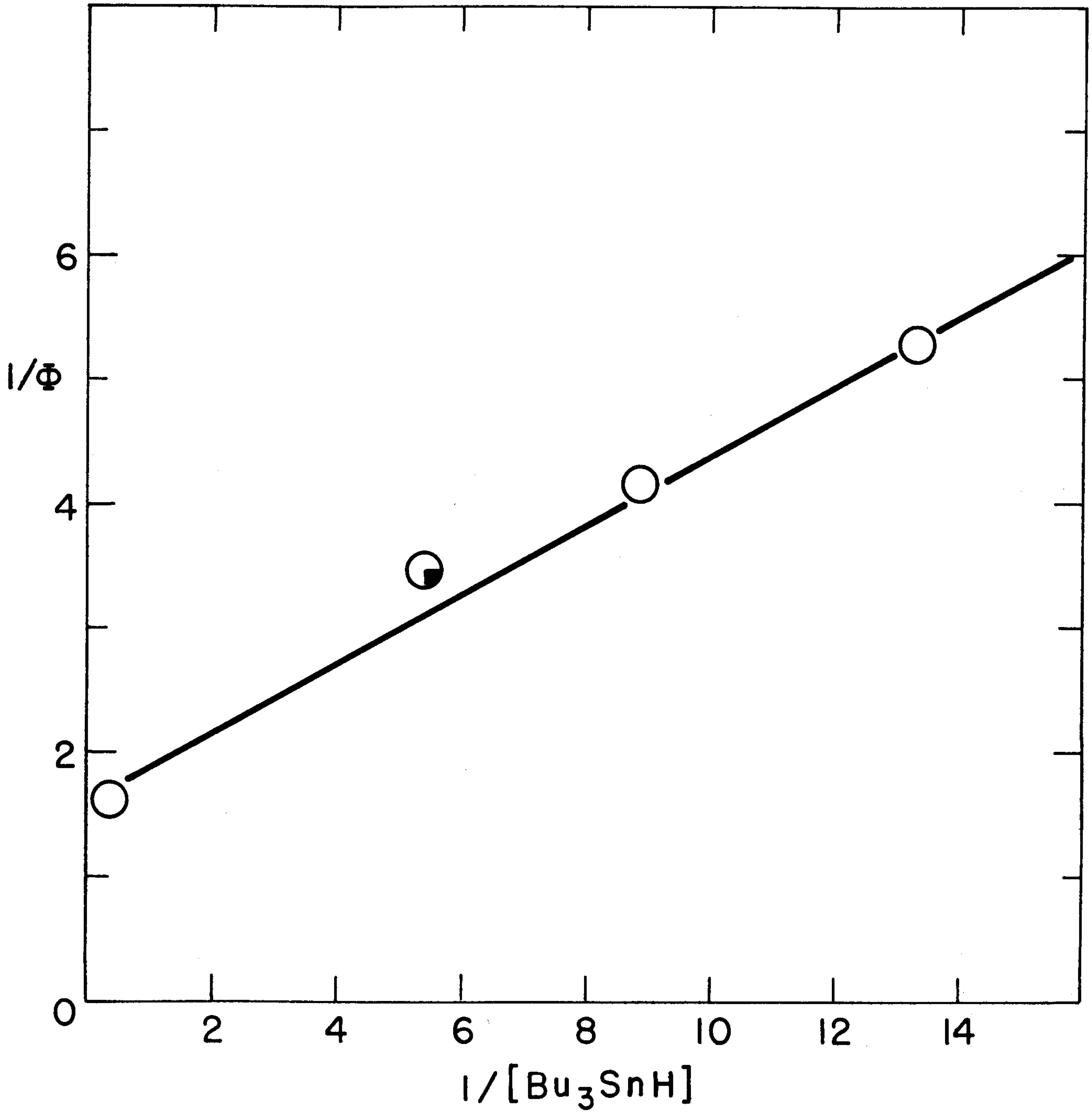
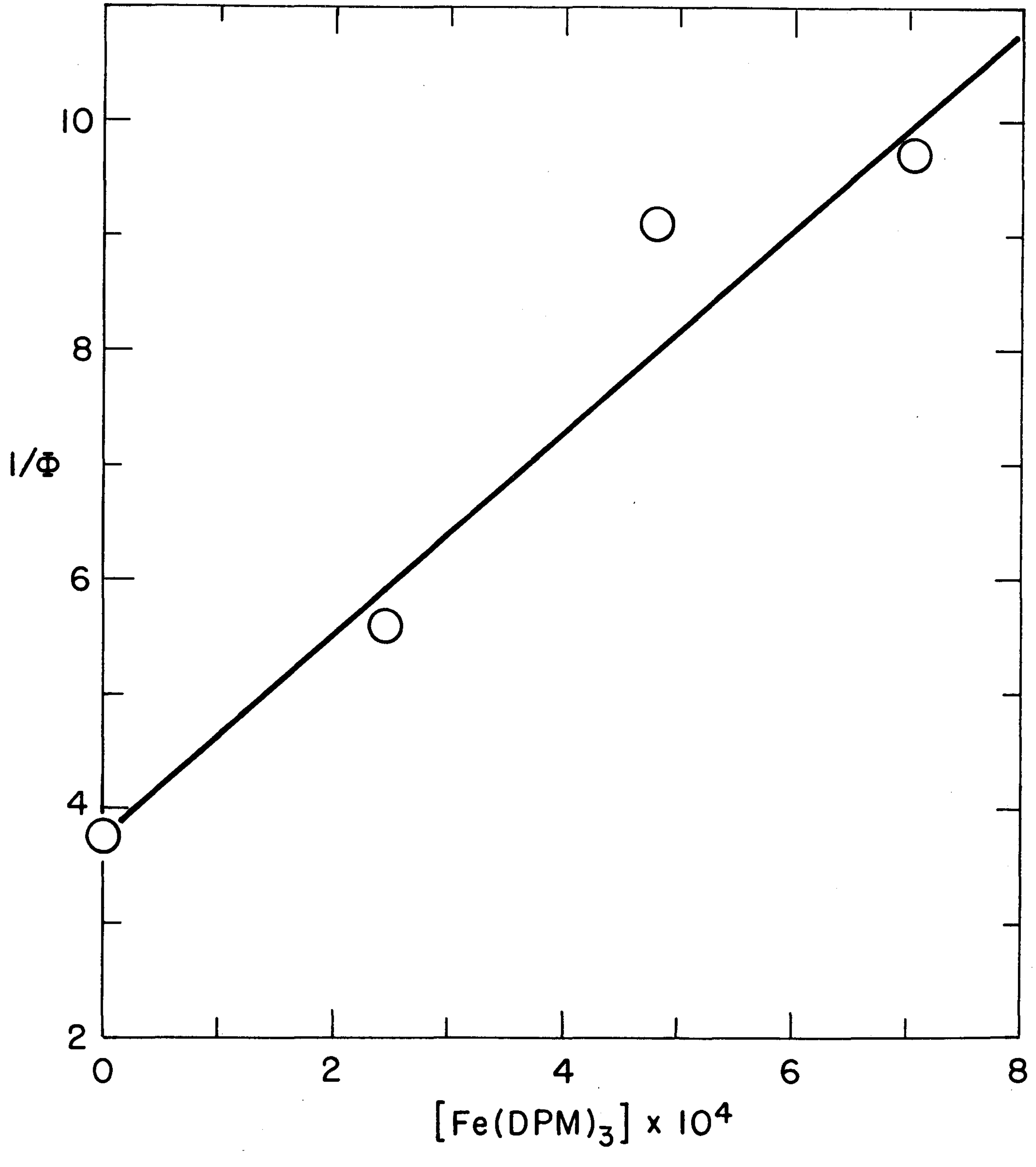

6
4
2
0
1/Φ
2
4
6
8
10
12
14
1/[Bu_3SnH]

Figure 4

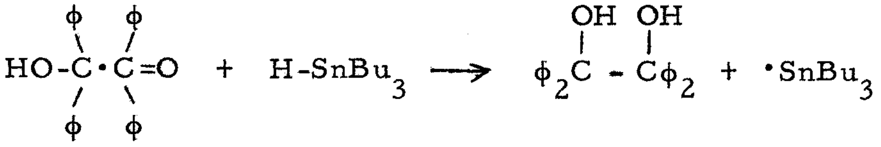
Quenching of the Photoreduction of 2-Acetonaphthone by Ferric Dipivaloylmethide.


10
8
1/Φ
6
4
2
0
2
4
6
8
[Fe(DPM)3] x 10^4

seems to be about the same as that for the chelate, lending further weight to the argument that the quenching reaction is diffusion-controlled.

The DPM chelates of gadolinium, erbium, zinc and chromium were added to certain runs and found to have little or no quenching ability. A systematic investigation of metal chelates as quenchers is in progress in these laboratories.

Benzophenone.— This compound was photoreduced by tributylstannane to give benzpinacol in nearly quantitative yield. The quantum yield for the reduction in the presence of 0.185 M hydrogen donor was found to be 1.3 at 3130 Å. The fact that the quantum yield is greater than unity is puzzling, since the virtually exclusive formation of benzpinacol makes a chain mechanism almost inconceivable. Hydrogen transfer to a diphenylhydroxymethyl radical - benzophenone complex could account for the result.



$$\mathrm{HO{-}}\overset{\phi}{\underset{\phi}{\mathrm{C}}}\cdot\overset{\phi}{\underset{\phi}{\mathrm{C}}}\mathrm{{=}O} + \mathrm{H{-}SnBu_3} \longrightarrow \phi_2\overset{\mathrm{OH}}{\mathrm{C}} - \overset{\mathrm{OH}}{\mathrm{C}}\phi_2 + {\cdot}\mathrm{SnBu_3}$$

As in the case of the naphthoyl compounds, no reaction was observed to take place in the dark.

Discussion

The low reactivity of excited states of 1-naphthaldehyde and 2-acetonaphthone toward secondary alcohols is genuine and not an artifact caused by reversal of the hydrogen transfer reaction:

$$R_2CO^* + R'_2CHOH \longrightarrow R_2\dot{C}OH + R'_2\dot{C}OH \qquad (10)$$

$$R_2\dot{C}OH + R'_2\dot{C}OH \longrightarrow R_2CO + R'_2CHOH \qquad (11)$$

Such a mechanism would have been very interesting as an example of a "cooling off" process involving temporary storage of material in the form of high energy intermediates. Radicals produced in reaction 10 would be vibrationally excited and would lose energy before disproportionation regenerated the original reactants with the carbonyl compound being produced in its ground electronic state. However, occurrence of reactions 10 and 11 should lead to racemization of an active secondary alcohol. Failure to observe any racemization after prolonged irradiation of 2-acetonaphthone in active 2-octanol excludes the mechanism.

Another possible explanation of the inert character of naphthoyl compounds would be found if the excited molecules did not decay by way of triplet states. The fact that they phosphoresce when irradiated in a glass at low temperature would not guarantee that intersystem crossing would be efficient at room temperature in fluid solutions. Such a possibility is disallowed, however, by the study of the characteristics of photoreduction of the two compounds by tributylstannane. The reactions show the characteristics that were used previously to infer that long-lived triplets are involved in photoreduction of benzophenone (7, 9, 10). Thus, significant reaction occurred in solutions in which the concentration of hydrogen donor was as low as 0.075 M and quenching by 3×10^{-4} M ferric chelate was easily measurable. The conclusion that irradiation of 2-acetonaphthone and 1-naphthaldehyde gives high yields of triplets seems inescapable.

The lowest triplet state of benzophenone lies 70 kcal. above the ground state (1). The lowest triplets of many dialkyl ketones, alkyl phenyl ketones and benzophenones are grouped surprisingly close together with excitation energies between 70 and 75 kcal. (17). They must all be $\underline{n} - \pi^*$ triplets, and the close grouping probably indicates a relatively high degree of localization of the π^* electron. In any event, the fact that compounds as different as acetone, acetophenone and benzophenone have triplet excitation energies within 4 kcal. of each other leads one to expect that nearly all $\underline{n} - \pi^*$ triplets of aldehydes and ketones will lie close to 70 kcal. above the ground states. However, the lowest triplet states of 1-naphthaldehyde and 2-acetonaphthone lie, respectively, at 57 and 59 kcal. above the ground states. The close similarity in position and structure of the phosphorescence spectra of these compounds and other naphthalene derivatives (1, 17) indicates that $\pi - \pi^*$ triplets of naphthoyl compounds lie lower than the $\underline{n} - \pi^*$ triplets.

There are two possible reasons for the low reactivity of the triplet states of naphthoyl compounds: First, they have less excitation energy; and, second, they have electronic structures different from those of carbonyl compounds that undergo easy photoreduction. The energetic argument alone is hardly enough to account for the disappearance of the hydrogen transfer reaction. With an aliphatic secondary alcohol as the donor, reaction 10 would be endothermic by less than 45 kcal.* with the ground state of the ketone. Therefore, the reaction with any of the triplets studied should be highly exothermic. Apparently abstraction by the naphthoyl triplets, unlike the abstraction reactions of benzophenone triplets, involves a significant activation energy. The result is not surprising since $\underline{n} - \pi^*$ excitation of benzophenone specifically produces an electron deficiency at the oxygen atom to which a new bond must be formed.

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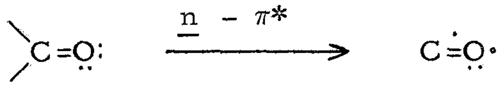
*A rough estimate for the heat of the reaction, $C_{10}H_7COCH_3$ + $RCHOHCH_3 \longrightarrow C_{10}H_7\underset{\cdot}{C}(OH)CH_3 + R\underset{\cdot}{C}(OH)CH_3$, can be made as follows: $D(C{=}O) - D(C{-}O) = 94$ kcal. (18); $D(RCH(CH_3){-}H) = 94$ kcal. (19); $D(O{-}H) = 110$ kcal. (18); R.E.$(C_{10}H_7\underset{\cdot}{C}(OH)CH_3)$ = R.E.$(1{-}C_{10}H_7CH_2\cdot)$ (20) + 7 kcal.** = 29 kcal.; excess R.E. of $R\underset{\cdot}{C}(OH)CH_3$ = 7 kcal.** The estimated heat of reaction is 42 kcal., which should be a maximum value.



If the triplets of 2-acetonaphthone and 1-naphthaldehyde have the π π^* configuration, the half-vacant, bonding orbital is spread over the entire system rather than being concentrated at the oxygen atom. Hydrogen abstraction by such a species would require extensive electronic reorganization and might therefore be an activated process. Although the Sn-H bond energy is not known, it must be rather low, increasing the exothermicity of abstraction by an excited molecule. Both this factor and the high polarizability of tin atoms must contrive to lower the activation energy for the reaction in which tributylstannane serves as the donor.***

**Stabilization of α-oxyradicals is well recognized but hard to document quantitatively. Walling (21) estimated stabilization by an α-ethoxy group of 8 kcal. A value of 11 kcal. for the resonance energy of $\cdot CH_2OH$ can be estimated from the rate of pyrolysis of ethyl alcohol (22).

***Charge transfer bonding, arising from partial transfer of the electron in the π^* orbital to tin, might contribute to the decrease in activation energy.

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12. This calculation is based on the formula:

    $\tau = g_u/g_\ell \; n^2 c \; 8\pi \bar{\nu}_m^2 \int \epsilon'(\bar{\nu}) \, d\bar{\nu}$, from ref. 1.

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PART II

TRIPLET-TRIPLET ENERGY TRANSFER IN SOLUTION

Introduction

Energy transfer between molecules has been of interest to chemists and physicists for many years. An important subcategory of intermolecular energy transfer (and one of particular concern to photochemistry) is non-radiative transfer of electronic excitation energy between molecules. For purposes of discussion, the speculation and experimental evidence for the latter phenomenon may be broken down into three general categories:

(1) Exciton migration in crystals, (2) fluorescence quenching and concentration depolarization in solution, and (3) triplet-triplet transfer in liquid or solid solution.

Exciton migration through inorganic crystals has been rather extensively studied. It is a short range effect requiring orbital overlap between donor and acceptor (1). The donor and acceptor are usually the same kind of molecule. Exciton migration has been detected in many of the oxides, halides and sulfides of copper, mercury, lead, cadmium, barium, and other metals (2). In a relatively pure crystal this type of energy transfer can go on successively between like molecules until it reaches an impurity molecule of lower electronic excitation energy. The impurity serves as a "trap" and cannot re-excite a host molecule, hence it must get rid of its energy some other way, often by fluorescence. A similar sort of energy transfer in organic crystals has been demonstrated for naphthalene (3, 4) and anthracene (3) with anthracene and naphthacene, respectively, serving as acceptors (traps).

Phenomena relating to the quenching of fluorescence (category 2) may or may not involve intermolecular excitation energy transfer. In fluorescence quenching by oxygen, the quencher may act chiefly as a paramagnetic catalyst for singlet-triplet interconversion and not receive electronic excitation energy itself (excess energy liberated in the process presumably being absorbed by solvent as vibrational energy). The numerous examples of quenching of the fluorescence of dyes by aromatic molecules (5) cannot involve electronic energy transfer because the energy of the lowest excited singlet states of the donors are much lower than the energies of the lowest excited singlet states of the acceptors (quenchers). Eisenbrand (6) has attributed quenching of this sort to compound formation between fluorescing molecule and quencher. For example, Weiss (7) regards the quenching of methylene blue fluorescence by phenylhydrazine as due to the formation of a charge-transfer complex. The dye presumably is reduced by the action of light and the hydrogen donor to yield a species incapable of fluorescence. Another general type of fluorescence quenching, known as concentration quenching, manifests itself by a decrease in fluorescence yield with increasing concentration of fluorescent material. This type of quenching is often attributed to purely chemical effects such as the formation of molecular aggregates to yield species that do not fluoresce upon excitation. Forster's book (5) contains a lengthy account of the various special cases and theories of concentration quenching.

Induced fluorescence is well known in the vapor (8) and liquid (9) states as well as the solid state (3, 4) and must involve singlet-singlet excitation energy-transfer. Lipsky and Burton (9) observed the fluorescence of terphenyl sensitized by toluene. They concluded from their measurements that the energy transfer was faster than the diffusion controlled rate, and they speculated about the possibility of a long-range effect. The theory of long-range energy transfer in solution has been invoked to explain concentration depolarization of fluorescence (10). If a dilute solution of a fluorescent substance is irradiated with polarized light, the observed fluorescence is ordinarily polarized. However, if the concentration of the fluorescent substance is increased, the polarization of the emission is decreased. The fact that this depolarization phenomenon persists in viscous media indicated to Perrin that some long-range (not nearest neighbor) effect is operating. Foster (11) estimates that this type of energy transfer process can take place across distances of 50-100 Å. According to him the efficiency of the process is proportional to the overlap between the donor emission spectrum and acceptor absorption spectrum, and inversely proportional to the sixth power of the intermolecular distance. For like molecules the overlap will be small (0-0 bands only). Foster emphasizes that this is not an emission-reabsorption process, but that the energy transfer is made possible due to a weak quantum mechanical coupling of the two transition dipole oscillators.

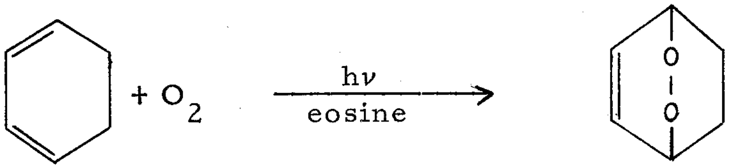
The preceding discussion has been concerned with energy transfer between molecules in singlet states. Our investigations are primarily concerned with category 3, the phenomenon of triplet-triplet transfer.

A molecule in a triplet state may be destroyed by a chemical reaction or it may lose energy and return to the ground singlet state by various means. The latter include (1) phosphorescence, (2) thermal deactivation, and (3) transfer of energy to another molecule with concomitant promotion of the latter to an excited electronic state. A foreign substance capable of acting as an acceptor in the transfer process may be a very efficient quencher. However, observation of very efficient quenching action does not necessarily imply that the quencher acts as an energy acceptor. Some molecules, such as paramagnetic species, may catalyze thermal deactivation by alleviating spin-conservation restrictions.

Triplet-triplet transfer in the glassy state at low temperature has been reported by Terenin and Ermolaev (12, 13, 14). They investigated several systems. A typical one was benzaldehyde and naphthalene in EPA. Irradiation of naphthalene alone in EPA with 3660 Å light produced no visible luminescence (since naphthalene does not absorb in this region). However, if benzaldehyde was added the phosphorescence of naphthalene was observed along with the characteristic emission of benzaldehyde. The lowest triplet state of naphthalene lies below the lowest triplet of benzaldehyde. Therefore it is assumed that the long-lived benzaldehyde triplet simply passes its energy to the naphthalene. Quite recently, Farmer, Gardner and McDowell (15) have reported very similar results with benzophenone as the donor. An EPA glass containing both the ketone and naphthalene was irradiated with light of a wavelength absorbed only by benzophenone. Naphthalene triplets, presumably formed by energy transfer from benzophenone triplets, were produced and detected by e.p.r. spectroscopy.

Bäckstrom and Sandros (16) have been the only investigators to observe induced phosphorescence in solution. They irradiated a solution containing benzophenone and biacetyl with light of a wavelength absorbed only by benzophenone, and observed phosphorescent emission from the biacetyl triplet. The same authors (17) have observed quenching of phosphorescence of biacetyl by certain polynuclear hydrocarbons. A quenching mechanism involving triplet-triplet energy transfer was proposed.

Photosensitized chemical reactions offer a promising approach to the study of triplet-triplet energy transfer in solution. Well known examples of photosensitized reactions are the formation of transannular peroxides from dienes. Various dyes are commonly used as sensitizers (18, 19, 20).



Other dye-sensitized oxidations by molecular oxygen are also known (21, 22, 23). The mechanism of these processes almost certainly cannot involve triplet-triplet transfer from the excited dye molecule to the substrate. The triplet states of the dyes are much lower than the triplet states of the acceptors so the transfer would be highly endothermic. The mechanism proposed by Schenck in 1948 seems to be the most reasonable (24). In this mechanism a triplet state of the dye (D) reacts with oxygen to form a labile complex which then oxidizes the substrate (S):

$$\begin{tikzcd}
h\nu + D \arrow[r] & D^* \arrow[r] & D^3 \arrow[dr, "O_2"] & \\
D + O_2S & DO_2S \arrow[l] & & DO_2 \arrow[ll, "S"']
\end{tikzcd}$$

Within the past year Schenck has published an account of the benzophenone-photosensitized addition of maleic anhydride to benzene (25). The mechanism is not clear, but it is nearly certain the reaction involves transfer of energy from the lowest triplet state of benzophenone to maleic anhydride. Unequivocal evidence for triplet-triplet transfer in other photosensitized chemical reactions has recently been obtained in these laboratories. Hammond, Leermakers, and Turro (26) found that benzophenone was an efficient sensitizer for the photodecomposition of ethyl pyruvate. Benzophenone, which is known to yield triplets quantitatively when irradiated in solution (27), was irradiated in the presence of ethyl pyruvate with light of appropriate wavelengths absorbed only by benzophenone. The ester decomposed with a quantum yield even higher than that for direct, unsensitized photolysis. The evidence overwhelmingly compels the assumption that triplet-triplet transfer has occurred. In another instance, Kopecky, Hammond, and Leermakers (28) showed that benzophenone served as a sensitizer for the decomposition of diazomethane. Triplet methylene was produced. Its chemistry showed nonstereospecific addition to double bonds rather than stereospecific addition to double bonds and indiscriminate insertion into C-H bonds characteristic of singlet methylene.

It was of interest to us to complement and extend the above findings to other systems in an attempt to elucidate the general rules governing triplet-triplet energy transfer in solution. Two techniques have been employed in this investigation. The first involves photosensitization of the cis-trans isomerization of piperylene (1,3-pentadiene) by various aryl carbonyl compounds. The second method involves the study of the effects of quenchers on the quantum yield in the photoreduction of benzophenone by benzhydrol. We believe that quenching is accomplished by energy transfer to the quencher:

$$(C_6H_5)_2CO^3 + Q \longrightarrow (C_6H_5)_2CO + Q^*$$

Relative quenching efficiencies of various compounds have been determined.

Experimental

Chemicals.— cis-Piperylene was obtained from mixed piperylene (29) obtained from K and K Chemicals. The mixture was heated under reflux with maleic anhydride to remove the trans-isomer. The cis-isomer was then distilled and a fraction boiling at 43-44° at atmospheric pressure was collected for use. 1-Naphthaldehyde (Eastman Kodak White Label) was vacuum distilled, the fraction boiling in the range 110-112° at 3 mm. was collected and used. Benzaldehyde (Matheson, Coleman, and Bell , Reagent Grade) was purified by distillation. The fraction boiling in the range 179-180° was collected. 9-Anthraldehyde (Aldrich Chemical Corp.) was recrystallized from acetic acid, m.p. 104°. 2-Acetonaphthone (Eastman Kodak White Label) was recrystallized from petroleum ether, m.p. 55-56°. Benzophenone (Matheson, Coleman and Bell, Reagent Grade, m.p. 47-48°), benzil (Matheson, Coleman and Bell, Reagent Grade, m.p. 94-95°), and dibenzalacetone (Eastman Kodak White Label, m.p. 112-113°) were used as furnished. Benzene (Mallinckrodt Analytical Reagent Grade) was used as furnished. Benzhydrol (Matheson, Coleman and Bell, Reagent Grade) was twice recrystallized from petroleum ether. Tributylstannane was prepared as described in Part I of this thesis. Naphthalene (Matheson, Coleman and Bell, Reagent Grade, m.p. 80-81°), azulene (Aldrich Chemical Corp., m.p. 101-102°), and maleic anhydride (Matheson, Coleman and Bell, Reagent Grade, m.p. 53-55°) were used as furnished. Purified cyclohexene and ferric dipivaloylmethide were furnished by Dr. Karl Kopecky. Naphthalene-d_8 was obtained from Merck, Sharp and Dohme and used without further purification.

Apparatus.— The light source, optical system, reaction cells, etc., for the quantum yield determinations have been described previously (27). The filter system, consisting of Corning glass filters 7-60 and 0-52 in series, isolated the 3660 Å Hg emission. For other experiments an immersion reactor (Engelhard Industries) was used with a Hanovia 200 w S-654A mercury vapor lamp as the light source. Vapor chromatography was carried out with a Loenco Model 15 instrument containing a column packed with tricresylphosphate.

Isomerization of cis-Piperylene Photosensitized by 1-Naphthaldehyde.— A benzene solution containing 0.10 M 1-naphthaldehyde and 0.8 M cis-piperylene was irradiated overnight in the immersion reactor. Vapor chromatographic analysis of the product mixture showed that 90% of the cis-piperylene had been converted to another compound with retention time about 20 seconds shorter than that of cis-piperylene at room temperature. The mixture was distilled and the volatile product was collected and purified by vapor chromatography. The infrared spectrum indicated that the new compound was trans-piperylene (30) and its ultraviolet spectrum exhibited a maximum at 2240 Å in agreement with the value reported in the literature for *trans*-piperylene (31). The maleic anhydride adduct was prepared, m.p. 60° (lit. value, 62° (32); the *cis* isomer does not form the adduct).

Determination of Photostationary Isomer Ratios with Various Sensitizers.— Benzene solutions containing 0.1 M aromatic carbonyl compound and 0.2 M *cis*-piperylene were irradiated in the immersion reactor with all light of wavelengths shorter than 2800 Å filtered out with an Engelhard Industries corex filter. Samples were withdrawn periodically and analyzed by vapor chromatography. Irradiation was continued until the *cis*/*trans* isomer ratio was observed to be constant (usually 3-4 hours). In general, the total diene concentration did not change. Some diene was consumed when benzil and dibenzal acetone were used as sensitizers.

Photoreduction of 9-Antraldehyde.— A solution containing 7.5 mmoles of 9-anthraldehyde and 20 mmoles of tributylstannane in 130 ml. benzene was irradiated for 8 hours. The solvent was then stripped off and petroleum ether was added. A white solid (0.4 g., 27%) separated out, m.p. 220-230°. Chromatography of the entire reaction mixture on alumina yielded this material pure, m.p. 228-232°. Treatment of 18 mg. of this compound with lead tetraacetate in acetic acid for 3 hours, followed by the addition of 2,4-dinitrophenylhydrazine reagent, yielded a brick-red solid (not weighed) which was recrystallized from ethanol-ethyl acetate, m.p. 271-275°. Authentic 9-anthraldehyde-2,4-dinitrophenylhydrazone was prepared, m.p. 277-282°; mixed m.p. 272-280°.

Determination of Quantum Yields.—

(1) Actinometry.— A benzophenone-benzhydrol actinometer was employed. Solutions 0.05 molar in benzophenone and 0.10 molar in benzhydrol were degassed and irradiated for a given length of time. The residual benzophenone was then determined spectrophotometrically. A quantum yield of 0.74 for the process is assumed.* The results obtained by this method were consistent with one determination using the uranyl oxalate actinometer. A solution 0.10 molar in oxalic acid and 0.03 molar in uranium acetate was irradiated. After 11,160 seconds the residual oxalic acid was titrated with 0.100 N permanganate. A quantum yield of 0.49 is assumed for the uranyl oxalate system (33).

(2) Photoreduction of Benzophenone.— Benzene solutions usually containing 0.05 M benzophenone, 0.10 M benzhydrol, and a quencher in low concentration (2-5 x 10^{-4} M) were placed in quartz cells, degassed, and irradiated. After a measured length of time the reaction was stopped and the residual benzophenone was determined spectrophotometrically after appropriate dilution.

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*This assumption is based on the extensive investigation of the system by W. M. Moore, Ph. D. Thesis, Iowa State College, 1959, and ref. 27, and on the slight revision of the data by Mr. R. P. Foss.

(3) Photoreduction of Anthraldehyde.— Benzene solutions containing 1.0×10^{-3} M 9-anthraldehyde and 0.148 M tributyl stannane, were degassed and irradiated. The cells were then opened and the residual anthraldehyde was determined by 25 fold dilution and measurement of the absorbence at 4000-4400 Å. In one experiment azulene (5.0×10^{-4} M) was included.

(4) Isomerization of Piperylene.— A benzene solution containing 0.05 M benzophenone and 0.10 M cis-piperylene was degassed and irradiated for 16,380 seconds. The extent of isomerization was determined by vapor chromatographic analysis of the reaction mixture.

Results and Discussion

Sensitized Isomerization of Piperylene

Piperylene (1,3-pentadiene) possesses a strong $\pi - \pi^*$ transition in the 2200-2300 Å region* but shows no absorption at wavelengths longer than 2500 Å. Irradiation of a benzene solution originally containing 0.2 M _cis_-piperylene and 0.1 M benzophenone, with all light of wavelengths shorter than 2800 Å filtered out, converted the _cis_-diene to a mixture of the _cis_ and _trans_ isomers. After three hours the composition of the mixture became constant, with the _trans_-isomer predominating in the ratio of about 4: 3. The quantum yield for the process was found to be about 0.3.

Use of other aromatic carbonyl compounds as sensitizers gave very interesting results. Benzil, 2-acetonaphthone and 1-naphthaldehyde sensitized the isomerization to give photostationary mixtures that were much richer in _trans_- than _cis_-diene. Dibenzalacetone, on the other hand, was essentially inert as a sensitizer. The data are summarized in Table I.

In no case was light absorbed by the diene; all light responsible for promoting the isomerization was absorbed by the sensitizer. From work performed in these laboratories it is known that benzophenone (27),

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* λ_{max} for _cis_ = 2280 Å, for _trans_, 2240 Å; ϵ_{max} in both cases is about 20,000.

Table I

Photosensitized *cis*-*trans* Isomerization of Piperylene

Carbonyl Compound	*trans*/*cis* Ratio at Stationary State	O-O Band in Phosphorescence Spectrum of Sensitizer (33)	Triplet Energy (kcal)
Acetophenone	I.23	3850 Å	74
Benzaldehyde	1.23	3960	72
Benzophenone	1.30	4100	70
Benzil	2.25	4630	62
2-Acetonaphthone	2.50	4830	59
1-Naphthaldehyde	10	5100	57
Dibenzalacetone	no isomerization	5400	53

2-acetonaphthone (35) and 1-naphthaldehyde (35) decay efficiently to triplet levels in solution at room temperature. In addition, acetophenone (36), benzaldehyde (37) and dibenzalacetone (38) have been found to undergo photoreduction reactions in solution, which seems to be a criterion for the existence of long-lived excited intermediates (e.g., triplet states). Benzil (16) phosphoresces in solution and hence must decay via the triplet state. All of the above compounds phosphoresce strongly in an EPA glass at low temperature (34), and the above evidence suggests strongly that decay via triplet levels takes place in solution at room temperature also. If this may be granted, one is forced to the conclusion that the sensitized isomerization involves energy transfer from the triplet state of the carbonyl compound to the diene, with production of the triplet state of the diene. The sensitizer triplets at 20,000-25,000 cm^{-1} (34) (or even the sensitizer singlets at 30,000-33,000 cm^{-1}) could not possibly excite the diene to the lowest excited singlet at 45,000 cm^{-1} (31) since such a process would be highly endothermic.

Direct, unsensitized isomerization has been reported to yield a photostationary composition of 73% cis and 27% trans after 12-24 hours starting from the cis-isomer (39). After irradiation of the cis-isomer with unfiltered light for three days we observed a composition of 52% cis and 48% trans. The efficiency is extremely low (partly because of the low intensity of the emission from the lamp at wavelengths shorter than 2500 Å), and the photostationary ratio may not have been reached. It may well be that isomerization via direct excitation of the diene to an upper singlet state (i.e., unsensitized photolysis) does not go through the triplet state, and that isomerization of the excited singlet is inefficient because it must compete with very fast singlet decay processes. It also may be the case that unsensitized isomerization does go through the triplet state but that singlet-triplet intersystem crossing in the diene molecule is very inefficient.

There is no report in the literature of observation of phosphorescence of simple conjugated dienes; therefore it is quite possible that the excited singlet states, produced by light absorption, do not decay by way of triplet levels. Consequently, the sensitized reactions are of considerable interest for two reasons: (1), a method is now available for the production of a group of potentially valuable chemical intermediates; (2), the use of a suitably graded series of sensitizers should provide an easy method for estimation of the energies of the triplet states of dienes, a matter of some theoretical interest (40).

Current notions (11, 12) would predict that energy transfer will not occur if the diene triplet is at higher energy than the triplet state of the sensitizer. However, at 0-20° C, the temperatures at which most of our experiments have been carried out, there is a reasonable possibility that slightly endothermic energy transfers may occur. These activated processes could take place between the triplet and vibrationally excited diene molecules. In any event, it is likely that the transfer efficiency will be low if the O — O band in the phosphorescence spectrum of the sensitizer lies at longer wavelengths than the corresponding transition of the diene. Characteristics of the phosphorescence spectra of the various sensitizers are included in Table I. Acetophenone, benzaldehyde and benzophenone gave stationary state compositions which only slightly favor the <u>trans</u> diene. Therefore we infer that the triplet energies of these carbonyl compounds lie above the energies of the lowest triplet states of both cis- and trans-piperylene. Benzil, 2-acetonaphthone and 1-naphthaldehyde establish stationary states in which the trans isomer predominates strongly. From this we infer that the S_g-T_1 transition of cis-piperylene lies at slightly longer wavelengths than that of the trans isomer, since energy transfer to the trans isomer has become relatively inefficient. Since dibenzalacetone showed no sensitizing action, the transitions in both dienes must be at shorter wavelengths (higher energy) than 5400 Å. This estimate agrees very well with the results of Evans (40), who observed a broad band in the 3500-5000 Å region (O-O band at 4800 Å) in the spectrum of butadiene in the presence of high pressures of oxygen. The oxygen perturbation method permits the direct spectrophotometric observation of singlet-triplet absorption. This transition becomes weakly allowed due to the presence of large concentrations of paramagnetic oxygen molecules. Results obtained in this manner have been open to some question because of the possibility of molecular compound formation with oxygen. Our agreement with Evans' results is important because it establishes the fact that S_g-T_1 transitions observed by the oxygen perturbation technique are not significantly altered (at least in the case of 1,3-dienes) by strong interactions with oxygen.

Two experiments were carried out in an attempt to induce triplet-triplet transfer between two hydrocarbons, a phenomenon which has not yet been reported in the literature. In the first experiment, a solution of naphthalene and cis-piperylene in benzene was irradiated for many hours. Isomerization proceeded extremely slowly and irradiation was discontinued. In the second experiment a benzene solution containing benzophenone, naphthalene, and cis-piperylene was irradiated for several hours. The photostationary state had the same composition as that established with only benzophenone as a sensitizer. In both experiments, naphthalene triplets must have been obtained efficiently.* The naphthalene triplet at 62 kcal. is several kcal. above the triplet of other compounds that do sensitize isomerization. The obvious conclusion from these experiments is that triplet-triplet transfer between the hydrocarbons naphthalene and piperylene is not efficient. However, more recent experiments in these laboratories have shown that the picture is more complicated. Quenching experiments (discussed in a later section) have indicated that the rate of energy transfer from benzophenone triplets to naphthalene is nearly identical to the rate of energy transfer from benzophenone to piperylene. Thus, if transfer from naphthalene triplets to piperylene is very inefficient, one would expect the rate of isomerization of piperylene sensitized by benzophenone to be reduced by half by

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*With reference to the first experiment, Porter and Wright (41) have found that irradiation of naphthalene solutions gives a high yield of triplets. With reference to the second experiment, naphthalene molecules that quench benzophenone triplets are presumably excited to their (the naphthalene molecules') triplet states. Most of the light was absorbed by benzophenone. Since benzophenone singlets decay exclusively via triplets (27), and since quenching by naphthalene is very efficient (discussed in a later section), naphthalene triplets must have been formed in an appreciable yield.

the addition of an equimolar quantity of naphthalene. Such an experiment has been recently carried out by Mr. N. J. Turro, who found that the rate of isomerization of piperylene was not reduced by the addition of naphthalene. The results of the above experiments appear to be irreconcilable. Further work is being done in these laboratories to clarify the overall picture of energy transfer between the triplet states of hydrocarbons.

Effect of Quenchers on the Photoreduction of Benzophenone.

From previous work in these laboratories (27) it is known that the photoreduction of benzophenone by benzhydrol in the presence of a quencher follows the rate law*:

$$\frac{1}{\phi} = \frac{1}{\phi'} + \frac{k_d}{\phi' k_r [DH]} + \frac{k_q [Q]}{\phi' k_r [DH]}$$

Measurement of the quantum yield, ϕ, for the photoreduction as a function of quencher concentration yielded values of k_q/k_r, the ratio of the rates of quenching to hydrogen abstraction. The data are given in Table II and figures 1-3.

The mechanism of the quenching action of ferric dipivaloylmethide is uncertain but the other compounds probably function as acceptors in the process of energy transfer. In every case in which the

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*See Part I of this thesis, pp. 3 and 4 , for an explanation of the symbols.

Table II[a]

Photoreduction of Benzophenone by Benzhydrol in the Presence of Quenchers

Quencher	[Quencher]	[Benzhydrol]	ϕ	k_q/k_r	E_T[b]	Ref.
2-Acetonaphthone	5×10^{-4}	0.20	0.30	790	59	34
2-Acetonaphthone	5×10^{-4}	0.10	0.20	730		
Naphthalene	5×10^{-4}	0.10	0.20	750	61	34
Naphthalene	2×10^{-4}	0.10	0.34			
<u>cis</u>-Piperylene	5×10^{-4}	0.10	0.21	750	55-60	e
<u>cis</u>-Piperylene	1.0×10^{-3}	0.10	0.104			
Benzil	4.4×10^{-4}	0.10	0.31	436	62	34
Cyclohexene	5×10^{-4}	0.10	0.67	30	?	
Azulene	5×10^{-4}	0.10	0.15			
Azulene	2×10^{-4}	0.10	0.25	1100	?	
Azulene	3×10^{-4}	0.10	0.20			
1-Naphthaldehyde	5×10^{-4}	0.10	0.17	880	57	34
1-Naphthaldehyde	2×10^{-4}	0.10	0.34			
Naphthalene-d_8	5×10^{-4}	0.10	0.18	840	61	34
Biacetyl	5×10^{-4}	0.10	0.41	c	56	34
Maleic anhydride	5×10^{-4}	0.10	0.58	d	?	
Ferric dipivaloylmethide	2×10^{-4}	0.10	0.48	365	-	
None	-	0.10	0.74	-	-	

a. Concentration of benzophenone = 0.05 M.
b. Energy of lowest triplet state (kcal.).
c. Quencher consumed in the reaction.
d. Quencher probably consumed by the Schenck (25) reaction.
e. See this thesis, Part II, preceding section.

Figure 1

Quenching of Photoreduction of Benzophenone by ○, Azulene, and ⊕, Naphthalene.

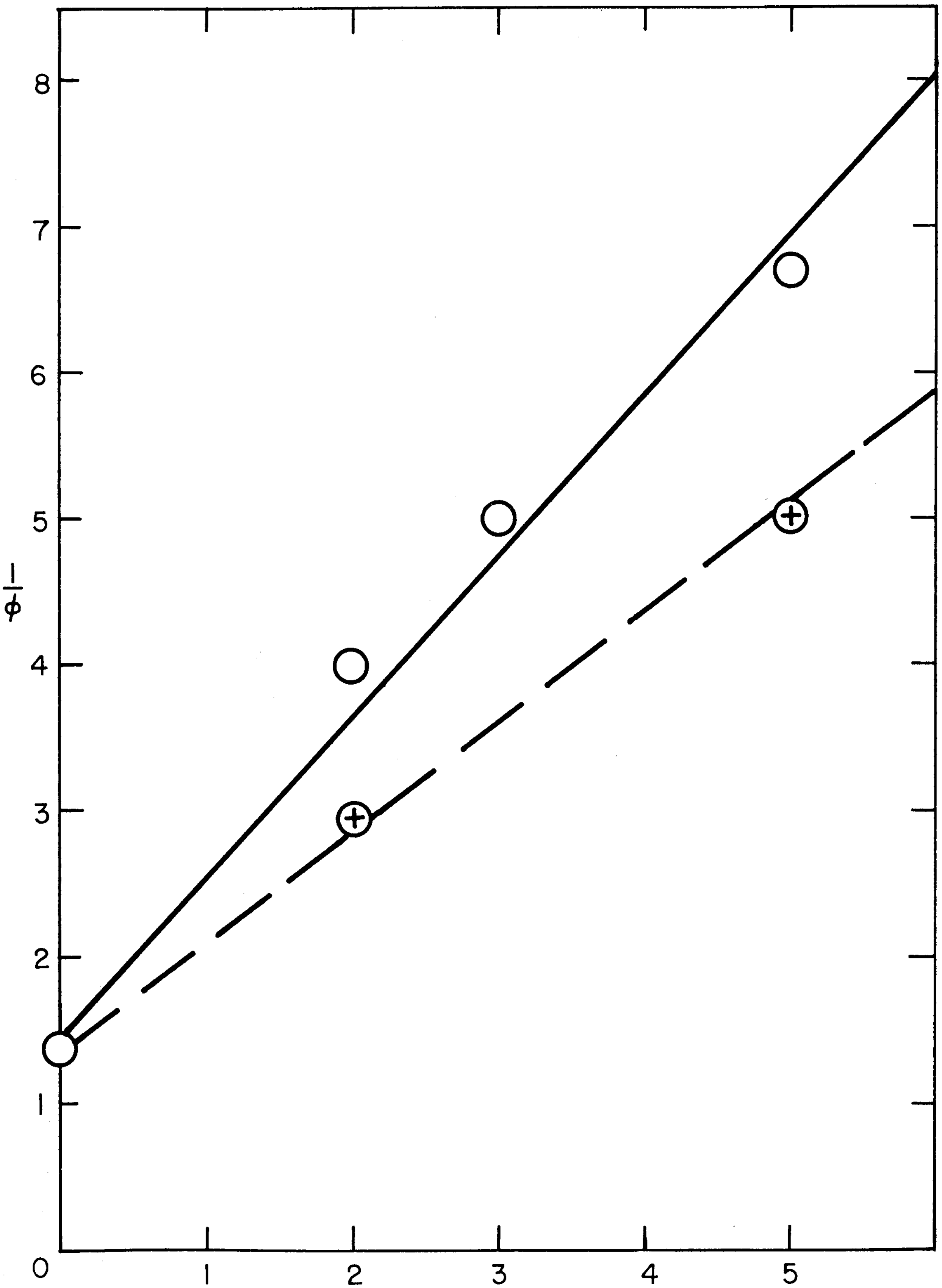

8
7
6
5
4
3
2
1
0
$\frac{1}{\phi}$
1
2
3
4
5
[QUENCHER] x10^{+4}

Figure 2

Quenching of Photoreduction of Benzophenone by Piperylene.

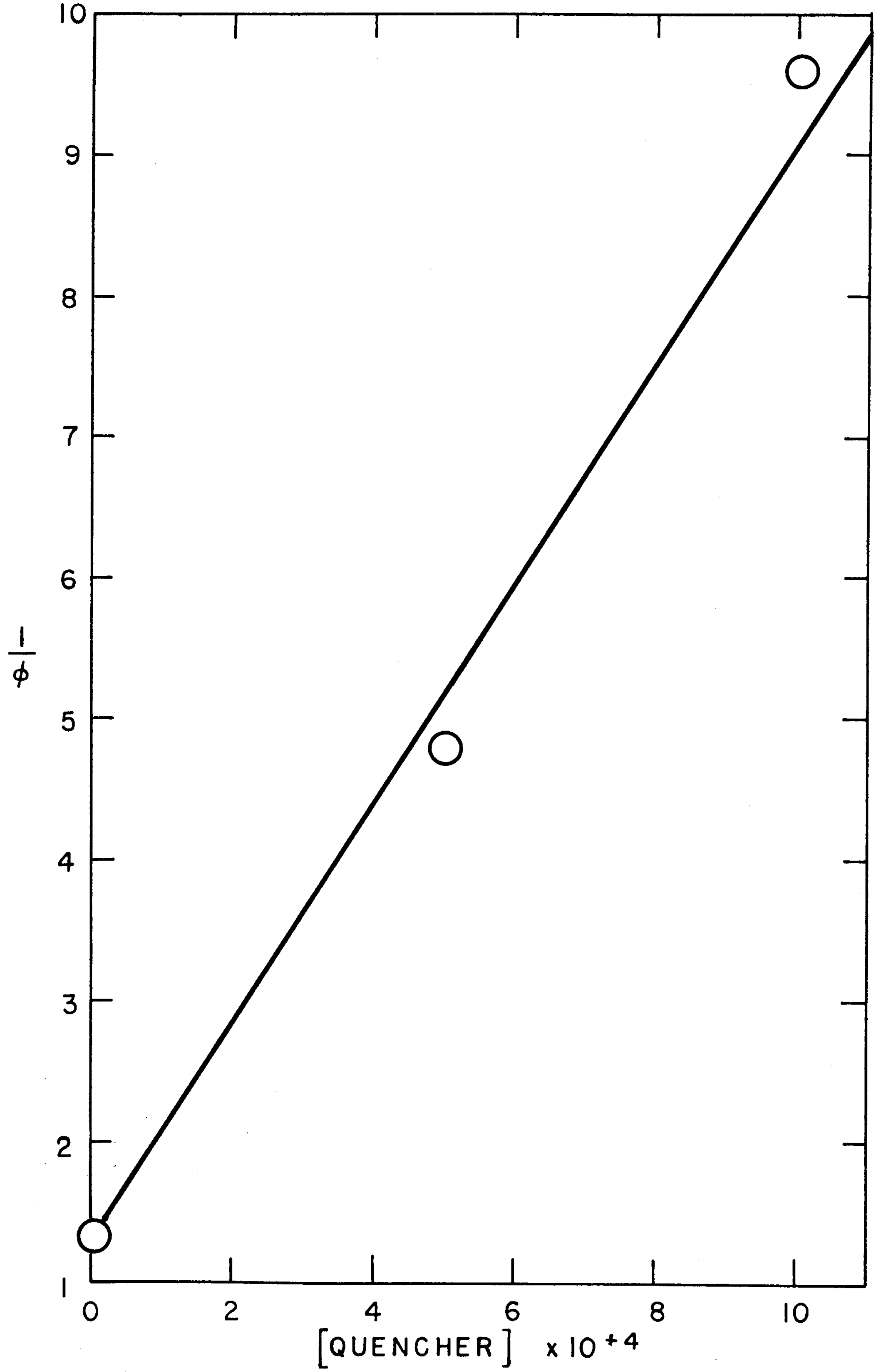
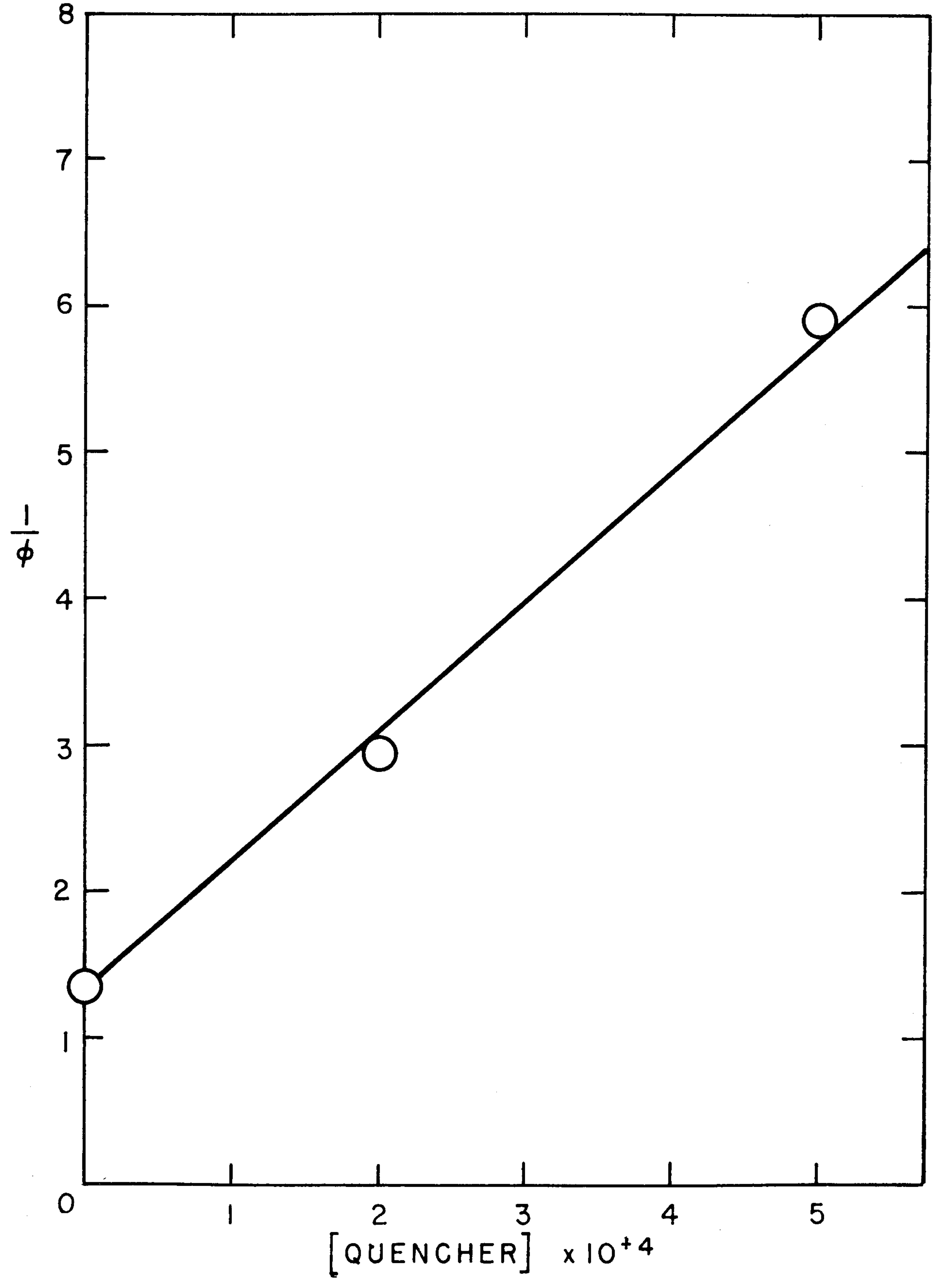

1/φ
10
9
8
7
6
5
4
3
2
1
0
2
4
6
8
10
[QUENCHER] x 10^{+4}

Figure 3

Quenching of Photoreduction of Benzophenone by 1-Naphthaldehyde.



8
7
6
5
4
3
2
1
0
$\frac{1}{\phi}$
1
2
3
4
5
[QUENCHER] x 10⁺⁴

energy of the lowest triplet state of the acceptor is known, the transfer would be exothermic since the lowest triplet of benzophenone lies 70 kcal. above the ground state (34). No information is available concerning the triplet states of azulene, cyclohexene and maleic anhydride. However, since the first singlet-singlet transition of azulene is found at 7000 Å (42 kcal.), the compound must have one, and probably more (42), triplet states lying below the lowest triplet of benzophenone. However, it seems very probable that energy transfer to cyclohexene would be endothermic. Evans (40) observed the S_g-T_1 transition of ethylene at 29,000 cm^{-1} (83 kcal.). Incorporation of the ethylenic function in a cyclic system might lower the S_g-T_1 excitation energy somewhat but it seems very doubtful that gap will be as low as 70 kcal. We believe that the relatively inefficient quenching by cyclohexene is probably characteristic of an energy transfer which is endothermic by a few kilocalories. If the argument is turned around, we can infer that the S_g-T_1 transition of maleic anhydride, a reasonably efficient quencher, must require 70 kcal. or less.

The quenching efficiencies of most of the compounds tested are grouped remarkably close together. Naphthalene, 1-naphthaldehyde, 2-acetonaphthone, and piperylene all have values of k_q/k_r around 800, and the most efficient quencher of all that were tested was azulene ($\frac{k_q}{k_r}$ = 1100).

The remarkable similarity in the relative rates of quenching by compounds as different as piperylene, acetonaphthone, and azulene (rates within a factor of two of each other) is compelling evidence for the existence of one common, rate-limiting factor. A diffusion-controlled process is implied. Bäckstrom and Sandros (16, 17) have previously assumed that energy transfers of this sort are diffusion controlled. Their experimentally determined rate constants for quenching of biacetyl phosphorescence by certain polynuclear aromatic hydrocarbons ($k_q \sim 10^9 \ell$ mole^{-1} sec^{-1}) are of the order of diffusion controlled rate constants. Since this process must involve triplet-triplet transfer, it is probably safe to assume that quenching of benzophenone triplets by energy transfer will be at least close to diffusion controlled if the process is not significantly endothermic.

Quenching Ability of Azulene.

As mentioned previously, azulene was observed to be the best of the tested quenchers. Calculations based on three measurements yielded a value of $k_q/k_r = 1100$ (fig. 1). Azulene presumably has more than one triplet below the lowest triplet of benzophenone. The lowest azulene triplet probably lies in the infrared, a few thousand wave numbers below the lowest excited singlet state at 15,000 cm^{-1} (6000-7000 Å) (42). Two more triplets, corresponding to the singlets obtained by the transitions at 3500 Å and 2800 Å (42), should lie below or near to the benzophenone triplet. It is presumed that benzophenone is quenched by excitation of azulene to an upper triplet, since this process best conserves electronic energy.

It was of interest to determine experimentally if azulene could also quench by energy transfer to its lowest triplet. 9-Anthraldehyde was selected as the donor, since the energy of its lowest triplet must be at least as low as that of anthracene (14,700 cm^{-1} or 42 kcal. (34)), and probably slightly lower. This value would be well below the expected energy of an upper triplet of azulene, hence energy transfer to an upper triplet would not be anticipated. With no azulene present, 9-anthraldehyde was photoreduced by 0.15 M tributylstannane with a quantum yield of 0.045 to give a 27% yield of the corresponding glycol, 1,2-di-9-anthrylethane-1,2-diol. Under similar conditions, in the presence of 5×10^{-4} M azulene, the quantum yield was reduced to 0.025 (table III). Thus, quenching was again found to be significant with k_q/k_r calculated to be 5300. Since the systems are different, of course, this number cannot be directly interpreted in terms of the data for the benzophenone-benzhydrol system. The conclusion to be drawn is that quenching by energy transfer to the lowest triplet of azulene does occur.

Because of our current interest in the triplet levels of azulene, we are now carrying out experiments to determine if emission from an upper triplet of azulene can be induced by benzophenone or another

Table III

Photoreduction of 9-Anthraldehyde by Tributylstannane in the Presence of Azulene

[Anthraldehyde]	[Stannane]	[Azulene]	ϕ	k_q/k_r
1.0×10^{-3}	0.148	-	0.045	-
1.0×10^{-3}	0.148	5×10^{-4}	0.025	5300

suitable sensitizer.* This emission (which has not previously been observed) might be T_4-T_1 or T_3-T_1 fluorescence.

Quenching by Ferric Dipivaloylmethide.

Ferric dipivaloylmethide was found to quench benzophenone with a rate of k_q/k_r equal to 365, in good agreement with the value obtained by Moore, Hammond and Foss (27). Thus it is a somewhat less efficient quencher than naphthalene, piperylene, azulene, etc. However, previous assumptions (27, 35) regarding the diffusion controlled nature of the ferric chelate quenching reaction are still probably valid to a first approximation. The rate is about 50% slower than that of the quenching reactions of naphthalene and its derivatives; but absolute rates of diffusion controlled reactions probably cannot be estimated to within a factor of two in any case.

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*This work is being done by G. W. Robinson, G. S. Hammond and P. A. Leermakers.

The mechanism of quenching is open to some interesting speculation. Chelated ferric ion is a paramagnetic species with one unpaired electron in a d orbital. The most attractive mechanism would be the formation of a weak charge-transfer complex between the triplet and the metal ion. Spin inversion would be allowed. The excited molecule, upon returning to the ground singlet state, could elevate the ferric chelate to a fully allowed, short-lived, excited electronic state. The excited chelate would then fluoresce or be quenched rapidly to the ground state by non-radiative processes. Fluorescence has not been observed, nor has it been carefully looked for. In an alternate mechanism the energy of the excited benzophenone molecule is directly absorbed by solvent molecules as vibrational energy. The iron in this case acts merely as a center of paramagnetic perturbation which helps to allow spin inversion in the benzophenone triplet.

Quenching Ability of Naphthalene-d_8.

Robinson and co-workers (43) and Hutchison and Mangam (44) have observed that the phosphorescence lifetime of naphthalene-d_8 at low temperatures is significantly longer than that of naphthalene. The explanation proposed (45) for the phenomenon is that the overlap integral between the ground vibrational state of the triplet and the highly excited vibrational states (60 kcal.) of the ground singlet is much greater for the hydrogen compound than for the deuterated molecule. This is because the vibrational quanta are smaller in the latter case, and hence the vibrational quantum number corresponding to the same energy will be larger. Thus, non-radiative decay from the naphthalene triplet will be faster than that from perdeuteronaphthalene triplet. This effect is expected for all processes where a large amount of electronic energy is changed into vibrational energy of the products providing the mechanism of the transfer explicitly involves the C-H or C-D bonds.

It was of interest to us to determine if deuterium substitution had any effect on the quenching ability of naphthalene. In the quenching situation, the system B^3N^0 (benzophenone triplet - naphthalene ground) goes to B^0N^3. The 10 kcal. separating the electronic energies of the two states appears as vibrational energy in B^0N^3. The result of the experiment was that naphthalene-d_8 and naphthalene have about the same quenching efficiency. In retrospect, this is a reasonable result. The energy separation in the B^3N^0-B^0N^3 transition is small enough so that the ground vibrational state of B^3N^0 need only overlap with a relatively low vibrational state of B^0N^3. Furthermore, in solution there appear to be other non-radiative pathways to the ground state which do not involve the C-H or C-D vibrations. Thus the effect of deuterium substitution is insignificant.

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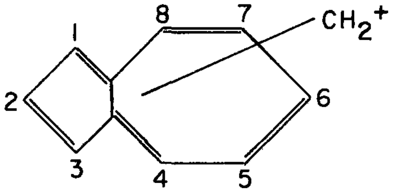
PROPOSITIONS

1. Simple molecular-orbital calculations* yield the following resonance energies for azulenyl-carbinyl cations (1):



I

			R.E.
1-	carbinyl	cation	3.470β
2-	"	"	3.686β
4-	"	"	4.394β
5-	"	"	4.148β
6-	"	"	4.378β

It is proposed that the corresponding bromides or tosylates be prepared and solvolyzed. It is predicted that a kinetic study of the system will show that the rates of solvolysis decrease in the following order:

4-isomer > 6-isomer > 5-isomer > 2-isomer > 1-isomer.

Syntheses of the azulenyl carbinols from which the bromides or tosylates will be made will be carried out based on Plattner's synthesis of azulene (1). The synthesis involves the diazoacetic ester ring expansion of indan with subsequent aromatization. This directly yields a mixture of the carboxylic esters in the 5 and 6 positions. The esters may be reduced to the carbinols with lithium aluminum hydride. To prepare the 1, 2 and 4 isomers the corresponding hydroxymethyl indans

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*The familiar LCAO method was employed. Funds for time on the computer were provided by Professor Hammond's PRF research grant.

would be employed as starting materials. Ring expansion would produce additional substitution in the 5 or 6 position, which would be eliminated by saponification and decarboxylation to yield the desired compounds.

A study of the sort proposed would yield information, in addition to that in the literature for other systems, concerning the reliability of simple M.O. methods in predicting reactivities or organic compounds.

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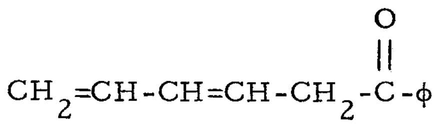
2. It is proposed that α-butadienyl-acetophenone (1) will show interesting and unusual photochemical behavior, the study of which may help elucidate the mechanism of triplet-triplet energy transfer.



$$CH_2{=}CH{-}CH{=}CH{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}\phi$$

I

Although the near ultraviolet spectrum of (I) should be nearly identical to that of acetophenone, it is predicted that the compound will not readily undergo the photoreduction reactions characteristic of acetophenone (1).

There are *two independent* conjugated centers in the molecule, *i.e,* the benzoyl system and the butadiene system. The molecule should possess three singlet-singlet transitions in the 4000-2000 Å region: an *n*-π^* transition at 3500-3000 Å and π-π^* transitions near 2500 Å and 2250 Å. Only the last transition, the one of highest energy, would be attributed to the butadiene function. However, since the S-T splitting for the butadiene transition is much larger than that for either acetophenone transition, the lowest triplet in the molecule should be that of the butadiene system (fig. 1) (2, 3, 4).

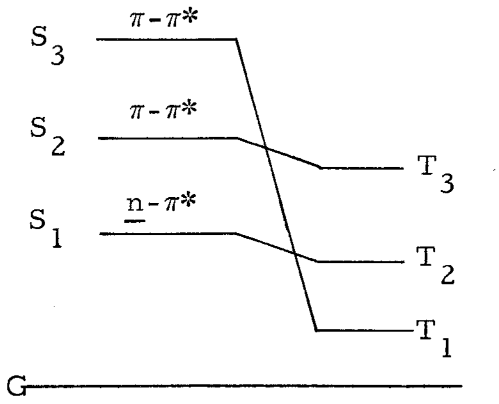


Figure 1

Thus, a quencher for the triplet energy of the benzoyl system is built into the molecule. Irradiation of the compound with light of wavelengths 2500-3500 Å should selectively excite only the benzoyl part of the system to the S_1 or S_2 singlet. The system will then quickly decay to the $\underline{n}-\pi^*$ triplet (T_2 in the diagram). If quenching (inter- or intramolecular) does not occur, this $\underline{n}-\pi^*$ triplet ought to easily abstract hydrogen from a suitable donor, or phosphoresce at low temperature.

It is proposed that a study be carried out in which quantum yields of photoreduction and phosphorescence (T_2-S_g and possibly T_1-S_g) are determined as a function of dienone concentration. If the quantum yields are essentially independent of concentration, T_2-T_1 quenching is intramolecular, accomplished by a distortion of the molecule which permits T_2-T_1 orbital overlap. If the quantum yields show a concentration dependence, then intermolecular quenching is important.

A careful analysis of the data from this and related systems ought to provide information about the nature and extent of orbital overlap required for triplet-triplet quenching.

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3. It is proposed that the technique of flash photolysis be employed in the study of triplet-triplet energy transfer between hydrocarbons. Bäckstrom and Sandros (1) have used the technique to measure rates of quenching of biacetyl phosphorescence by aromatic hydrocarbons and other compounds. In some cases the mechanism of quenching was triplet-triplet transfer from biacetyl to the quencher. Porter and Wright (2, 3) and Livingston and Tanner (4) have employed flash photolysis to study quenching of naphthalene and anthracene triplets. As quenchers they employed oxygen, various paramagnetic metal ions, and various organic compounds, none of which quenched by the triplet-triplet transfer mechanism.

There have been no reported cases in the literature of induced phosphorescence or quenching of triplet states in which the mechanism is triplet-triplet energy transfer between hydrocarbons (aromatics, dienes, etc. that possess low-lying triplet states).

Attempts have been made in these laboratories to observe triplet energy transfer from naphthalene to piperylene by chemical means, but the results are confusing (5).

It is proposed that two systems be studied in which the rates of triplet-triplet energy transfer between hydrocarbons may be easily measured. The two systems proposed are anthracene plus azulene and naphthalene plus piperylene. These systems are well suited for study because in both cases the triplet states of the donors (anthracene and naphthalene) are: 1) obtained in high yield in solution by the light flash, 2) long-lived (10^{-3} and 10^{-4} sec. lifetimes in hexane (3)), and 3) of higher energies than those of the acceptors (azulene and piperylene). The T_1-T_2 absorption spectra of the donor triplets are known (2, 4). The concentration of triplet species is followed by the optical density of its T_1-T_2 transition.

It is believed that rates of triplet-triplet quenching are diffusion controlled (1, 5). Whether this is true in the special case of quenching between hydrocarbons is the concern of this proposition. If, as has been suggested by Hammond (6), the presence of a dipole moment in one of the molecules is necessary for efficient quenching, then azulene should be a good quencher for anthracene even though piperylene may be a poor quencher for naphthalene.

Knowledge concerning the rates and mechanisms of triplet-triplet energy transfer is of significant importance. The fact that something unusual is suspected in the transfer between pure hydrocarbons would make the above experiments especially interesting.

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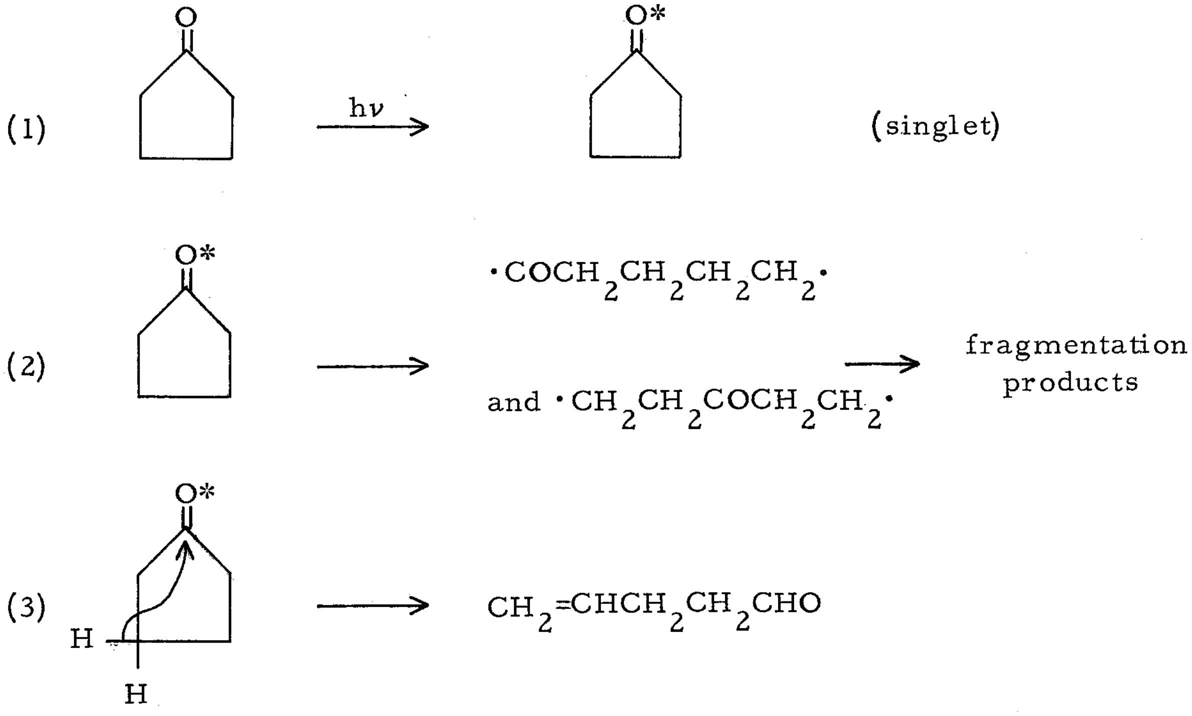
4. Srinivasan (1) has studied the photolysis of cyclopentanone in the vapor phase, and has observed carbon monoxide, ethylene and cyclobutane as fragmentation products, and 4-pentenal as the isomerized product. The irradiation used was 3130 Å.

He proposed the following overall mechanism:



$\cdot COCH_2CH_2CH_2CH_2\cdot$

and $\cdot CH_2CH_2COCH_2CH_2\cdot$

$CH_2{=}CHCH_2CH_2CHO$

In step 3, he proposed a direct hydrogen atom transfer to the carbon of the excited carbonyl prior to rupture of the ring system. That β (or γ) hydrogen was involved in the transfer was ascertained by photolyzing cyclopentanone-2, 2, 5, 5 d_4, in which case the isomerized product was found to be $CD_2{=}CHCH_2CD_2CHO$.

Since increasing pressure (either by the addition of carbon dioxide, oxygen, or more cyclopentanone) increases the quantum yield of the aldehyde from about 0.05 to double or triple that value, and at the same time decreases the quantum yield of fragmentation products, the author proposed that the higher vibrational levels of the excited singlet yield fragmentation products, the quenched lower levels yield the pentenal. The singlet rather than the triplet state is assumed, since oxygen does not inhibit the reaction. He rules out the $\cdot COCH_2CH_2CH_2CH_2\cdot$ diradical as an intermediate for pentenal formation because this would presumably be the same intermediate that forms the fragmentation products, and pressure effects should not be in the opposite direction in the two cases.

The above mechanism is highly improbable because direct abstraction of a hydrogen by the excited species (excited by an $\underline{n} \rightarrow \pi$ transition, the only transition of an unconjugated carbonyl group near 3130 Å) would situate the hydrogen on oxygen rather than on carbon.

It is proposed that the same intermediate diradical <u>does</u> give rise to the isomerized and fragmentation products. Thus, light absorption by the ketone gives rise to a vibrationally excited "hot" diradical which can form the fragmentation products immediately or which can be quenched by collision to a lower energy species. The quenched diradical will now take the easier path, <u>i.e.</u>, gamma hydrogen abstraction through a 5-membered ring transition state rather than the more energy-demanding fragmentation.

The following experimental evidence supports the above hypthesis: a) Increased pressure favors pentenal formation (quenching the diradical to lower vibrational states). b) Increased temperature favors fragmentation products (higher temperatures excite higher vibrational levels). c) Although the liquid phase photolysis has not been studied in the cyclopentanone system, it has been studied in the case of cyclohexanone (2). In the vapor phase photolysis of cyclohexanone at room temperature, the quantum yield of 5-hexenal is about 4 times that of the fragmentation products. In the liquid phase the ratio increases to about 10 to 1. Vibrationally excited species are more easily quenched in the condensed than in the vapor phase.

It should be relatively easy to distinguish experimentally between the two mechanisms. If a 1-3 hydrogen shift occurs before ring rupture, then a photolyzed sample of cyclohexanone-3, 3 d_2 should show a pronounced product isotope effect favoring $CH_2{=}CHCH_2CD_2CH_2CHO$ over the other possibility, $CH_2{=}CDCH_2CH_2CH_2CDO$. If the rupture occurs before hydrogen transfer, there is an equal probability of 1-6 rupture and 1-2 rupture; the radical has no choice which hydrogen to abstract, and ideally there would be no isotope effect. However, abstraction in the latter mechanism is competing with the fragmentation process. For this reason cyclohexanone (where, in the condensed phase, fragmentation is only one-tenth as important as isomerization) is chosen as the ketone for investigation. It is assumed that cyclopentanone and cyclohexanone react by the same mechanism.

The investigation is important from two standpoints. First, if Srinivasan's mechanism should happen to be right, then current thinking on the nature of *n*-π^* excited states would have to be revised. Secondly, if the mechanism proposed herein is correct, then more information would be available on the difference in chemistry of vibrationally "hot" and vibrationally quenched free radicals.

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5. It is proposed that absorption and emission spectra of 1-acetylazulene be studied in rare gas matrices at 4.2°K. The compound, easily prepared by the Friedel-Crafts acylation of azulene with acetic anhydride (1), ought to furnish spectroscopic information about the triplet states of the azulene nucleus (a matter of some theoretical interest (2)). Such information has not been obtained by a study of azulene by various workers (3,4) because of inefficient S-T intersystem crossing, or fast T_n-S_g non-radiative quenching, or both, under the conditions employed.*

1-Acetyl azulene ought to possess an n-π* singlet absorption with the O-O band at around 3700 Å (5), slightly lower in energy than the S_2 singlet (O-O band) of the unsubstituted azulene nucleus (2).

It has become fairly well established that intersystem crossing in molecules containing a heteroatom as part of the conjugated system is often very efficient (6). Because of the very low energy of the T_1 triplet (2) in azulene (and presumably in acetyl azulene) and because intersystem crossing taking place through the n-π* singlet should yield the T_3 or T_4 triplet, it is proposed that irradiation of acetyl azulene

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*Very recently (and subsequent to the original formulation of this proposition) Robinson, Leermakers and Hammond in these laboratories have observed what is very possibly T_n-T_1 emission of azulene in Xenon and Krypton at 4.2°K and in acetophenone at 77°K.

with 2000-3500 Å light at low temperatures may lead to the observation of T_n-T_1 fluorescence. The intersystem crossing and subsequent triplet-triplet emission ought to be especially facilitated by the use of solid Xenon or Krypton as solvents.

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6. In 1957 Doering and Knox (1) observed that tropylium ion could be reduced by zinc dust to the dimer of cycloheptatriene. He postulated as an intermediate the cycloheptatrienyl free radical. It is proposed that this interesting species be generated by an unequivocal synthesis, and that the properties and stability of the radical be investigated.

Theory predicts that the radical should have appreciable resonance energy (2.54β)(1), although it would presumably be unstable with respect to the cation (R.E. 2.99β) in the presence of oxidizing agents. It is quite possible that the calculated value of the resonance energy of the radical is not a good approximation to the correct value. The calculated ΔR.E. in generating the radical from cycloheptatriene is 1.9β or 36 kcal. Thus the apparently stable dimer obtained by Doering would have a C-C bond joining the monomers of less than 10 kcal., a rather unreasonable figure.

It is proposed that 1) the *t*-butyl perester or diacyl peroxide of 1-methyl-2,4,6-cycloheptatriene-1-carboxylic acid (Appendix A) be decomposed in a variety of solvents of varying hydrogen atom donating ability; and 2) Doering's dimer be subjected to a kinetic pyrolytic study to determine the energy of the C-C bond joining the monomers. With regard to the first part of the proposition, the decomposition of the perester or peroxide will yield *methyl* cycloheptatrienyl radical. The methyl group serves only to facilitate the synthesis of the starting compound (Appendix A). Measurement of the relative amounts of dimer formation, hydrogen abstraction, and oxidation to the cation in various media should yield information concerning the stability of the radical.

Appendix A

The synthesis of the perester and peroxide might conveniently be carried out as follows:

The reaction of α-methyl diazoacetic ester with benzene, with subsequent heating, should yield 1-methyl-2, 4, 6-cycloheptatriene-1-carboxylic acid. Further reaction with $SOCl_2$ and *t*-butyl hydroperoxide will yield the perester. Reaction of the acid chloride with hydrogen peroxide and sodium hydroxide will lead to the formation of the peroxide. Non-methylated cycloheptatriene carboxylic acids are known (2), but they are easily interconverted. The presence of the methyl group serves to give the correct positioning of the double bonds unambiguously.

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