THE PHOTOREACTIONS OF N-METHYL-2-PYRIDONE

Thesis by

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ABSTRACT

In studying the photochemistry of N-methyl-2-pyridone, four products were observed. Besides the previously known dimer and bicyclic monomer, two new dimers were isolated.

The quantum yields of product formation were measured, and it was found that only one intermediate was involved. From sensitization and quenching experiments, the lowest excited singlet state appears to be that intermediate although a highly reactive, ground state isomer cannot be ruled out. Some spectroscopic evidence for this isomer is given.

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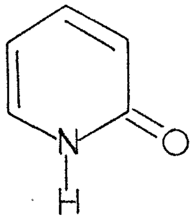
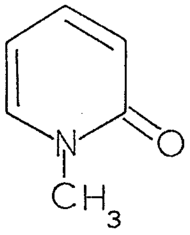
INTRODUCTION

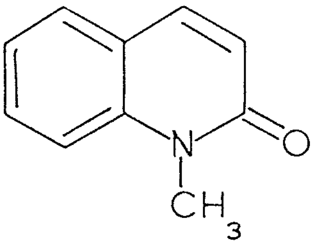
In studying the photochemistry of α,β unsaturated lactams, Taylor and Paudler[1] irradiated 2-pyridone(I), N-methyl-2-pyridone(II), and N-methylquinolone(III).



I

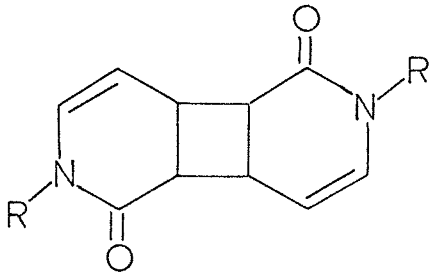


II



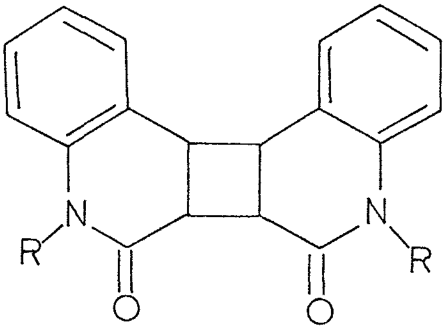
III

The products which were isolated were determined to be dimers and from UV and dipole moment measurements the structures were assigned as head-to-tail cyclobutane dimers(IV). However in the case of the quinolone the structure was assigned as head-to-head(V) because of the large dipole moment.



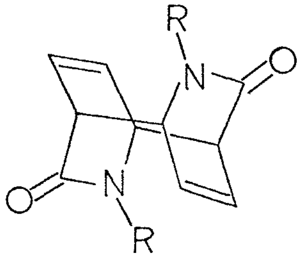
IV

Several groups,[2,3,4] at about the same time, reported that the structure assigned for the pyridone



V

dimers was not the cyclobutane dimer but actually a 1,4-1,4 adduct(VI). This determination was based on UV, NMR, and IR analysis. The isolated dimer showed no strong UV absorption which would be expected for a vinyl

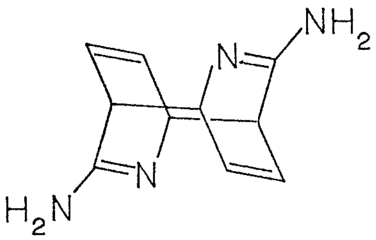


VI

lactam;[4] there was no vinyl lactam stretching in the IR; and the NMR was not consistent with a cyclobutane dimer. Later work[5] employing X-ray crystallographic techniques gave conclusive evidence that VI was the correct structure.

Two papers[2b,6] reported on the dimerization of various substituted 2-pyridones. Methyl substituents on the ring did not seem to hinder the reaction, and a variety of groups on the nitrogen also did not affect the dimerization. In all cases the dimers had the same structure, as determined by spectral and chemical analysis.

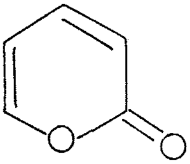
One of these papers[2b] also reports that the 2-aminopyridines undergo a dimerization, yielding products which can be chemically related to the pyridone dimers. For this reason they were assigned a similar structure(VII).



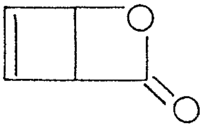
VII

In all of these cases the pyridones were irradiated in aqueous solution and only one dimer was isolated. The dimer usually crystallized out on the walls of the vessel and was collected.

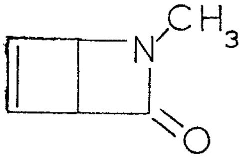
As a synthetic approach to cyclobutadiene, Corey and Streith[7] irradiated N-methyl-2-pyridone and 2-pyrone(VIII) in dilute ether solution, obtaining the internal photocyclization products IX and X. The structures were consistent with the



VIII



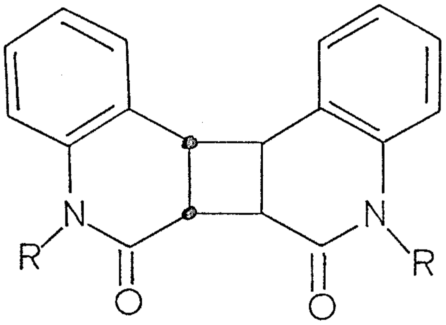
IX



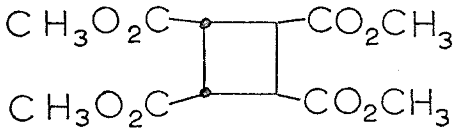
X

UV, IR, and NMR data. IX was found to form a Diels-Alder adduct with 2,5-diphenyl-3,4-isobenzofuran. However no data were given as to whether X would do likewise.

Because of the error in assignment of the structure of the pyridone dimers, Buchardt[8] reinvestigated the quinolone dimer. With the aid of spectroscopic as well as chemical evidence, it was found that indeed the dimers were of the cyclobutane type (XI). The configuration around the cyclobutane ring was assigned by degradation of the dimer to the tetramethylcyclobutane tetracarboxylate(XII) which was the same as that formed from the trans head-to-head dimer of coumarin. The structure of the dimer then



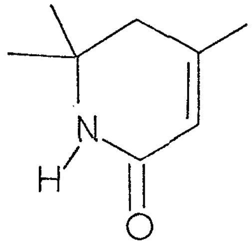
XI



XII

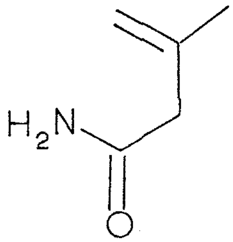
seemed to be conclusively proven.

Another type of reaction which has been observed in pyridone systems is a photocleavage. 4,6,6-Trimethyl-5,6-dihydro-2(1H)pyridone(XIII), on irradiation in water,

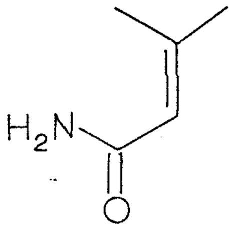


XIII

gave three products:[9] acetone, compound XIV, and compound XV. This can be thought of as proceeding through a

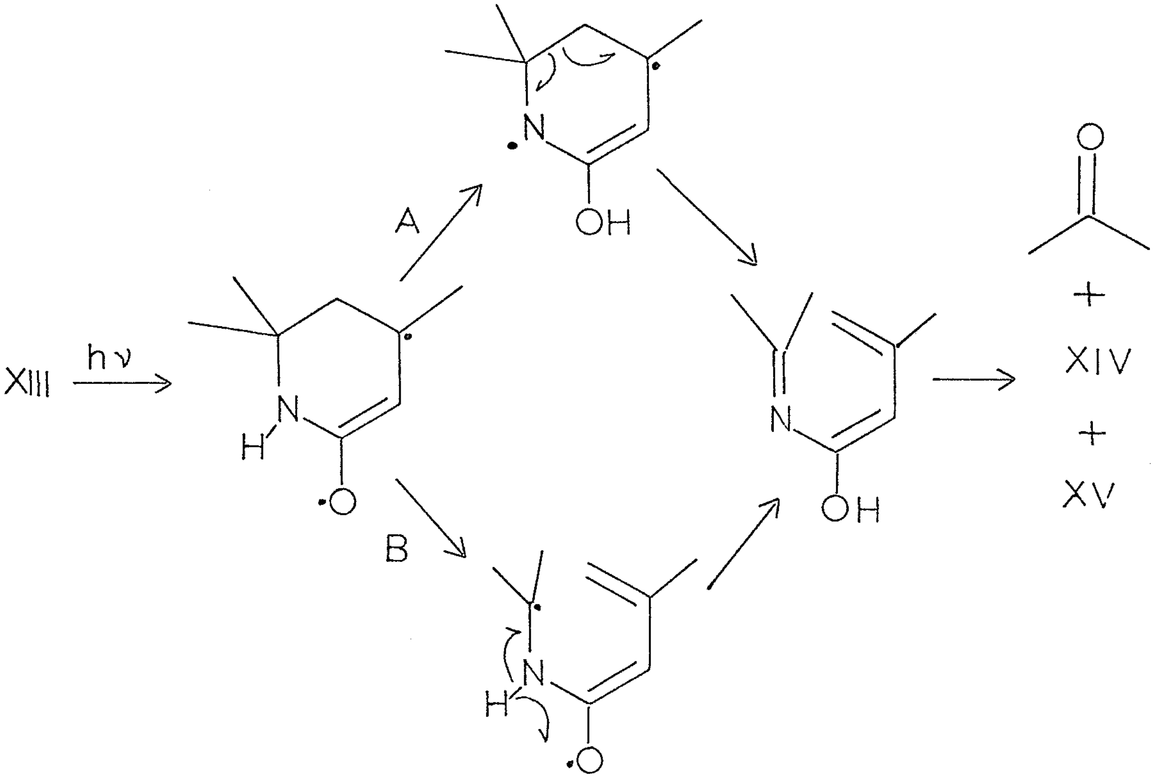


XIV



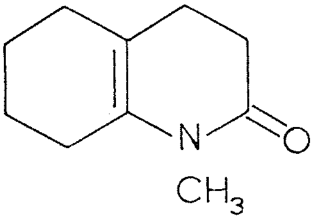
XV

cleavage to yield an intermediate which is hydrolyzed to give the products. Irradiation in dry t-butyl alcohol yielded a difficultly isolable product which was unstable to moisture. A mechanism formulated to account for the products went as follows:

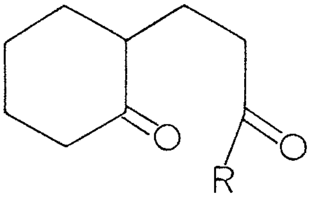


It was found that irradiation of the N-methyl or N-acetyl derivatives led to no new products.

Another cleavage reaction was observed[10] in the irradiation of 1-methyl-1,2,3,4,5,6,7,8-octahydro-2-quinolone(XVI), in methanol, cyclohexylamine and n-butylamine, to give the ring opened product (XVII). This was formu-



XVI



R = OMe

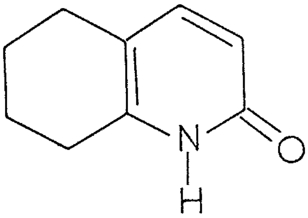
= NHC_6H_{11}

= NHBu

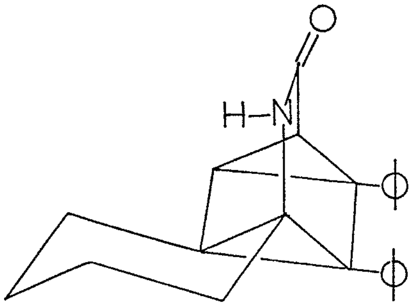
XVII

lated as proceeding through a ketene intermediate.

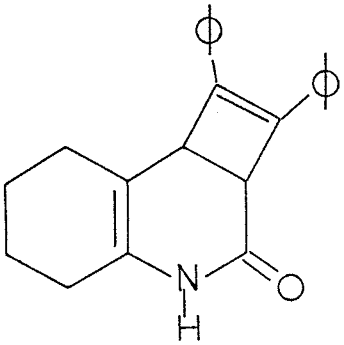
There are also several reports[11,12,13] of photochemical cycloaddition reactions to the olefinic bonds of pyridones. Irradiation[11] of a methanolic solution of 5,6,7,8-tetrahydroquinolone(XVIII) and diphenylacetylene yielded an insoluble dimer (structure not determined except that it had a nonconjugated lactam) and two minor products XIX and XX. XIX was present in greater amounts and on photolysis at 2537 Å would yield XX. However XX was found to be a primary photoproduct of the pyridone(XVIII). The quadricyclic product XIX was thought to proceed through an intermediate diene analogous to norbornadiene. Similar products were obtained from the N-methylated pyridone, although no dimeric material could be isolated in this case.



XVIII

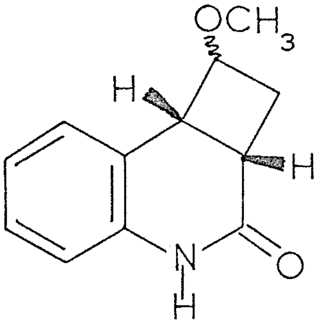


XIX

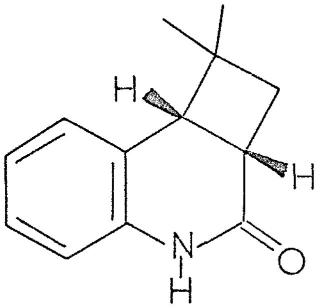


XX

Other workers[12,13] investigated the addition of olefins to quinolone. Evanega and Fabiny[12] studied the photoaddition of tetramethylethylene, isopropylene, methylvinyl ether and cyclopentene to quinolone. All the adducts formed were of the cyclobutane type and of a specific stereochemistry, as shown by the product with methylvinyl ether(XXI). The products obtained were with the OCH_3 cis and trans to the protons. Likewise with isopropylene only one adduct was formed (XXII). In the case of the adduct with cyclopentene only the trans cyclobutane was found. The reported dimer of quinolone was also found and on dilution of the reaction solution with a constant ratio of reactants, the ratio of the dimer to photoadduct decreased indicating that two different excited states were responsible for the two reactions. All the work was



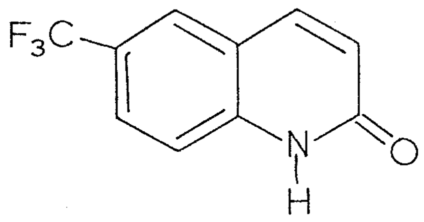
XXI



XXII

done on directly irradiated systems and no sensitization was reported.

Another group observed[13] the photosensitized cycloaddition of olefins to N-methyl-6-trifluoromethylquinolone(XXIII). The photodimer was found and also, in all cases except one, a single photoadduct. The olefins used were N-methylmaleimide, maleic anhydride, diethylmaleate, ethylacrylate, acrylic acid, N-methyl-3-carbomethoxy-1,2,5,6-tetrahydropyridine, N-methyl-1,2,5,6-tetrahydropyridine (2 adducts), cyclopentene and ethylene. The structures for these adducts were argumentatively and spectroscopically related to those of Evanega,[12] who had done some deuterium labeling work in structure determination.



XXIII

In a theoretical paper dealing with photochemical monomolecular reactions, Malrieu looked at the conversion of N-methyl-2-pyridone to the bicyclic isomer X. It was noted that the 4,5 and 3,6 bonds shortened in the excited state and the 3,4 and 5,6 bonds lengthened. This calculation was carried out on the lowest π-π^*, and n-π^* singlet states and the lowest π-π^* triplet state, and all showed the same effect. This paper was interesting but not of much significance.

In contrast to the 2-pyridones, the oxygen analogue, 2-pyrone(XXIV), undergoes more varied photochemical reactions[15,17,20] as shown in Figure 1. In a study[15] of the direct photolysis of 4,6-dimethyl-2-pyrone(XXV), three dimers were found: XXVI, XXVII, and XXVIII. Of these XXVI and XXVII were found to be converted to 1,3,5,6-tetramethylcyclooctatetraene on heating. Thus they were assigned the indicated structures. The third dimer was assigned its structure on spectral evidence and because it was rapidly converted to XXVI at 160°C. This is indicative of a Cope Rearrangement and requires the indicated stereochemistry.[16] However if the irradiation is carried out in methanol[17] instead of benzene, then a ring-opened product was formed. Presumably the pyrone opened to a ketene which then added methanol to yield the unsaturated keto ester (XXIX). Chapman[18] has not been able to observe this ketene directly as in other systems[19] but thinks this is due to its extremely short lifetime.

In a more recent paper, Pirkle and McKendry[20] investigated the multiplicity of the reactive excited states of 2-pyrone. When 2-pyrone was irradiated in a

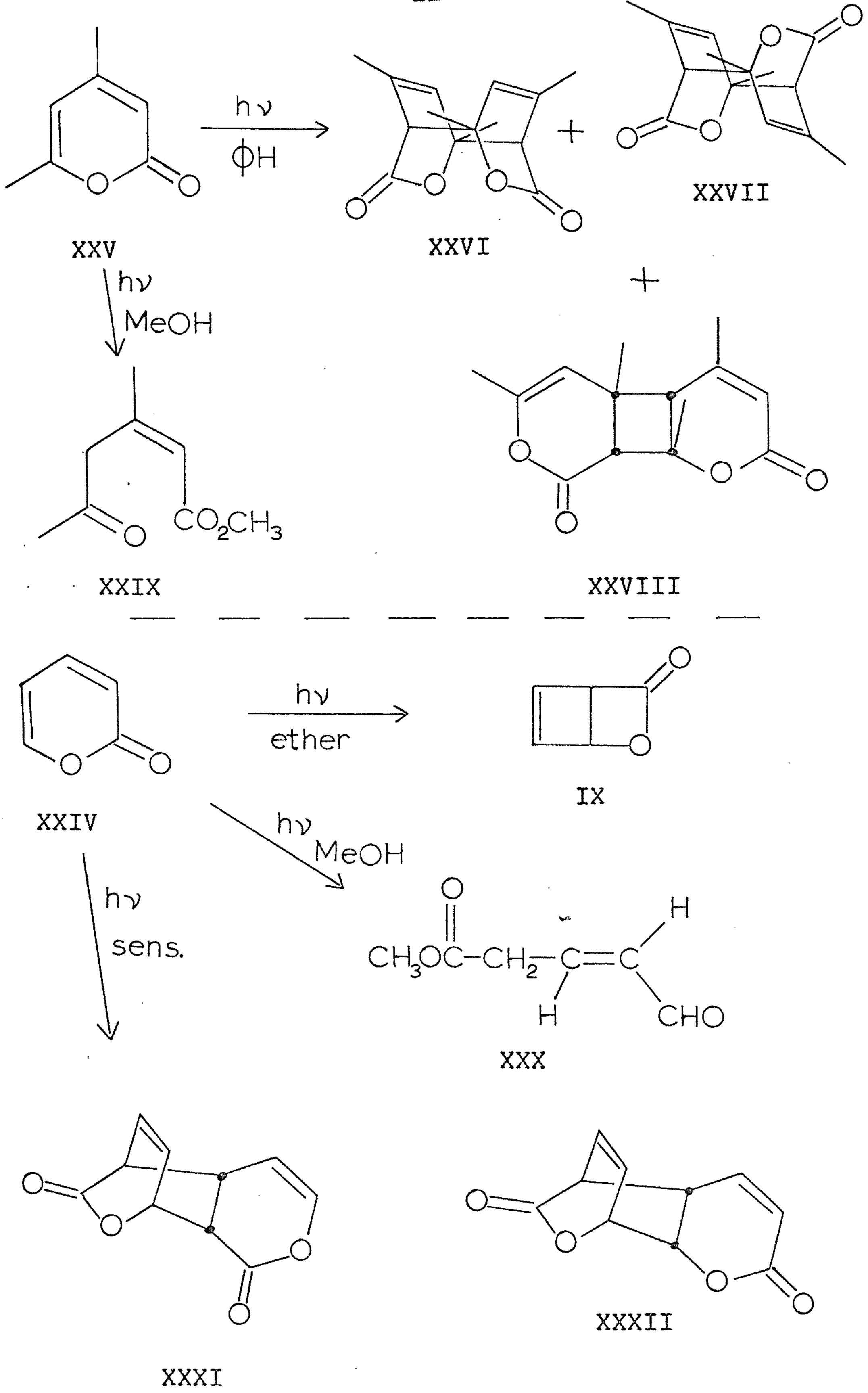
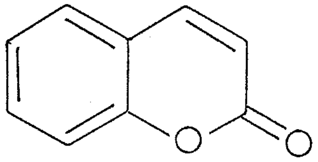

hν
ϕH
XXV
XXVI
+
XXVII
+
hν
MeOH
CO2CH3
XXIX
XXVIII
hν
ether
XXIV
IX
hν
MeOH
hν
sens.
CH3OC–CH2–C=C
H
H
CHO
XXX
XXXI
XXXII

Figure 1

methanol--ether (90:10) mixture, an almost quantitative yield of ring-opened product XXX was isolated. However if a sensitizer was added no XXX was observed; but instead two dimers, XXXI and XXXII. Since the formation of neither IX nor XXX could be quenched by 0.1 M piperylene and neither formed on sensitization, it was assumed that they follow from the excited singlet state. The dimers, XXXI and XXXII, most likely came from the triplet state because of their appearance only on sensitization. This work then gave some mechanistic basis for the photochemistry of 2-pyrones; and how extensive the analogy between this and the reactions of 2-pyridone is, it is not known.

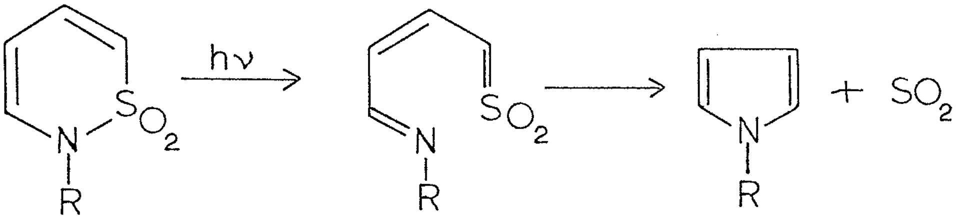
The oxygen analog of 2-quinolone, coumarin (XXXIII), has been the subject of numerous investigations and all four cyclobutane dimers are known. The mechanism appears to be quite complex and the products vary with the conditions.



XXXIII

A comprehensive look at these investigations is beyond the scope of this introduction, but one can obtain a more detailed account in reference 21. One interesting observation of the coumarin system was the production of ethylcoumarate on irradiation[22] of coumarin in ethanol. Attempts[23] to identify an intermediate responsible for the ring-opened product have not been very conclusive.

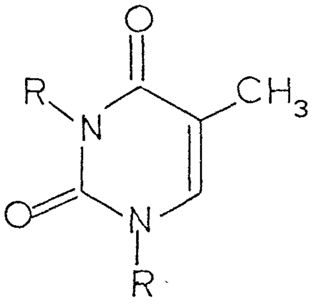
The photolysis of unsaturated sultams[24] also lead to ring opening. This might be considered an analog to the 2-pyridone system.



This ring opening, through a ketene intermediate, appears to be a quite general reaction[17,19,25]; and in many cases the intermediate itself has been observed[19] at low temperature using infrared spectroscopy.

Finally, the nucleic acid bases undergo[26] both dimerization and hydration under the influence of ultraviolet light, particularly thymine(XXXIV). It forms a cyclobutane dimer which is thought to be mainly responsible for the biological damage of DNA on UV irradiation. This dimerization has been the subject of numerous investigations and its mechanism is still open to question.

N-methyl-2-pyridone can be considered as a model



XXXIV

compound for the pyrimidine bases, and thus understanding the mechanism of its photoreactions might be very useful. Our investigation had the following objectives: a) determining if other products (cyclobutane dimers and ring-opened compounds) are formed as in similar systems; b) measuring the quantum efficiencies of all processes with the purpose of elucidating the mechanism; and c) studying any ground state intermediates responsible for the various reactions.

RESULTS AND DISCUSSION

Because several products[2,7] from the irradiation of N-methyl-2-pyridone (NM2P) are known and only one from 2-pyridone, the former was chosen to undertake the investigation. On irradiation of a solution of NM2P in ethanol on a preparative scale, a solid product formed on the walls of the vessel. This was collected and found to be identical in all properties to dimer D, previously reported.[2,3,4] (This was referred to as dimer VI in the Introduction.) However all attempts to analyze quantitatively for it failed (gas chromatography, UV, IR, NMR). Because of this, another product, seen in the vapor phase chromatogram, was tackled first. This product was isolated by column chromatography and found to be identical in spectral properties with the bicyclic isomer, P, reported by Corey and Streith[7] (referred to as X in the Introduction).

With the dimerization reaction a concentration dependence on the quantum yields might be expected, so the quantum yield for formation of the bicyclic isomer was measured as a function of the concentration of NM2P. These values are shown in Table I and plotted in Figures 2 and 3. All quantitative irradiations were carried out at 3130 Å unless otherwise noted. It is possible to see that the quantum yield for the formation of P decreases

TABLE I

Quantum Yield of Formation of P at Various Concentrations of NM2P

	$[\text{NM2P}]_{\text{ave}}$ (M)	Φ_P
Run 1:	0.0086	0.0093 ± 0.0003
		0.0094 ± 0.0001
	0.047	0.0093 ± 0.00005
		0.0091 ± 0.0002
	0.085	0.0089 ± 0.0002
		0.0093 ± 0.0002
	0.269	0.0079 ± 0.0001
		0.0075 ± 0.0001
Run 2:	0.0086	0.0096 ± 0.0001
		0.0094 ± 0.0002
	0.018	0.0091 ± 0.0001
		0.0092 ± 0.0001
	0.093	0.0089 ± 0.0001
		0.0090 ± 0.0001
	0.186	0.0082 ± 0.0002
		0.0082 ± 0.0001
	0.470	0.0071 ± 0.0002
		0.0069 ± 0.0003

TABLE I (cont'd)

	$[NM2P]_{ave}$ (M)	Φ_P
Run 3:	0.0078	0.0089 ± 0.0003
		0.0084 ± 0.0004
	0.086	0.0084 ± 0.0004
		0.0080 ± 0.0002
	0.193	0.0080 ± 0.0001
		0.0079 ± 0.0003
	0.260	0.0071 ± 0.0001
		0.0077 ± 0.0002
	0.435	0.0069 ± 0.0003
		0.0068 ± 0.0003

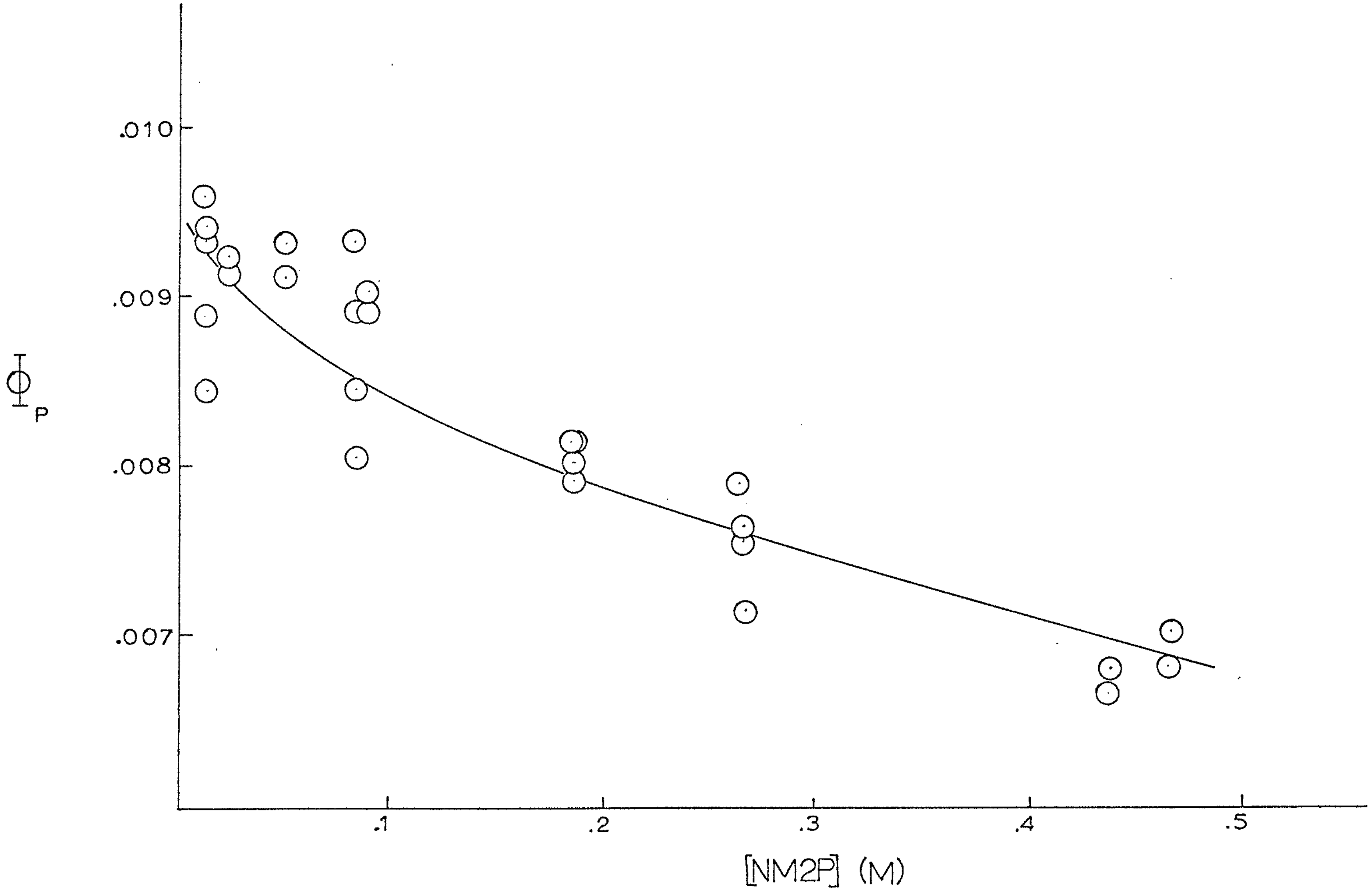


Figure 2. Quantum Yield of P at Various Concentrations of NM2P

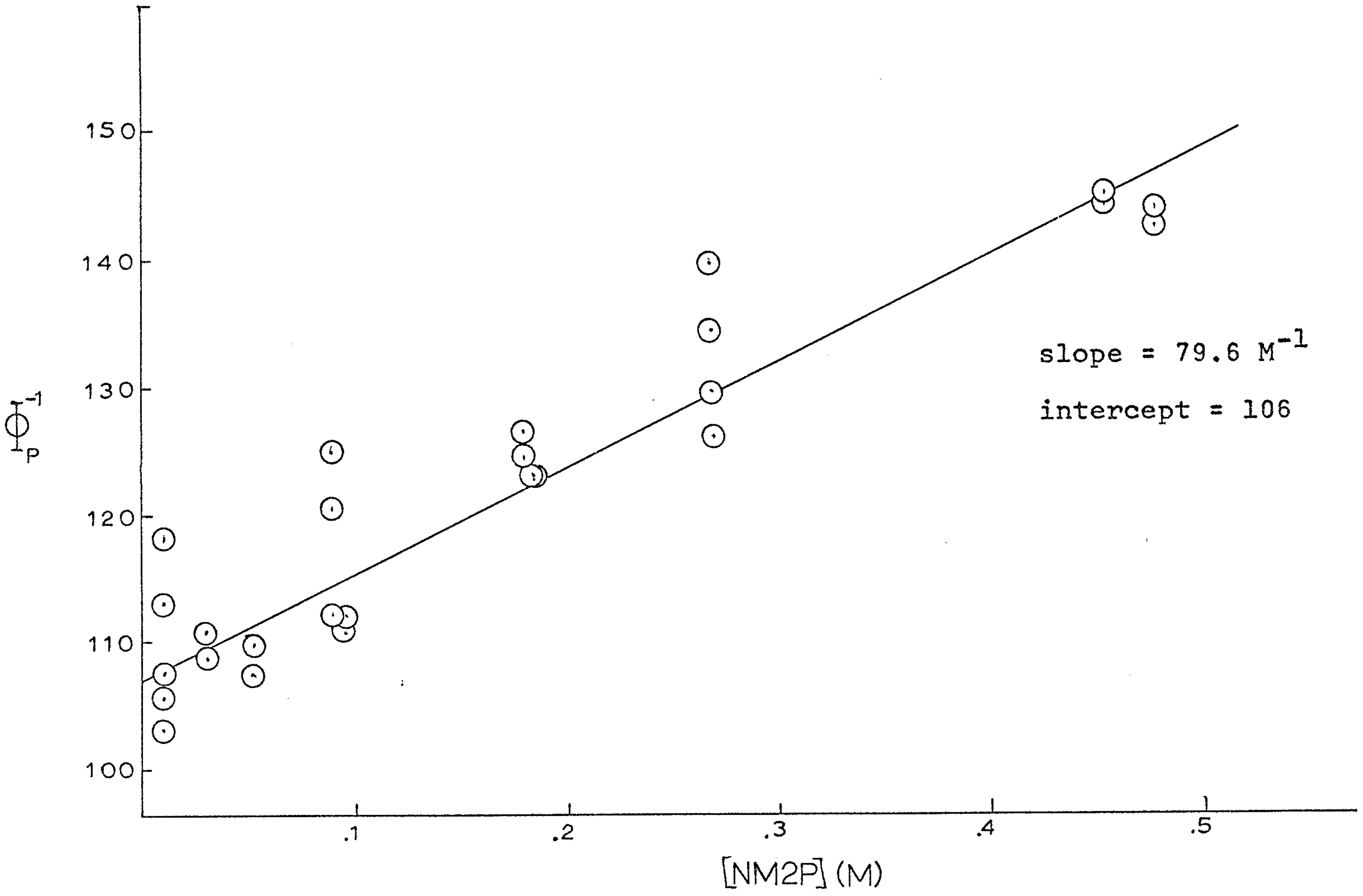


Figure 3. Reciprocal of Quantum Yield of P at Various Concentrations of NM2P

with increasing concentration, thus indicating that some dimerization must be occurring from a precursor to P. The large scatter of the points is a consequence of the uncertainty brought into the measurements on calibration of the VPC. However within any one run the trend of decreasing quantum yield of formation of P is definitely real.

The ease in analysis for P enabled several control experiments to be done. There is the possibility that the quantum yield of P might be dependent on irradiation time or that P reacts with NM2P either thermally or photochemically. This was easily checked and the observed data are given in Table II. All tubes were of the same concentration, 0.011 M in NM2P, and were irradiated for different lengths of time. The total photons absorbed varied by a factor of three without a detectable change in the quantum yield.

Tubes were prepared also in which P had been added before irradiation. On irradiation and analysis, the added P had no effect whatsoever on the quantum yield of P; and P seemed to be thermally stable over the period checked. This rules out any photoreactions of P with NM2P or any other perturbations due to energy transfer from NM2P to the product.

TABLE II

Effect of Total Amount of Irradiation on the Quantum Yield of P

I (einsteins)	Φ_P
3.5×10^{-4}	0.0090 ± 0.0004
	0.0088 ± 0.0004
6.0×10^{-4}	0.0088 ± 0.0002
	0.0089 ± 0.0002
8.3×10^{-4}	0.0091 ± 0.0003
	0.0090 ± 0.0003
11.1×10^{-4}	0.0091 ± 0.0003
	0.0090 ± 0.0003

The effect of solvent on the quantum yield of P was also measured. This is shown in Table III. As can be seen the effect is rather minor and eliminates any solvent-dependent process which is then competitive with the formation of P.

The quantum efficiency of disappearance of NM2P was measured two ways as noted in the Experimental Section. The analysis could be carried out by VPC at high temperatures or it could be done by UV spectroscopy. Since the latter was the most facile, it was used in a majority of cases. After irradiation the tubes were opened, diluted and the absorption read at 320 nm or 330 nm. The quantum efficiency was measured as a function of the concentration of NM2P and the results are shown in Table IV. From a plot of these data it is possible to note that the quantum efficiency decreases with decreasing concentration until the production of P becomes the dominant process (at about 10^{-2}M NM2P). If we neglect the points at low concentration a straight line may be obtained by a plot of reciprocal quantum efficiency for disappearance of NM2P against reciprocal concentration as shown in Figure 5.

As a check that nothing else in solution was absorbing significantly at the analyzing wavelengths, the quantum efficiency was measured at as low a conversion as possible--usually about 15-20%--and at several wavelengths.

TABLE III

Solvent Effects on the Quantum Yield of P

Solvent	Φ_P (relative to ethanol)
ethanol	1.00
isopropyl alcohol	0.96
benzene	0.77
95% ethanol	1.03

TABLE IV^{+}

Quantum Efficiency for Disappearance of NM2P at Various Concentrations

	$[NM2P]_{ave}$ (M)	Φ_{-NM2P}
Run* 1:	0.0086	0.010
	0.0084	0.011
	0.181	0.134
	0.181	0.137
	0.278	0.160
	0.276	0.169
	0.463	0.263
Run* 2:	0.093	0.061
	0.093	0.061
	0.184	0.132
	0.186	0.118
	0.279	0.170
	0.280	0.163
	0.470	0.251
	0.467	0.277
Run# 3:	0.0088	0.013
	0.0090	0.011
	0.096	0.060
	0.096	0.062

TABLE IV(cont'd.)

	$[NM2P]_{ave}$ (M)	Φ_{-NM2P}
	0.193	0.118
	0.190	0.138
	0.288	0.188
	0.288	0.188
	0.483	0.287
	0.481	0.296
Run$^{\#}$ 4:	0.0009	0.009
	0.0042	0.011
	0.0042	0.011
	0.0083	0.013
	0.0083	0.013
Run$^{\#}$ 5:	0.022	0.020
	0.093	0.064
	0.186	0.106
	0.270	0.154
	0.493	0.259
Run$^{\circ}$ 6:	0.052	0.027 ± 0.001
	0.051	0.029 ± 0.002
	0.507	0.180 ± 0.009
	0.506	0.225 ± 0.001
	0.091	0.042 ± 0.001

TABLE IV(cont'd.)

$[\text{NM2P}]_{\text{ave}}$(M)	$\Phi_{\text{-NM2P}}$
0.090	0.058 ± 0.001
0.090	0.049 ± 0.001

[+] the error in measurement of $\Phi_{\text{-NM2P}}$ by UV is estimated at 10%

[*] optical density read at 330nm

[#] optical density read at 320nm

[o] measurement made by VPC

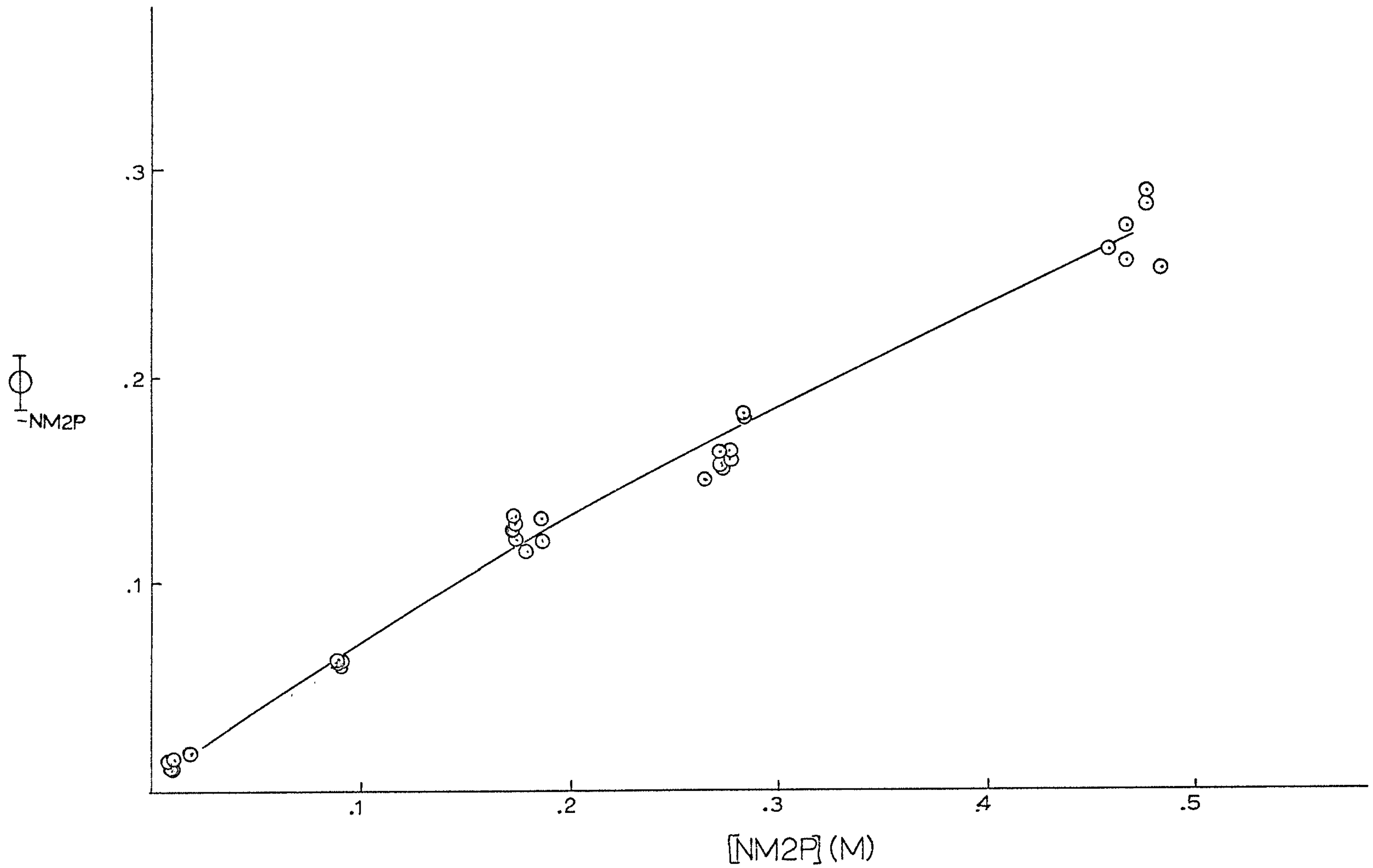


Figure 4. Quantum Efficiency for Disappearance of NM2P at Various Concentrations in Ethanol.

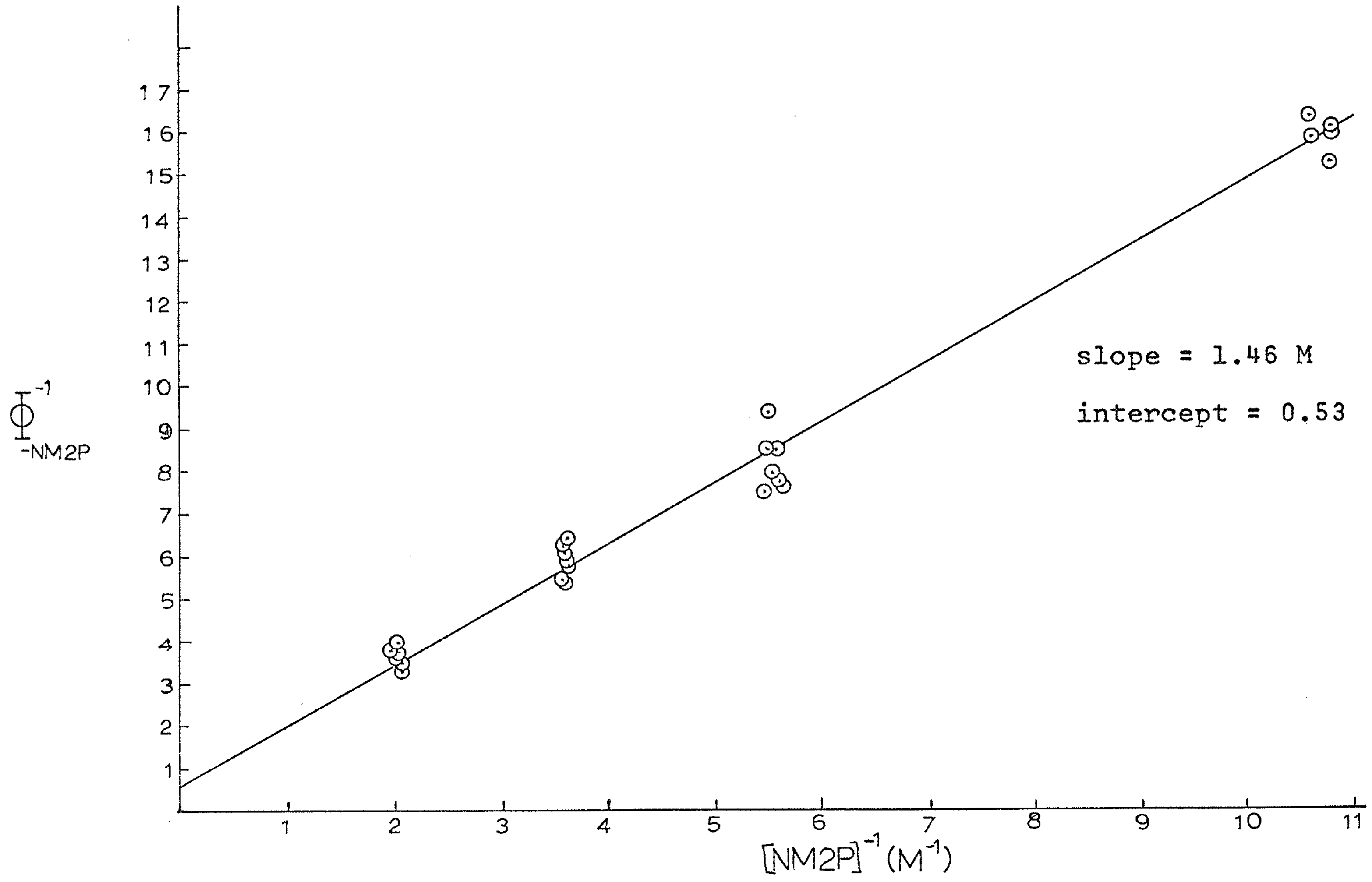


Figure 5. Reciprocal of Quantum Efficiency for Disappearance versus Reciprocal Concentration.

The same values within experimental error were obtained. Also the quantum efficiencies were measured by VPC and are shown in Table IV. These values have a much higher experimental error because of the low conversions and because the internal standard had to be added after irradiation. However the VPC values are the same or if anything less than the values measured by UV spectroscopy. The opposite trend would be expected if another species was absorbing.

In a similar control experiment, the effect of total photons absorbed on the disappearance quantum efficiency was investigated as shown in Table V. Samples were prepared with 0.010 M NM2P and irradiated up to 50% conversion.

The effect of solvent on the disappearance quantum efficiency has also been investigated. The data in Table VI and Figure 6 show the quantum efficiency for disappearance of NM2P as a function of concentration in benzene solution. These values are almost identical to those in ethanol and further substantiate that solvent is not an important factor in the reactions of NM2P.

With the data on the quantum yield of P and the quantum efficiency for disappearance of NM2P, it appeared that we need only measure the quantum yield of dimer D to account for the rest of the NM2P which was disappearing.

TABLE V[+]

Effect of Total Amount of Irradiation on Disappearance Quantum Efficiencies

I(einsteins)	$\Phi_{\text{-NM2P}}$
4.6×10^{-4}	0.014
	0.013
6.5×10^{-4}	0.013
	0.013
9.2×10^{-4}	0.012
	0.013
11.3×10^{-4}	0.013
	0.012

[+] error estimated at 10%; all optical densities measured at 320nm; initial concentration of NM2P is 1×10^{-2} M.

TABLE VI[#]

Quantum Efficiency for Disappearance of NM2P in Benzene

	$[NM2P]_{ave}$ (M)	Φ_{-NM2P}
Run 1:	0.020	0.019
	0.024	0.023
	0.083	0.063
	0.093	0.072
	0.173	0.126
	0.193	0.142
	0.256	0.160
	0.296	0.191
	0.435	0.223
	0.486	0.256
Run 2:	0.026	0.026
	0.100	0.076
	0.197	0.139
	0.250	0.163
	0.358	0.221

[#] optical density read at 320 nm; all values done in benzene as solvent; errors estimated at 7%.

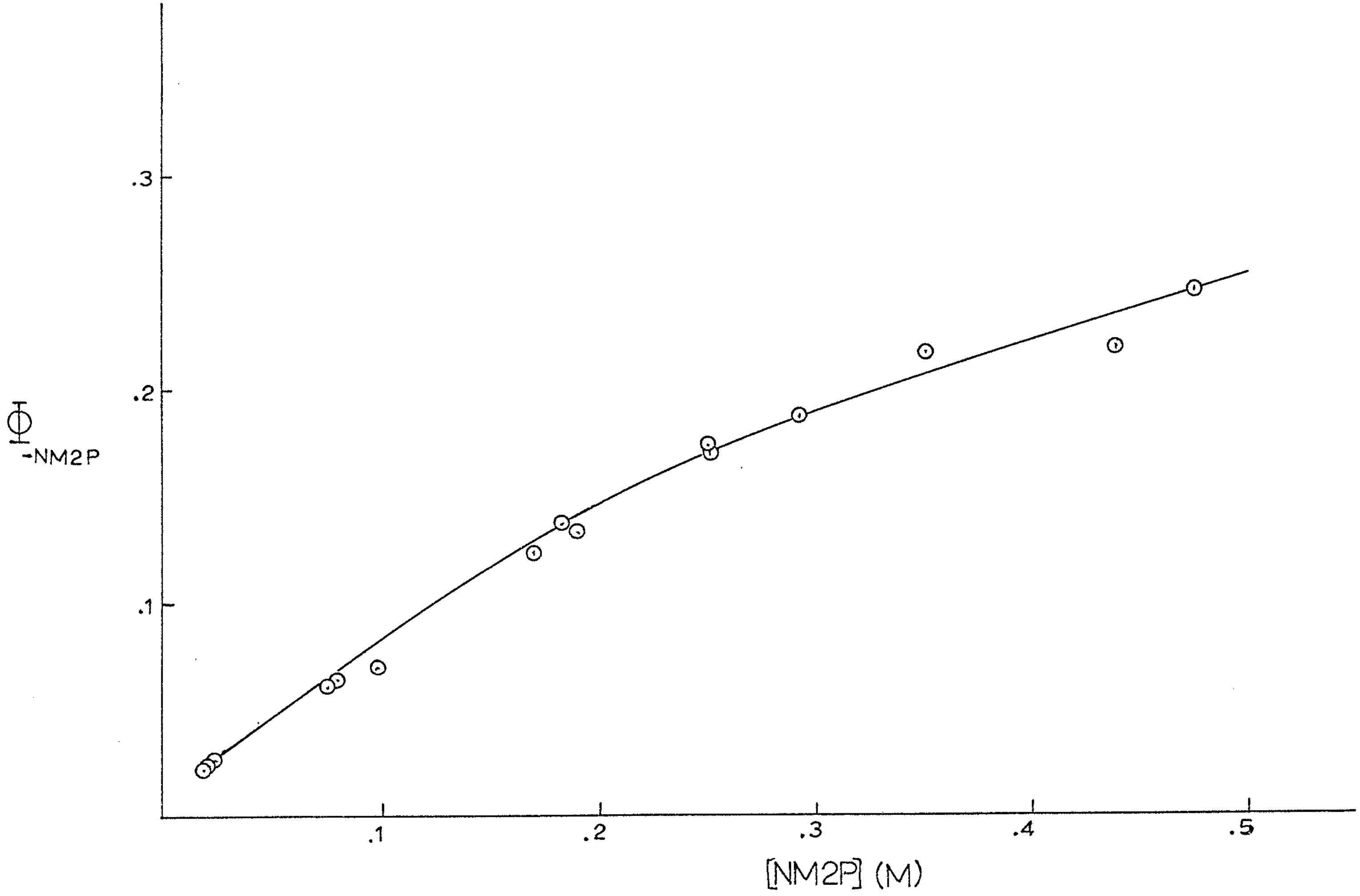


Figure 6. Quantum Efficiency for Disappearance of NM2P at Various Concentrations in Benzene.

As pointed out before, it was not easy to analyze for this dimer. However because of the ease of methylation of 2-pyridone, it was possible to label NM2P with carbon-14 and thus carry out analysis by isotope dilution. The procedure used is outlined in the Experimental Section. All the tubes were prepared with known amounts of labeled NM2P and the irradiations carried out as before. In ethanol solution dimer D did not separate out of solution at moderate conversions, so the analysis was quite easy. The data, shown in Table VII, however were rather surprising. If one doubles the quantum yield of D and adds it to the quantum yield of P then it is expected that this will equal the quantum efficiency for disappearance of NM2P. This was not the case at all and more than 50% of the NM2P which disappears is not accounted for in the amount obtained. This led us to look for other products.

The data for the quantum yield of D, plotted in Figure 7 and Figure 8, give very good straight lines. As would be expected, this quantum yield decreases to zero as the concentration of NM2P decreases; and it would be expected to level off to some value at high enough concentrations as indicated by the nonzero intercept of the reciprocal plot.

Now that another product had been implicated it was necessary to undertake a search for this. No other

TABLE VII*

Quantum Yield of Formation of Dimer D at Various Concentrations of NM2P

	$[NM2P]_{ave}$ (M)	Φ_D
Run:	0.087	0.011
		0.010
	0.172	0.022
		0.022
	0.265	0.031
		0.032
	0.373	0.041
	0.429	0.050
		0.050
Run 2:	0.092	0.011
		0.012
	0.176	0.023
		0.022
	0.266	0.032
		0.033
	0.342	0.042
		0.040
	0.452	0.053

[*] errors in experimental technique estimated to be 4%

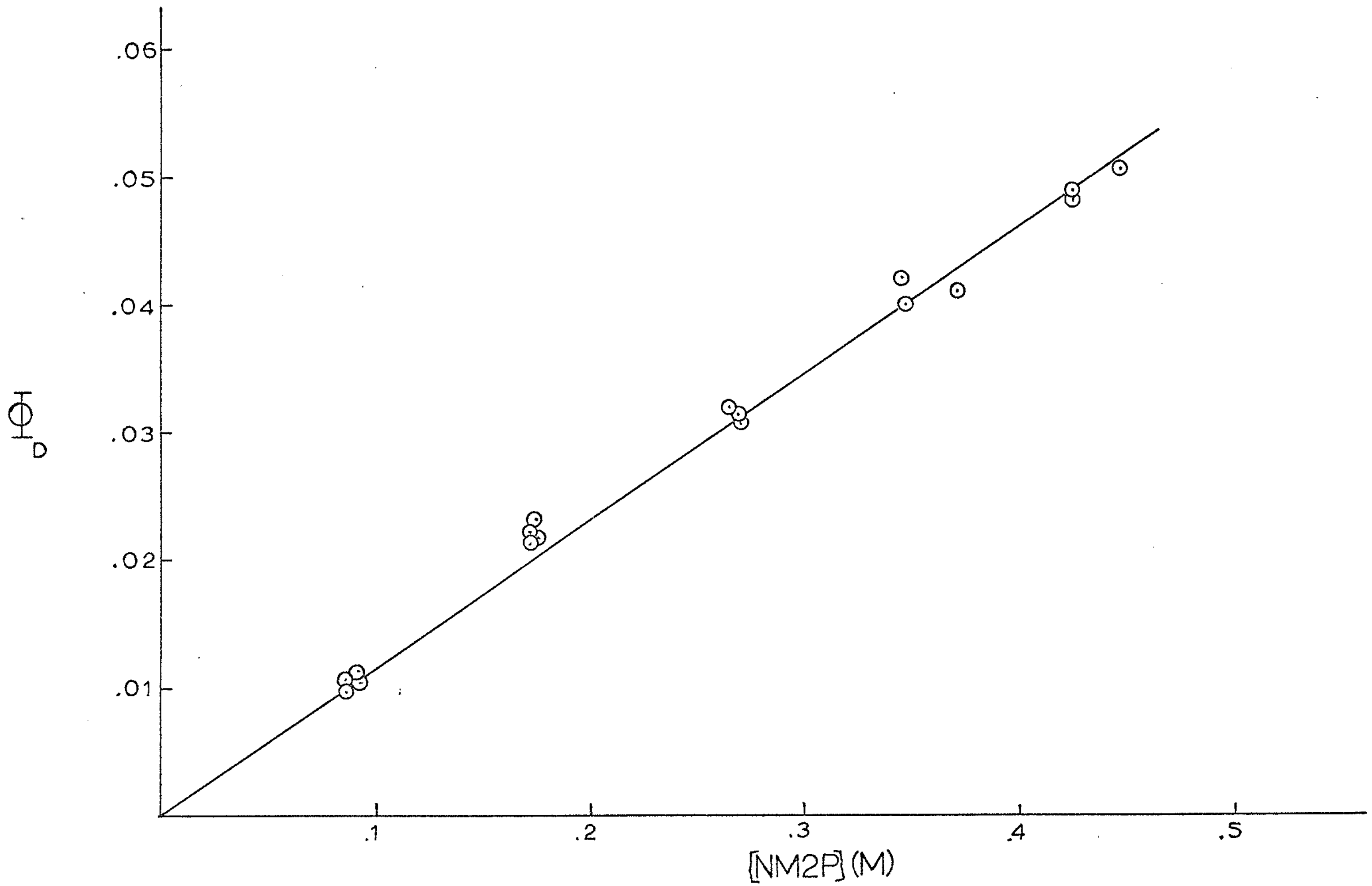


Figure 7. Quantum Yield of Dimer D at Various Concentrations of NM2P.

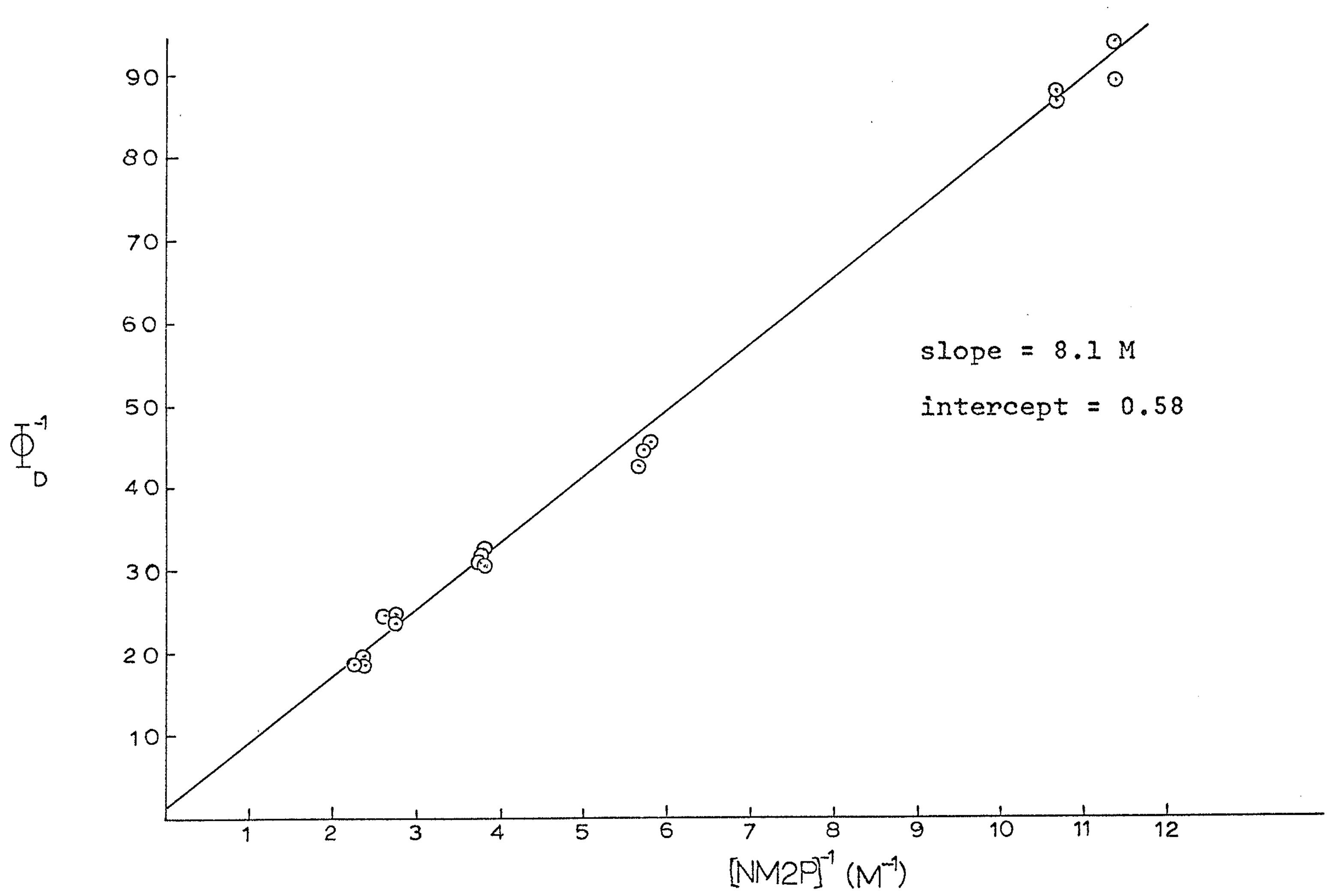
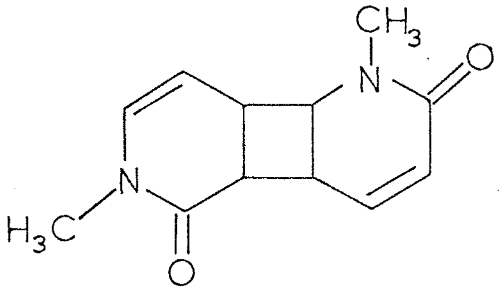


Figure 8. Reciprocal of Quantum Yield of Dimer D versus Reciprocal Concentration.

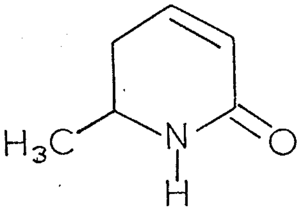
products were seen in the VPC and efforts to separate an irradiated mixture by chromatography on a silica gel column yielded only P and impure NM2P. However if a tube of neat NM2P was irradiated for several days and then the solid dimer D filtered off, a liquid fraction was obtained. Separation of this mixture on a silica gel TLC plate with 20% methanol in ether afforded a poor separation but several spots were noted. Use of thick silica gel plates, where overloading was not a problem, gave a much better separation and two new spots were observed. One was very close to the NM2P, and one very close to the place where dimer D would be expected.

The first spot was isolated and found to be a viscous oil. The spectral data showed that it was a new compound and definitely a dimer. The appearance of two distinct N-methyl singlets in the NMR (spectrum given in the Experimental Section) indicated that it was not a symmetrical dimer ruling out 1,4-1,4 adducts. A 220 MHz spectrum gave most of the couplings and it is believed that the compound is dimer M. This structure is supported by the

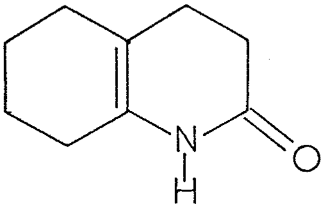


M

UV absorption spectrum which showed a λ_{max} = 265 nm. This is quite similar to absorption of some model compounds shown below:



λ_{max}	ε[27]
2560	2200
2510	2600
2470	2600
2360	2600



λ_{max}	ε[4]
2530	4900

The IR spectrum of the neat dimer showed a very broad carbonyl stretch at 1665 cm^{-1} and another strong band at 1610 cm^{-1}. The exact structure of the dimer, including the stereochemistry about the cyclobutane ring, is not known however. Because only a small amount can be easily isolated at any one time, it has not been possible to send off a sample for elemental analysis or do any degradative studies on the compound. An attempt to measure the molecular weight by mass spectrometry yielded only m/e = 109, indicating that the dimer easily splits apart.

The other new product isolated is a very minor one and only NMR spectral data are available (spectrum in Experimental Section). This is referred to as dimer T and a structure proposal would be very sketchy at this time. Dimer T is a white solid and shows four vinyl protons and four bridgehead protons at about the same chemical shifts as those of dimer D.[3] The N-methyl protons are shifted slightly, and for this reason it is believed to be another 1,4-1,4 dimer of differing stereochemistry. It was only possible to isolate about 1 mg of this material so further treatment was impossible. Further structure proof will be dependent on finding a means to isolate larger amounts of each product than are possible by TLC techniques.

The labeled NM2P proved to be a boon in measuring the quantum yields of formation of dimers M and T. The detailed procedure of analysis is given in the Experimental Section; but, simply, it consisted of opening the irradiated tubes and placing a portion of the solution on a TLC plate. After development the spots corresponding to NM2P, dimer M, and dimer T were scraped off and the silica gel counted in a scintillation counter. The NM2P served as internal standard and the quantum yields are shown in the following tables. The plots corresponding to these quantum yields are also given.

Now all of the NM2P can be accounted for and it is possible to devise a mechanism to account for the observed photochemistry. Since the yield of P decreases with increasing concentration, at least one of the dimers

TABLE VIII

Quantum Yield of Formation of Dimer M at Various Concentrations of NM2P

	$[NM2P]_{ave}$ (M)	Φ_M
Run 1:	0.080	0.011 ± 0.0001
		0.011 ± 0.0003
	0.195	0.025 ± 0.001
	0.260	0.034 ± 0.002
		0.034 ± 0.002
	0.350	0.043 ± 0.002
	0.480	0.056 ± 0.004
		0.059 ± 0.002
Run 2:	0.105	0.014 ± 0.001
		0.014 ± 0.0002
	0.175	0.022 ± 0.001
		0.021 ± 0.0001
	0.285	0.035 ± 0.002
		0.034 ± 0.002
	0.363	0.040 ± 0.003
		0.040 ± 0.002
	0.500	0.057 ± 0.0004
		0.050 ± 0.001

TABLE IX

Quantum Yield of Formation of Dimer T at Various Concentrations of NM2P

	$[NM2P]_{ave}$ (M)	Φ_T
Run 1:	0.080	0.0039 ± 0.0002
		0.0039 ± 0.0002
	0.195	0.0095 ± 0.0002
	0.260	0.0113 ± 0.0003
		0.0118 ± 0.0002
	0.480	0.0199 ± 0.0014
		0.0214 ± 0.0004
Run 2:	0.105	0.0040 ± 0.0008
		0.0044 ± 0.0002
	0.175	0.0078 ± 0.0002
		0.0065 ± 0.0005
	0.285	0.0109 ± 0.0013
		0.0123 ± 0.0006
	0.363	0.0130 ± 0.0014
		0.0137 ± 0.0003
	0.500	0.0206 ± 0.0008
		0.0175 ± 0.0008

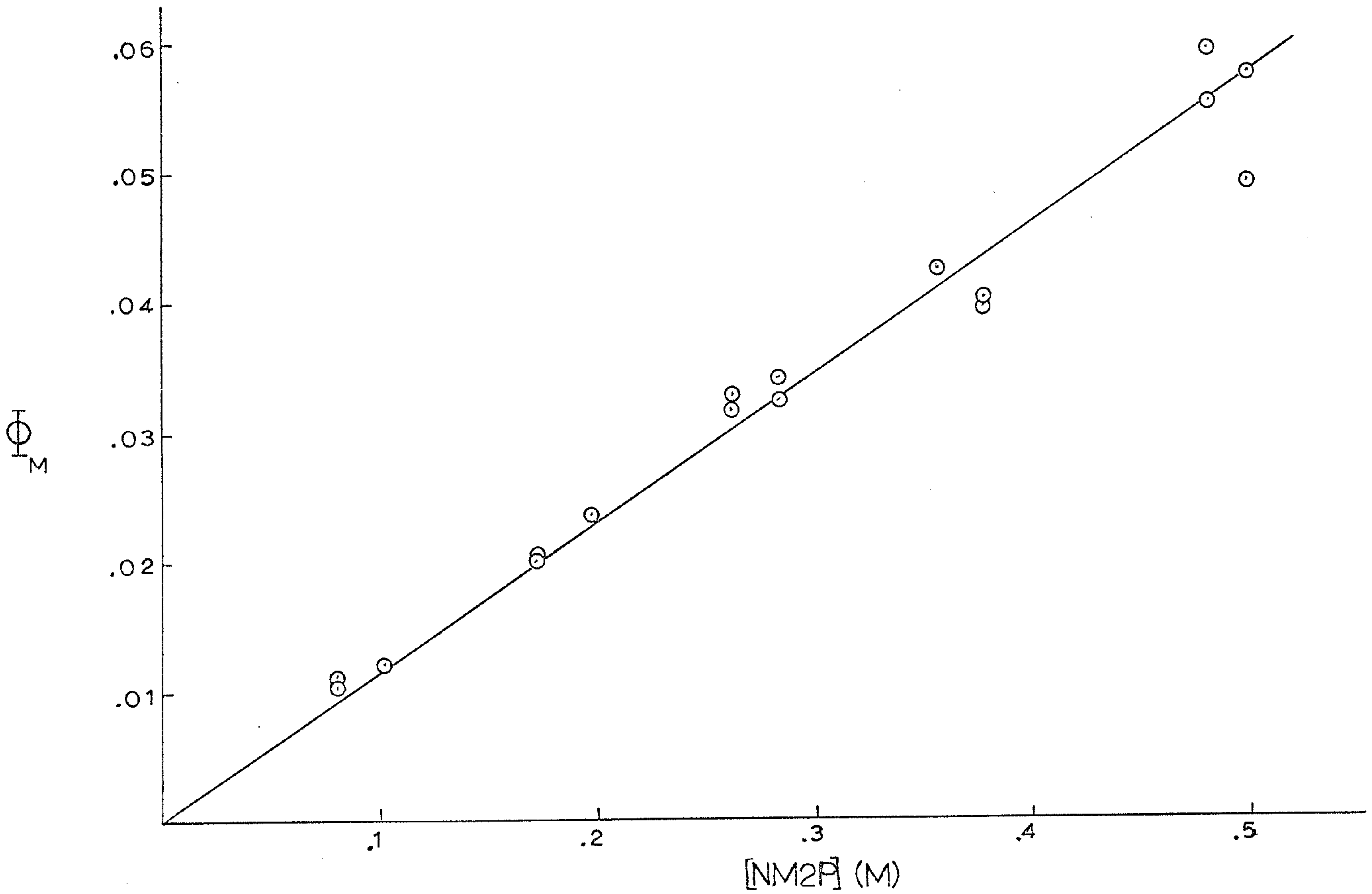


Figure 9. Quantum Yield of Dimer M at Various Concentrations of NM2P.

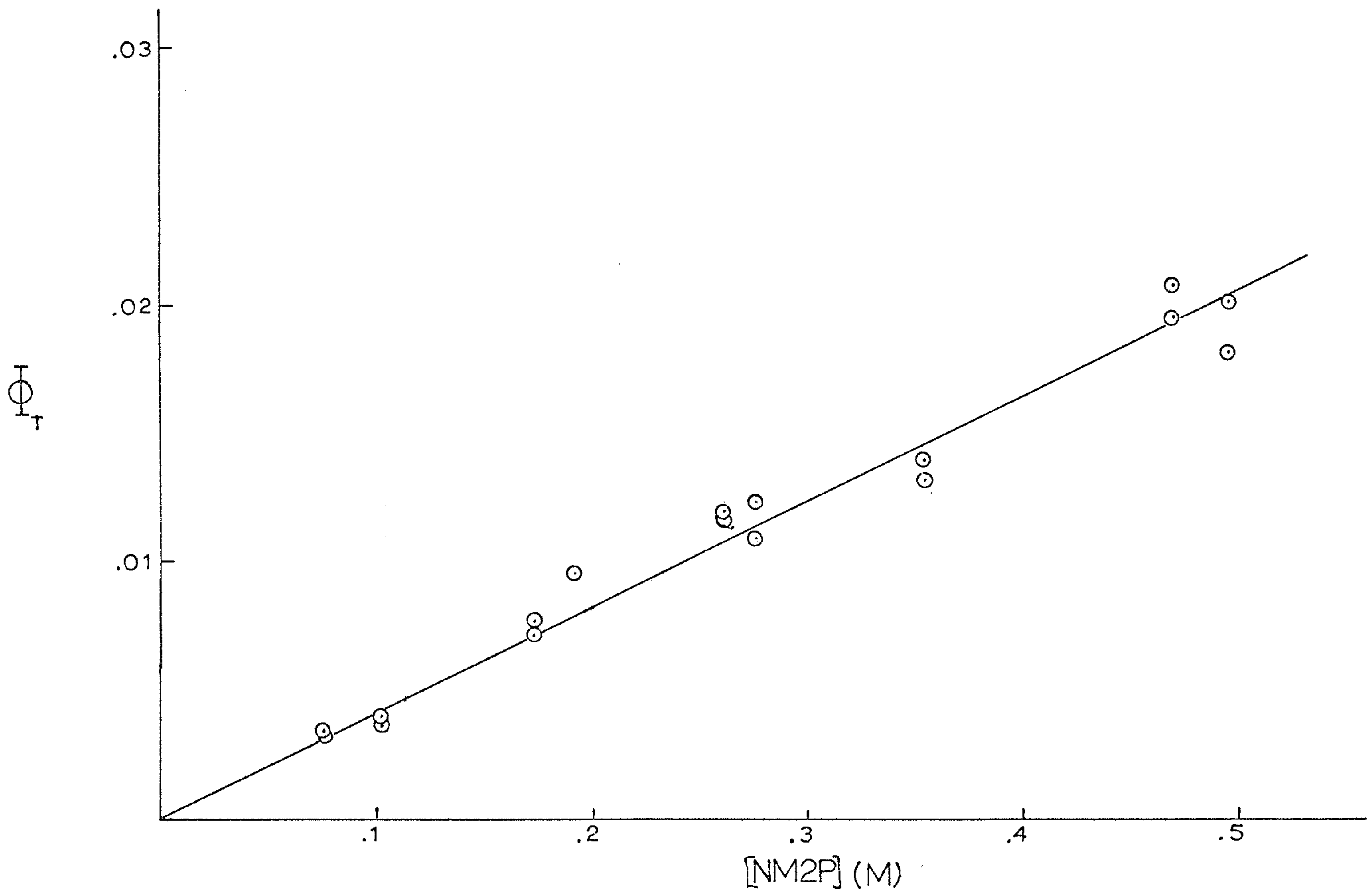


Figure 10. Quantum Yield of Dimer T at Various Concentrations of NM2P.

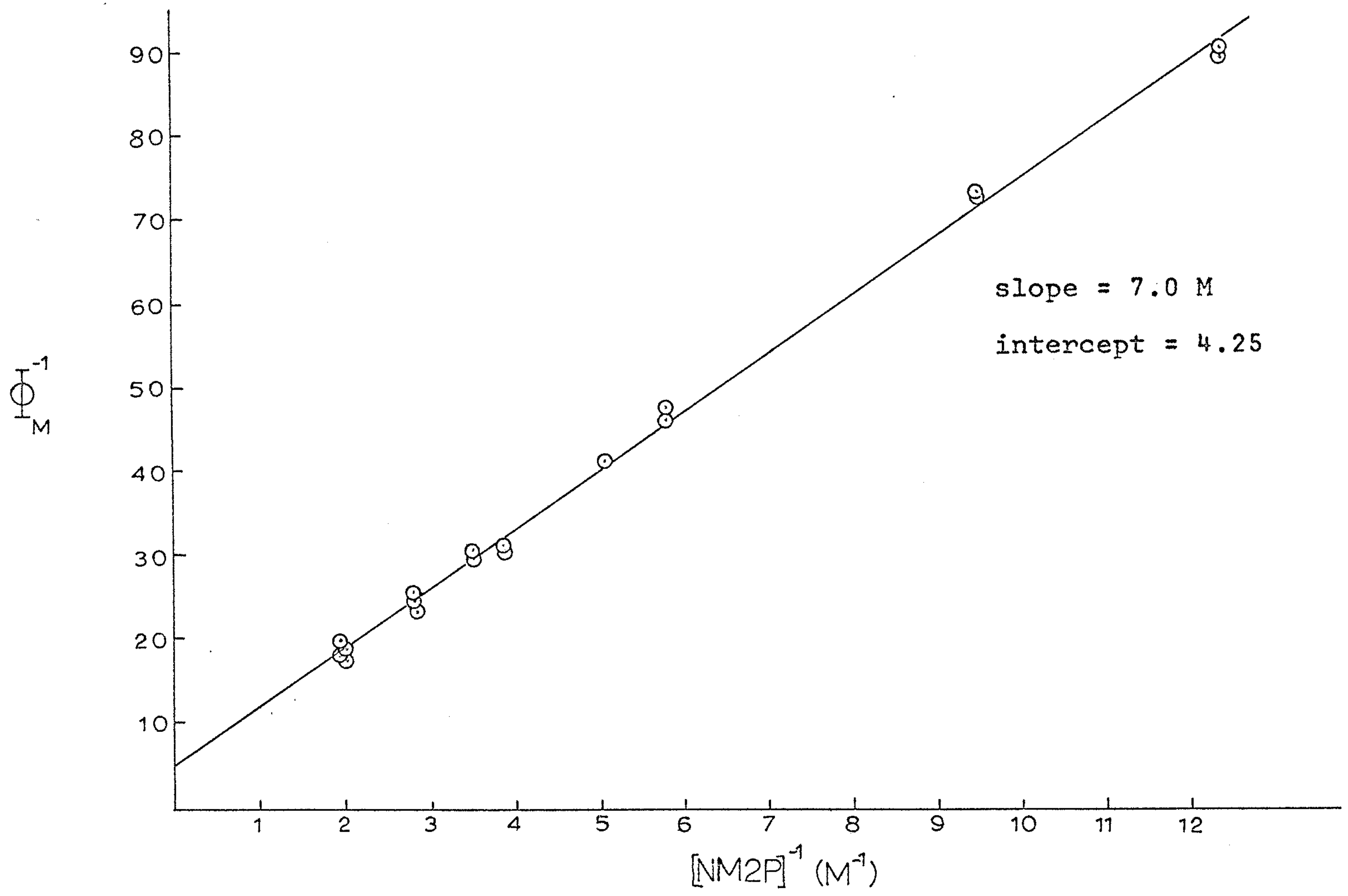


Figure 11. Reciprocal of Quantum Yield of Dimer M versus Reciprocal Concentration.

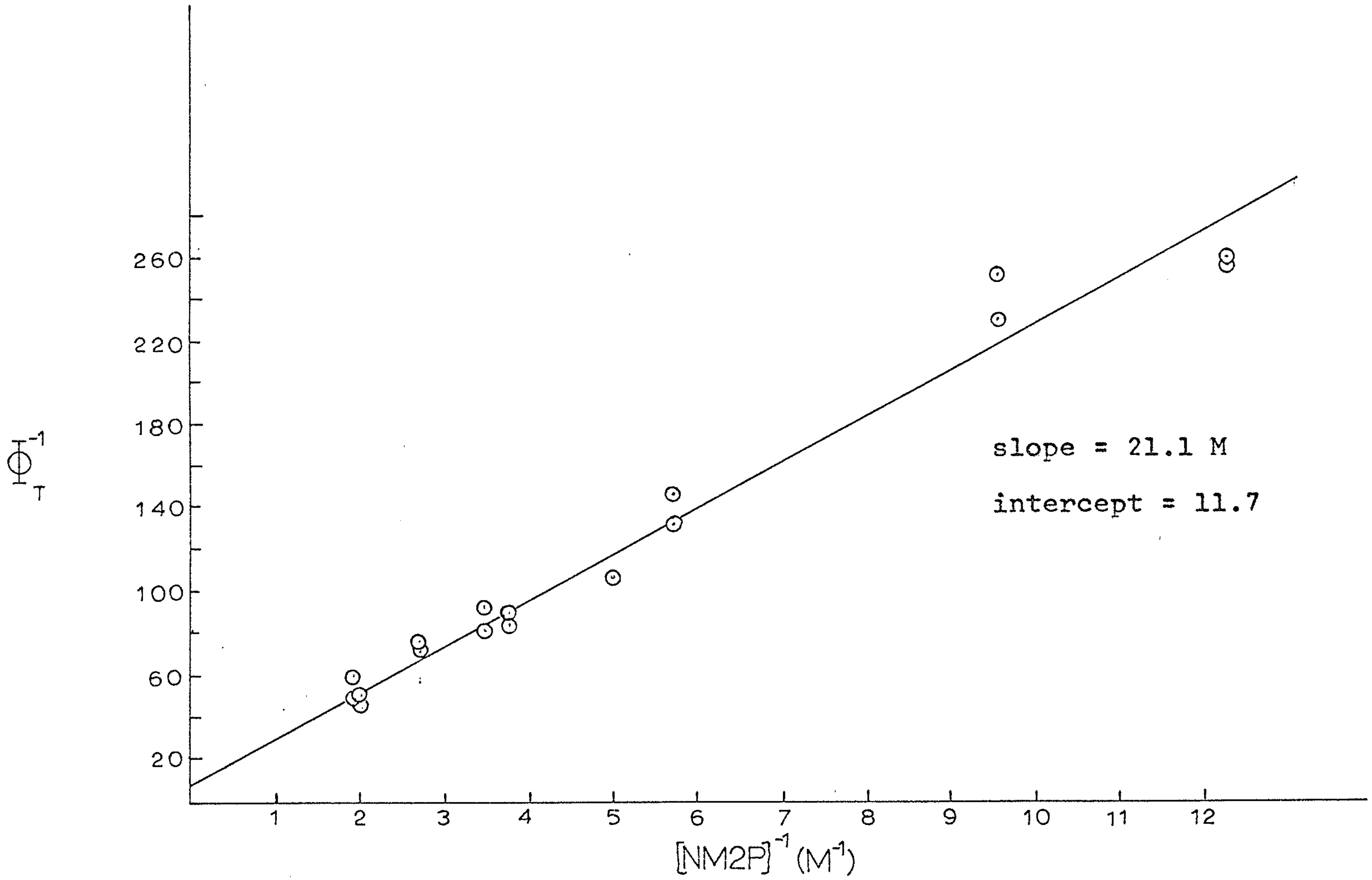


Figure 12. Reciprocal of Quantum Yield of Dimer T versus Reciprocal Concentration.

must be forming from the same excited state or from a precursor to that leading to P. As a means of testing the lowest singlet excited state, it is possible to measure the quantum yield of fluorescence as a function of concentration of NM2P. If P is forming from S_1 then we would expect quantum yield of fluorescence to decrease in a manner similar to quantum yield of P. These values were measured at Bell Laboratories by Dr. Angelo A. Lamola and shown in Table X. These were repeated several times and an average of four runs on two sets of identical tubes reported. Another set of samples was made up and the fluorescence intensity measured. They showed about the same trend with a slight decrease at higher concentrations. The decrease, however, could be due to peculiarities in the optical path caused by the very high optical density. If it is assumed that this decrease is real, then one must account for the fact that the decrease is not as large as that for the quantum yield of P. However the experimental errors of the measurements are large enough to explain the discrepancy.

Attempts to measure a decrease in lifetime of the singlet state of NM2P with increasing concentration also led to clouded results. Since the fluorescent state of naphthalene could be quenched by dienes[28] to give a Stern-Volmer plot with slope $k_q \tau_s$, it was thought that

TABLE X*

Intensity of Fluorescence at Various Concentrations of NM2P

[NM2P] (M)	I_F
0.0126	66
0.0518	68
0.1043	67
0.3109	59
0.5142	55

*the error is estimated at 5 to 10%

quenching of the fluorescence of NM2P by tetramethylbutadiene at various NM2P concentrations could give a measure of changing τ_s. A typical plot of the data is shown in Figure 13 for [NM2P] = 3×10^{-4} M. When the concentration was increased the slope went down as shown in Table XI but the error was such that it was extremely difficult to say that this was due to a self-quenching of fluorescence and not just some fortuitous geometry effects in the measurements.

Direct measurement of the fluorescence lifetime was not possible using the TRW Nanosecond Spectral System;[29] but a more indirect method, described in the Experimental Section proved useful, yielding a value of 0.2 nsec ±0.2 nsec at 0.098 M. These data neither rule out S_1 nor strongly implicate it as the reactive state in the photoreactions.

More successful results were obtained when the possibility of a reaction from the triplet state was investigated. The standard test for the intermediacy of a triplet state is the quenchability of the reaction with suitable triplet quenchers, and the possibility of triplet sensitization. Both these tests were employed. In preliminary work, the quantum yield of intersystem crossing, Φ_{ISC}, was measured using the method of Lamola.[30] This consists of using NM2P as a sensitizer for the cis-trans isomerization of a diene, cis-piperylene. An actinometer

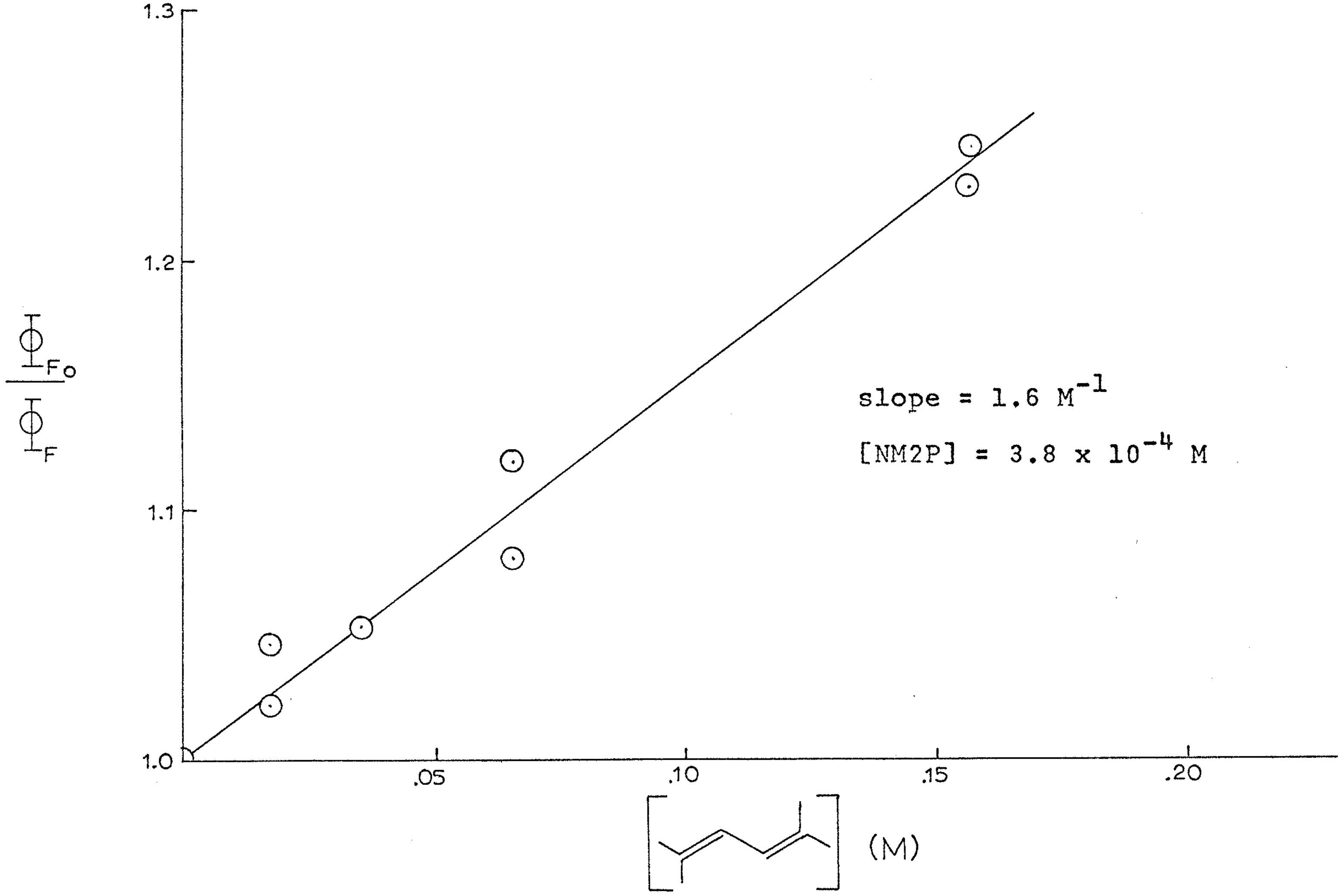


Figure 13. Stern-Volmer Plot for Quenching of Fluorescence of NM2P with Tetramethylbutadiene.

TABLE XI*

Slopes of the Stern-Volmer Plots for Quenching of the Fluorescence of NM2P with Tetramethylbutadiene at Various Concentrations

[NM2P] (M)	$k_q\tau$ (M^{-1})
3×10^{-4}	1.6
1×10^{-2}	0.83
1×10^{-1}	0.72
2×10^{-1}	0.44

*error estimated at 40%

of benzophenone--cis-piperylene was used, and even after twelve hours of irradiation only a very slight amount of isomerization had taken place. The amount of isomerization is shown in Table XII. The benzophenone tubes were irradiated for only two hours while those of NM2P were irradiated for twelve hours and thus it is possible to estimate that the quantum yield of intersystem crossing is less than 0.007. The amount of trans-piperylene is just about at out level of detection and could also be due to a small amount of direct irradiation or thermal isomerization. This experiment was repeated with the same results; and correlates well with the fact that phosphorescence, while observable, was very much weaker than fluorescence.

The phosphorescence was measured at 77°K in an alcoholic glass and the triplet energy found to be 69.2 kcal/mole by estimating the 0-0 band to be at 4133 Å. The phosphorescence of 2-pyridone was similar and of about the same energy.

Piperylene was found to quench the phosphorescence of 2-pyridone, as would be expected, so that the observed small intersystem crossing quantum yield is not due to a lack of energy transfer.

Sensitization experiments were undertaken using xanthone (E_T = 74.2 kcal/mole)[31] and various concentrations of NM2P. At low concentrations (10^{-3} M in NM2P) none of the isomer P appeared on irradiation of the system at 2537 Å,

TABLE XII*

Sensitization of Isomerization of cis-Piperylene

Sensitizer	Piperylene (0.05M)	
	% cis	% trans
Benzophenone (0.05M)	90.9	9.1
NM2P (0.089M)	99.7	0.3

*cis-piperylene is 0.05 M.

where the sensitizer absorbed all the light. Likewise experiments carried out at higher concentration (0.1 M in NM2P) showed no P nor any disappearance of NM2P on irradiation at 3660 Å. These analyses were carried out by VPC. Finally in a third experiment at 0.3 M NM2P, no dimers at all could be detected under conditions at which they had been observed previously. In all these cases the xanthone absorbed the light and it appeared to be photostable. The solutions did turn yellow on irradiation, but this could be due to a very minute amount of reaction which could not be detected in our system.

In order to show that the xanthone triplets were actually being quenched by the NM2P, tubes were prepared and the phosphorescence of xanthone was quenched by NM2P. At 77°K in an alcoholic glass 0.1 M NM2P quenched better than 50% of the phosphorescence of xanthone, indicating that the triplet energy is in all probability being transferred in fluid solution to the NM2P.

Various quenchers were also added to NM2P in an effort to measure the quenching of product formation. Using cis-piperylene, no quenching of the formation of P was observed up to 0.25 M in cis-piperylene. This was a higher concentration than used in measuring the quantum yield of intersystem crossing and all triplets should be easily quenched. In other systems[28] the piperylenes were found to be singlet quenchers of relatively low reactivity; because of this and the short lifetime of the singlet state of NM2P, no singlets should be quenched.

Tetramethylbutadiene was also used as a quencher for the formation of P. A plot of the Stern-Volmer relation is shown in Figure 14. Quenching is noted here and the slope gives a value of $k_q\tau$ of 2.7 M^{-1}. If one assumes that a triplet state is being quenched then the quenching rate constant will be rather small because triplet lifetimes of T_1 are normally about 10^{-6} sec, or longer, in fluid solution. Dienes are good triplet quenchers and would be expected to quench at the diffusion controlled rate. This small amount of quenching is best explained in terms of singlet quenching as proposed by Hammond and co-workers.[28] Tetramethylbutadiene is known as an efficient quencher of naphthalene singlets and this probably is also true here with NM2P. Likewise the slope of this plot is similar to that of Figure 13 in which the fluorescence of NM2P is quenched. The increased slope could be due to the fact of competitive absorption since the solutions turn bright orange on irradiation.

Finally quenching by trans-piperylene of the disappearance of NM2P was also undertaken. A plot of this data is shown in Figure 15. The result was quite unexpected in that the disappearance of NM2P was enhanced by added

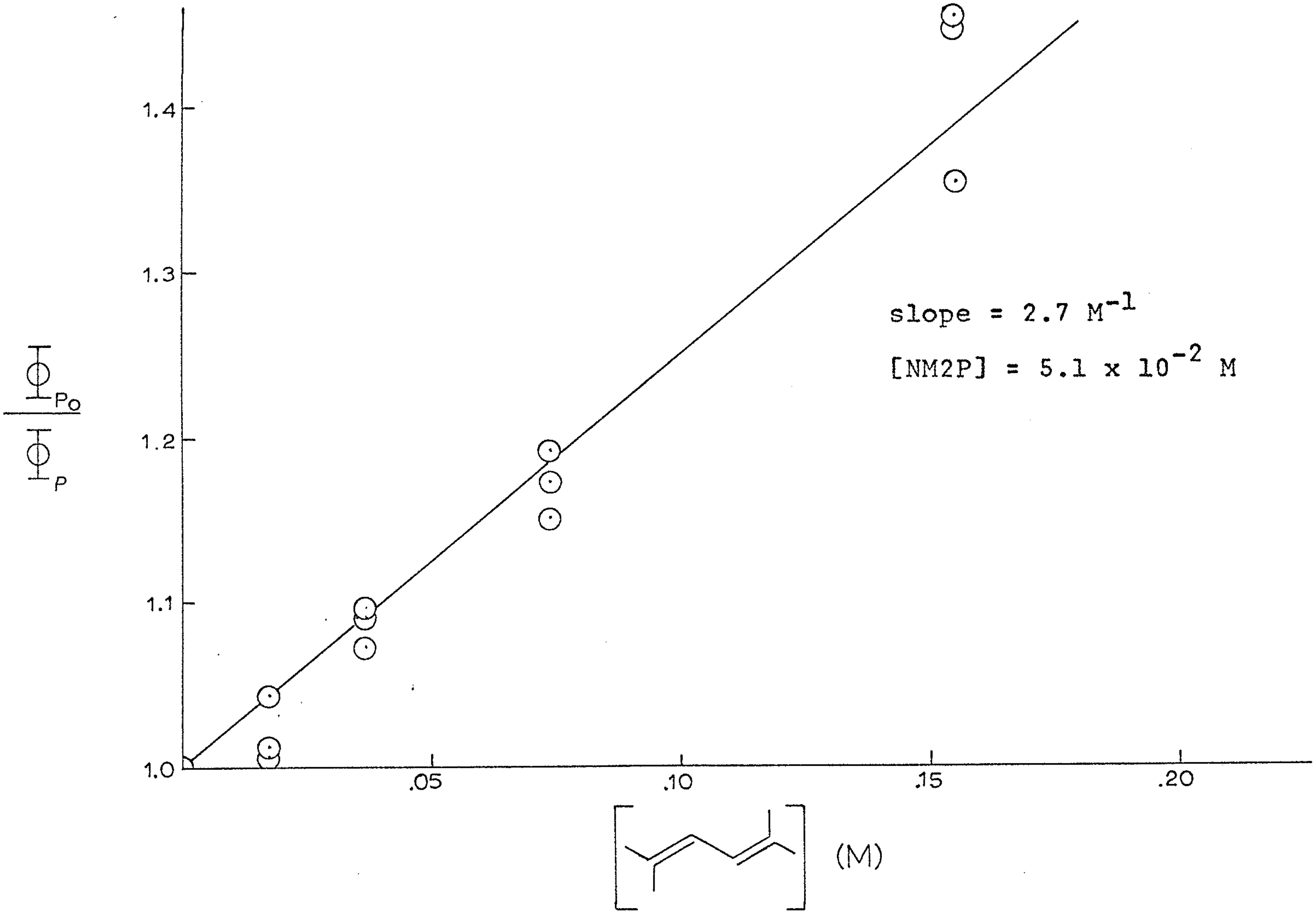


Figure 14. Stern-Volmer Plot for Quenching of Formation of P with Tetramethylbutadiene.

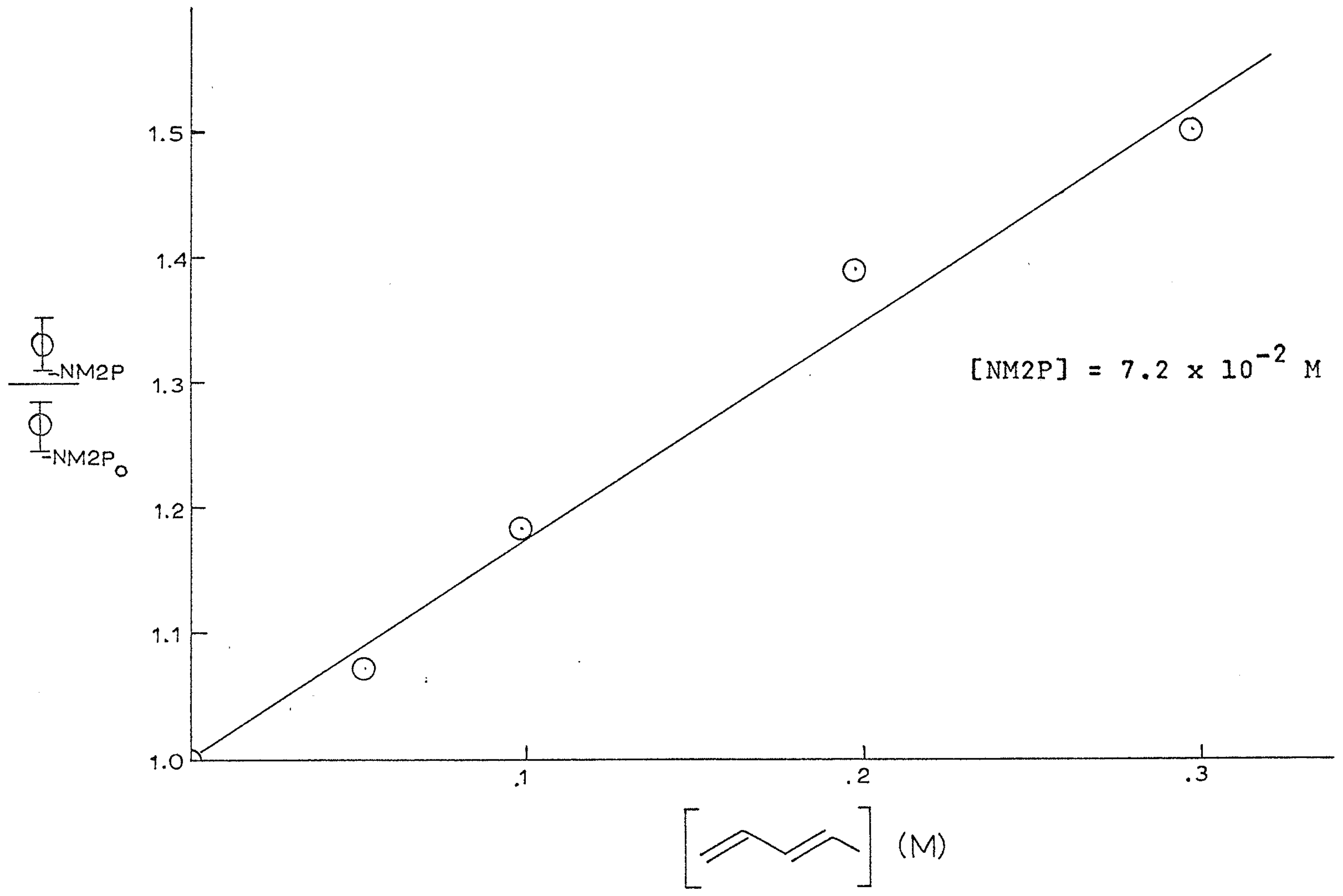


Figure 15. Stern-Volmer Plot for Quenching of Disappearance of NM2P with trans-Piperylene.

diene. It seems reasonable that this side reaction does not involve the triplet state; if a triplet of NM2P is formed then some of its energy should be transferred to piperylene before reaction. Then the piperylene should isomerize to some extent because this has been shown to be quite efficient.[30] Most likely this new reaction is taking place from some intermediate that is not the singlet and is different from that leading to P because of the lack of effect on the quantum yield of P by added diene. This is an interesting side reaction but not closely connected to the product forming steps of the photolysis.

Thus T_1 seems to be ruled out as the state leading to product formation. Likewise other states may be ruled out. S_2 is not involved because irradiation at 3130 Å puts light into only the lowest absorption band, presumably S_1. Likewise S_2 is believed to have a very short lifetime due to facile internal conversion to S_1. Similar arguements can be used to dispute the intermediacy of a "hot" ground state. The lifetime of vibrationally excited states is assumed to be of the order of vibrational lifetimes, 10^{-12} sec; and in order to see a quantum yield of 0.06, the excited state would have to be trapped at a rate of 6×10^{10} $sec^{-1}M$. If one assumes a diffusion controlled reaction of rate 10^{10} sec^{-1} then a concentration of trapping agent of 6 M would be necessary. However a concentration of NM2P of only 0.1 M is necessary to see a quantum efficiency of 0.06, thus "hot" ground states are eliminated.

With S_1 for NM2P being at 88 kcal/mole, it is possible that there is another triplet state below this but above 74 kcal/mole. Thus sensitization would be ineffective. However, again because of efficient internal conversion, this would be expected to have a very short lifetime and thus not be important in the reaction.

The reactive state in the photolysis appears to be the lowest excited singlet state but whether it goes directly to dimers or through a metastable reaction intermediate is not yet possible to determine. It is most likely that all of the dimers form from the same state because the ratio of the amounts of various dimers is a constant with increasing concentration of NM2P. Also the kinetics require that P and one of the dimers form from the same intermediate.

As a means of studying this intermediate, if present, several low temperature experiments were undertaken. A solution of NM2P, 10^{-4} M in EPA, was placed in a square cell, cooled to 77°K, and the absorption spectrum recorded on the Cary 14. The sample, still at 77°K, was irradiated with a 2500 watt lamp and the spectrum recorded again. A yellow color had become visible. The sample was warmed until melting and then refrozen and the spectrum recorded a third time. Figure 16 shows the change in absorption. The fact that another absorption appeared, on disappearance of NM2P, which was apparently stable at 77°K and which on warming then disappeared to give back NM2P seems to indicate that a reactive intermediate is forming from NM2P. This experiment was repeated several times. The UV is not much of a help in determining the structure of the intermediate so some low temperature IR experiments were undertaken.

Dr. O. L. Chapman has had great success in observing ketene intermediates[19] produced in many photochemical systems. He then performed some experiments for us in which a sample of NM2P, in ethanol and neat, was cooled to -196°C and irradiated. The IR spectrum was then recorded. With painstaking care the conditions were changed again and again, but no intermediate could be observed under the conditions in which it had been seen in the UV. Most likely the unreacted NM2P absorptions hid those of the intermediate. This most certainly rules out intermediates in which the carbonyl absorption would be clearly visible, such as a ketene.

A third set of low temperature experiments was carried out by observing the ESR signal produced on

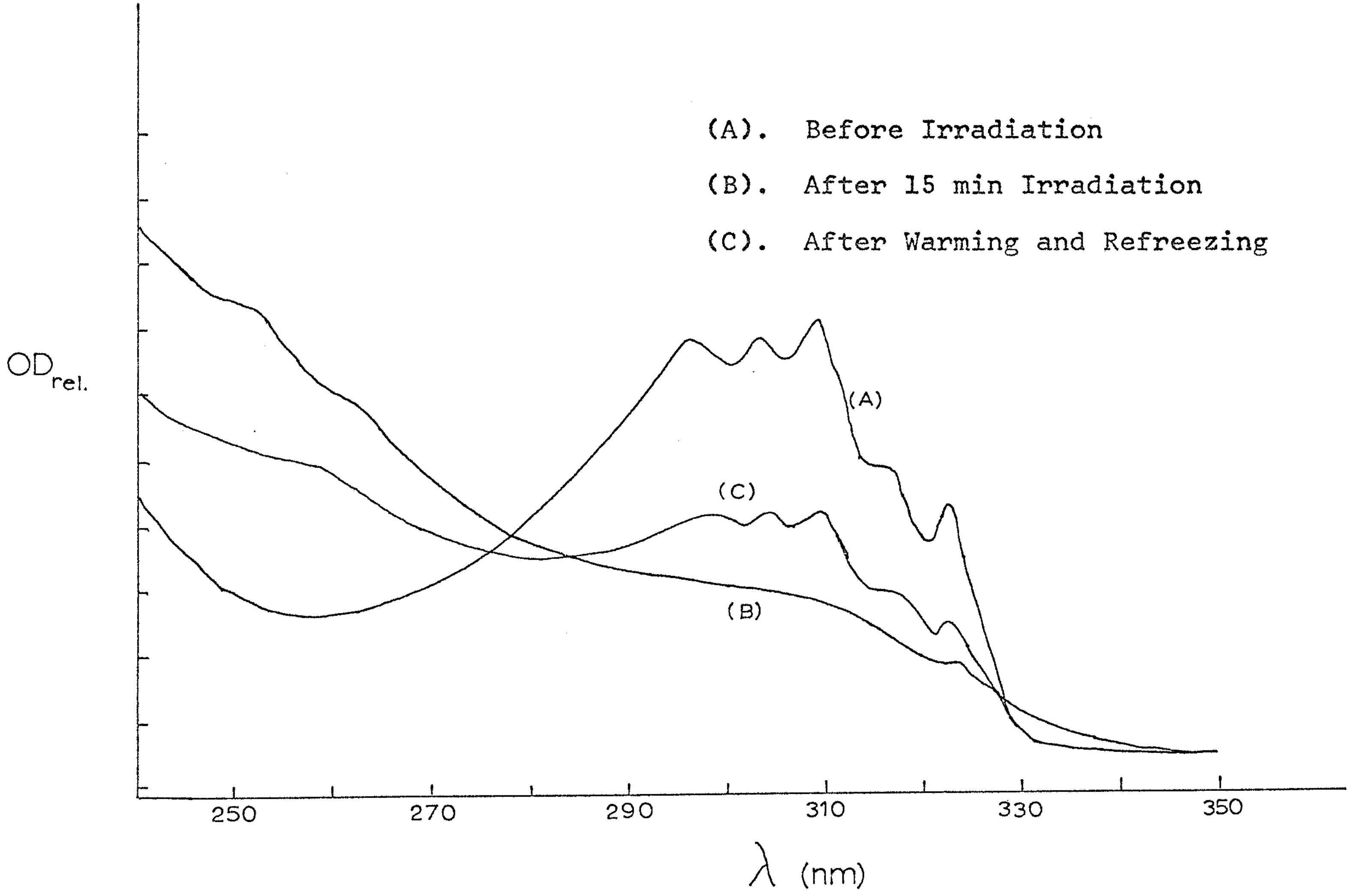


Figure 16. Change in Absorption on Irradiation of NM2P at 77°K.

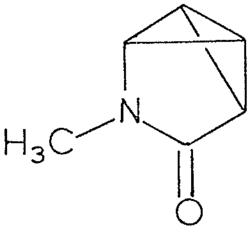
irradiation. A solution of 0.03 M NM2P was irradiated at 77°K in the cavity of an ESR spectrometer and a signal consisting of two lines observed. This also was found to be stable at low temperature and disappear on warming; and a yellow color was present in the tube after irradiation. Whether this signal is due to the same intermediate or just some impurities in the solvent is not known.

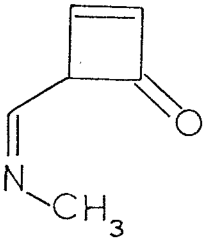
Finally irradiations were undertaken in an effort to trap the intermediate. Because of the lack of solvent effects and because all the NM2P can be accounted for, ethanol has no effect on the intermediate. Irradiation of NM2P in ethanol with various amounts of hydrogen ion yielded diminished amounts of P, but it was found that P was not thermally stable to acid so the results were meaningless.

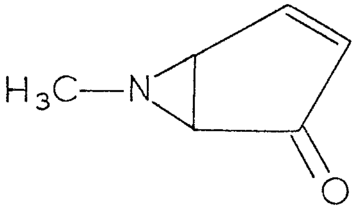
Likewise irradiation in the presence of cyclohexylamine yielded a white crystalline product, but this also formed on thermal reaction with product P. Thus the trapping experiments proved to be of little value.

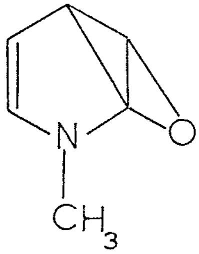
As a control experiment, a sample was prepared identical to that for the low temperature UV experiment, but in this case it was carried out at room temperature. This gave the expected results in that the NM2P absorption disappeared and that due to the products appeared. Flash photolysis experiments performed on similar solutions failed to produce any transient absorptions at room temperature, thus indicating that this intermediate reacts very rapidly at room temperature in fluid solutions.

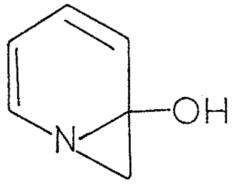
Some possible structures for this intermediate are shown below:

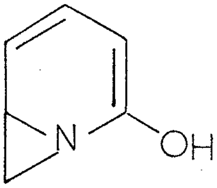












None of these seem to be what is needed to account for the observed results: reaction with NM2P to yield dimers or reaction with dienes to yield some products.

A mechanism can now be devised to account for the experimental results:

$$\begin{array}{rcll}
\mathrm{NM2P} & \xrightarrow{h\nu} & \mathrm{NM2P}^1 & aI \\
\mathrm{NM2P}^1 & \longrightarrow & \mathrm{NM2P} & k_1 \\
\mathrm{NM2P}^1 & \longrightarrow & \mathrm{NM2P} + h\nu & k_2 \\
\mathrm{NM2P}^1 & \longrightarrow & \mathrm{P} & k_3 \\
\mathrm{NM2P} + \mathrm{NM2P}^1 & \longrightarrow & \mathrm{D} & k_4 \\
\mathrm{NM2P} + \mathrm{NM2P}^1 & \longrightarrow & \mathrm{M} & k_5 \\
\mathrm{NM2P} + \mathrm{NM2P}^1 & \longrightarrow & \mathrm{T} & k_6 \\
\mathrm{NM2P}^1 & \longrightarrow & \mathrm{Z} & k_7 \\
\mathrm{diene} + \mathrm{Z} & \longrightarrow & \mathrm{products} & k_8 \\
\mathrm{Z} & \longrightarrow & \mathrm{NM2P} & k_9
\end{array}$$

Z = reactive intermediate

It is possible to find expressions for the quantum yields and to show that indeed the data do fit them.

$$\Phi_P = \frac{k_3}{k_1 + k_2 + k_3 + k_7 + (k_4 + k_5 + k_6)\,[\mathrm{NM2P}]}$$

$$\Phi_D = \frac{k_4\,[\mathrm{NM2P}]}{k_1 + k_2 + k_3 + k_7 + (k_4 + k_5 + k_6)\,[\mathrm{NM2P}]}$$

$$\Phi_M = \frac{k_5\,[\mathrm{NM2P}]}{k_1 + k_2 + k_3 + k_7 + (k_4 + k_5 + k_6)\,[\mathrm{NM2P}]}$$

$$\Phi_T = \frac{k_6\,[\mathrm{NM2P}]}{k_1 + k_2 + k_3 + k_7 + (k_4 + k_5 + k_6)\,[\mathrm{NM2P}]}$$

$$\Phi_F = \frac{k_2}{k_1 + k_2 + k_3 + k_7 + (k_4 + k_5 + k_6)\,[\mathrm{NM2P}]}$$

and at [diene] = 0

$$\Phi_{-NM2P} = \frac{k_3 + 2(k_4 + k_5 + k_6)\,[NM2P]}{k_1 + k_2 + k_3 + k_7 + (k_4 + k_5 + k_6)\,[NM2P]}$$

This then predicts that the reciprocal of the quantum yield of P versus the concentration of NM2P should be a straight line as is seen, and that the reciprocal of the quantum yield of dimerization, for any dimer, versus the reciprocal of NM2P concentration should also be straight. And finally, if we assume that $k_3 << 2(k_4 + k_5 + k_6)$ [NM2P] then the plot of the reciprocal of the disappearance quantum efficiency versus the reciprocal of NM2P concentration should be straight. Also the fluorescence yield should decrease with increasing concentration. If one notes that the plot of dimerization quantum yield as a function of NM2P concentration is linear and that the fluorescence of NM2P is weak, then it can be argued that $k_1 + k_2 + k_3 + k_7 >> (k_4 + k_5 + k_6)$ [NM2P] and that $k_1 + k_7 >> k_2 + k_3$. This says that the radiationless decay paths predominate over emission or reaction at low NM2P concentration.

As another check it is possible to see that from the reciprocal plots, ratios of intercepts to slopes or vice versa should give the same values in all cases. These were calculated and shown below:

Φ^{-1}_{-NM2P} vs $[NM2P]^{-1}$ $\qquad \frac{\text{slope}}{\text{int}} = 2.76$

$$\Phi_M^{-1} \quad \text{vs } [\text{NM2P}]^{-1} \qquad \frac{\text{slope}}{\text{int}} = 1.66$$

$$\Phi_T^{-1} \quad \text{vs } [\text{NM2P}]^{-1} \qquad \frac{\text{slope}}{\text{int}} = 1.80$$

$$\Phi_P^{-1} \quad \text{vs } [\text{NM2P}]^{-1} \qquad \frac{\text{int}}{\text{slope}} = 1.32$$

This is a remarkable correlation because the experimental errors in determining the intercept are great as shown by the plot of the reciprocal of the quantum yield of D versus the reciprocal of NM2P concentration. If one inspects the graph these points fall identically on top of the same points for dimer M but from the least squares fit the value of the intercept is off to such an extent that the ratio above is a factor ten larger. This is most certainly due to the experimental errors.

As pointed out before because of the uncertainty in the measurement of the quantum yield of fluorescence at various concentrations, it is still possible that the lowest excited singlet is not involved and the reaction proceeds through a nonfluorescent, excited intermediate. With such a kinetic scheme, the same straight lines are predicted and the same slope/intercept correlation. Thus unless more refined measurements of the quantum yield of fluorescence are possible, these cannot be distinguished.

There are still several unanswered questions in the photochemistry of N-methyl-2-pyridone. The structure of dimers M and T must be proven when a more viable technique is found for isolating them. Some degradative studies will have to be undertaken in order to prove the stereochemistry about the ring junctions. The nature of the intermediate has still to be investigated. Finally, the most interesting aspects of the investigation might turn out to be the apparent photoreaction between NM2P and the diene quenchers. As shown in Figure 14, there is a definite reaction between NM2P and *trans*-piperylene; and with tetramethylbutadiene an orange color is produced on irradiation which is stable at room temperature in a degassed tube but bleaches on opening of the tube. The ESR spectrum does not show a signal from the orange species so nothing is known of it.

EXPERIMENTAL

Materials

N-methyl-2-pyridone(Aldrich) was purified by distillation to yield a colorless liquid. This was stored in a freezer to prevent decomposition.

N-methyl(^{14}C)-2-pyridone was prepared by a method similar to that for O-methylation.[32] The glass apparatus had two arms and could be degassed. In the left arm 10.0 g of 2-pyridone(Matheson, Coleman and Bell) and 20.7 g of potassium carbonate(Baker Adamson) were placed with 125 ml of reagent acetone. In the other arm were placed 6.25 ml of methyl iodide(Matheson, Coleman and Bell) along with the ampoule of methyl(^{14}C) iodide (Tracerlab, 71 mg, 1.0 mc/mM, lot number 70-45-8). Both arms were cooled in liquid nitrogen and the apparatus degassed and sealed off. Then the methyl iodide was distilled into the left arm and that sealed off. The tube was heated in an oil bath at 65-70°C for three days. The tube was broken, the solid separated and the liquid distilled to remove all volatiles. The remaining residue was then separated by preparative gas chromatography on an 8 ft x 3/8 in, 25% Carbowax 20M (30/60 Chromosorb W) column, maintained at 180°C. To the main product was added 4.0 g of unlabeled N-methyl-2-pyridone and this distilled to give 6.0 g of purified N-methyl-2-pyridone (specific activity 3.15×10^6 cpm/mM) which was stored in the refrigerator.

Xanthone(Matheson, Coleman and Bell) was recrystallized from ligroin prior to use.

Hexadecane(Matheson, Coleman and Bell, Spectroquality) was used without purification.

1-Methylnaphthalene(obtained from L. M. Stephenson) was distilled before use.

Benzophenone(Matheson, Coleman and Bell) was recrystallized from ligroin before use.

2,3-Benzofluorene(Aldrich) was used without purification.

d,l-Camphorquinone(Aldrich) was used without purification.

Cyclohexylamine(Matheson, Coleman and Bell) was distilled before use.

Solvents--Absolute ethanol was refluxed over magnesium turnings and distilled. Benzene(Baker Analyzed Reagent) was stirred over sulfuric acid for several weeks, washed with dilute base and water, and dried over magnesium sulfate. Finally it was distilled from phosphorous pentoxide through a column packed with glass beads. Ether (Mallinkrodt, Anhydrous) was used without purification. EPA(Matheson, Coleman and Bell) was from a fresh bottle and used without purification. Methanol(Matheson, Coleman and Bell, Spectroquality) was used without further treatment. Isopropyl alcohol(Baker Analyzed, Reagent Grade) was used without purification.

Quenchers--*Cis*-piperylene(Columbia) was distilled from lithium aluminum hydride prior to use and showed less than 0.1% *trans* by VPC. *Trans*-piperylene(Columbia) was treated in the same manner as the *cis*. Tetramethylbutadiene (obtained from L. M. Stephenson) was distilled from lithium aluminum hydride and stored in the freezer.

Scintillation Solution (Bray's Solution)--This was prepared by adding the following:

60 g of naphthalene(Eastman Organics, recrystallized)
4 g of PPO (Packard)
0.2 g of POPOP (Pilot)
100 ml of methanol(Matheson, Coleman and Bell)
20 ml of ethylene glycol(Matheson, Coleman and Bell)

and diluting them to 1 liter with p-dioxane(Eastman Organics, Reagent Grade).

Quantum Yields

The desired amount of N-methyl-2-pyridone was weighed into a volumetric flask and diluted to volume. Hexadecane was also added as an internal standard for the analysis of the bicyclic product, P. In the quenching experiments the proper amount of quencher was delivered by λ-pipet to the flasks. For the sensitization experiments a saturated solution of xanthone in ethanol was used to dissolve the N-methyl-2-pyridone. This was enough to insure that all of the light went into the sensitizer at 3660Å.

Three milliliter samples of the solutions were then placed in pyrex culture tubes (13 x 100 mm) which were constricted and the tubes degassed by three freeze-pump-thaw cycles to a vacuum of 5×10^{-4} mm. Hg. In the case of irradiations at 2537Å, quartz tubes of 13 mm od were used. All tubes were stored in the dark before and after irradiation.

Irradiation of Samples

All quantum yield tubes were irradiated in a merry-go-round apparatus[33] to insure equal irradiation. The light source was a Hanovia 450 watt medium pressure mercury lamp with the appropriate filter system to isolate 3130Å or 3660Å. For 2537Å irradiations a 600 watt Hanovia low pressure lamp(Z1500-118) was used. The merry-go-round was operated in a water bath which could be kept at room temperature by external cooling.

Filters

a) 3130Å. Two filter systems were used. The first was 6 mm of a potassium chromate solution (127 mg K_2CrO_4 in 250 ml of 1% CO_3^{-2} in H_2O) and 10 mm of a cobalt sulfate solution (250 g of $CoSO_4 \cdot 7H_2O$ in 1 liter of H_2O). The second was a Corning 7-54 filter and 5 mm of a potassium chromate solution (528 mg of K_2CrO_4 in 1 liter of 1% CO_3^{-2} in H_2O) which was recirculated through the lamp cooling well.

The potassium chromate solution isolates a band at 3130Å and another in the visible. The second filter in each case absorbs in the visible thus isolating only the 3130Å line. For specific details of these filter solutions see references 33 and 34.

b) 3660Å. Corning 7-37 and 0-52 glass filters which fit into the merry-go-round were used to isolate the 3660Å line. This filter transmitted about 20% of the light with a 100Å band width.[30]

c) 2537Å. Oriel Optics 2537Å interference filters were used. They have a band width of 250Å with a maximum transmission of 20% at 2537Å.[33]

Actinometry

Two methods of actinometry were used. In the attempts to measure the quantum yield of intersystem crossing by isomerization of *cis*-piperylene,[30] a benzophenone--*cis*-piperylene actinometer was used. This was a tube of 0.05M benzophenone and 0.05M *cis*-piperylene irradiated at the same time as the N-methyl-2-pyridone tubes. The relative amounts of conversion can be used to measure the quantum yield of intersystem crossing for N-methyl-2-pyridone.

Potassium ferrioxalate was more extensively used as an actinometer. In general, the method is the same as that of Hatchard and Parker[35] with some modifications.

The potassium ferrioxalate was prepared by diluting 3.0 ml of 0.2000M ferric ammoniumsulfate and 3.0 ml of 0.6000M potassium oxalate to 100 ml with 0.1N sulfuric acid. This solution was stored in the dark. Three milliliters of it were irradiated and 1 ml withdrawn and diluted along with 2 ml of 0.1% o-phenanthroline solution and 1 ml of the acetate/acetic acid buffer to 10.0 ml. The OD was then read at 510 nm on a Beckman DU Spectrophotometer. The intensity was calculated from the following formula:

$$I = \frac{(OD) \times F \times (V)}{\phi \times A \times t}$$

where I = intensity in ein/min

OD = optical density at 510 nm

V = volume of $K_3Fe(C_2O_4)_3$ solution irradiated in liters

ϕ = quantum yield--1.21 at 3660Å, 1.24 at 3130Å, 1.25 at 2537Å

A = amount of light absorbed (>0.999)

t = time of irradiation in min.

$$F = \frac{\text{Volume of dilution} \times 10^{-3}}{\text{Volume of aliquot} \times \varepsilon}$$

ε = 11,030

In irradiations carried out for long times, the lamp intensity was measured every four or five hours and the total lamp intensity measured by graphical integration. This method is also described by Vesley[34a] and Hyndman.[34b]

Analysis

Analysis for the bicyclic isomer, P, was carried out on a Loenco Model 160 or Model 70 gas chromatograph with flame ionization detection and a recorder equipped with disc chart integration. The column used was a 4 ft x 1/4 in, 20% Carbowax 20M on 60/80 Chromosorb G maintained at 120°C. Hexadecane was the internal standard.

N-methyl-2-pyridone was determined in two ways. First, the above column could be used if maintained at 180°C with 1-methylnaphthalene as an internal standard. This was added as a solution after irradiation. The preferred method of analysis however was by UV spectroscopy. After irradiation the tubes were opened and the solution diluted until the OD at 3200Å or 3300Å was between 0.2 and 0.7. This was then compared to samples which had not been irradiated. Each method seemed to give similar quantum yields but those measured by VPC had a larger experimental error.

Analysis for the *anti*-*trans* dimer D was done by reverse isotope dilution. The irradiated tubes, prepared with N-methyl(^{14}C)-2-pyridone, were opened and 2 ml of the solution added to a weighed amount of unlabeled dimer. This was shaken to insure homogeneity and then the solvent removed. The dimer was recrystallized from ethyl acetate and then a weighed amount placed in 15 ml of Bray's Solution and counted on the scintillation counter (Packard TriCarb). From this the quantum yields could be calculated.

Analysis for the other two dimers was carried out in a different fashion. Tubes, again prepared with labeled N-methyl-2-pyridone, were opened after irradiation and concentrated by evaporating the ethanol. The solution was streaked on thick silica gel chromatography plates and eluted with 20% methanol in ether. The plates were then placed in front of a UV light and the spots corresponding to the pyridone and the dimers scraped off and collected separately. The silica gel was added to 15 ml of Bray's Solution and again counted on the scintillation counter. A 1 ml aliquot of the solution from the tube was diluted and the amount of pyridone present measured by UV. This then served as the internal standard for the analysis.

To serve as a check, portions of the plate on which spots did not appear were scraped off and counted giving only slightly above the background count of 30 cpm. The spots gave counts from 200 to 10,000 cpm so it is believed that this method of analysis is quite dependable. The reproducibility was excellent.

Emission Studies

The phosphorescence of N-methyl-2-pyridone was measured at 77°K with the apparatus previously described.[31]

In order to check that N-methyl-2-pyridone will quench xanthone triplets, solutions were prepared with xanthone and N-methyl-2-pyridone in 3 mm od quartz tubes. The emission was observed at 77°K on an Aminco-Bowman Spectrofluorimeter. The excitation light used was such that essentially all of the light went into the xanthone.

All of the fluorescence quenching experiments were carried out on solutions prepared in a manner similar to that in the previous section. The solutions were placed in tubes and degassed. Originally true bore pyrex tubes were used but it was found that pyrex culture tubes were just as satisfactory. The relative fluorescence intensities were measured on the Aminco-Bowman Spectrofluorimeter.

The measurements of quantum yield of fluorescence at various concentrations of N-methyl-2-pyridone were carried out by Dr. Angelo A. Lamola at Bell Telephone Laboratories on an apparatus previously described.[36]

Fluorescence lifetimes were measured in two ways. Lifetimes of 20 nsec or longer could be measured on the TRW Model 31A Nanosecond Spectral System with a Model 32A Decay Time Computer, and RCA Type 931A photomultiplier tube and a Tektronix 556 oscilloscope with a 1A1 and a B plug in. For N-methyl-2-pyridone this method indicated a lifetime of less than 2 or 3 nsec so another method was tried. A compound with singlet energy lower than the pyridone can be used as a quencher and from the slope of the Stern-Volmer plot, a value of $k_q\tau$ can be obtained. In order to get a value for k_q, the same compound can be used to quench another whose lifetime is known. A value of k_q can be calculated and thus the lifetime of N-methyl-2-pyridone be found. This method requires that in both systems k_q is the same, but this appears to be a reasonable assumption. In this investigation d,l-camphorquinone was used as the quencher of the fluorescence of NM2P. This gave a Stern-Volmer plot which curved upward at high camphorquinone concentrations due to competitive absorption, but a value of $k_q\tau = 2.46\ M^{-1}$ was obtained at low camphorquinone concentration. Then the fluorescence of 2,3-benzofluorene was quenched to give a value of $k_q\tau = 325\ M^{-1}$. Since the fluorescence lifetime of 2,3-benzofluorene was measured independently as 33.9 nsec, the lifetime of NM2P could be calculated as 0.2 nsec.

Low Temperature Experiments

Several low temperature experiments were undertaken in an effort to observe intermediates. A solution of N-methyl-2-pyridone in EPA was placed in a quartz Beckman UV cell and cooled to 77°K in the low temperature Dewar of a Cary Model 14 Spectrophotometer. The UV spectrum was recorded and then the Dewar was placed in front of a 2500 watt, high pressure, mercury-xenon Hanovia lamp with a pyrex filter. After irradiation the spectrum was recorded again. Finally the sample was warmed, refrozen and the spectrum recorded a third time.

Dr. Orville L. Chapman performed some low temperature irradiations in which the IR was monitored. These were carried out in a cooled IR cell at room temperature, -80°C and -190°C through a pyrex filter, with an apparatus previously described.[19a]

Irradiation and monitoring the EPR signals were also carried out. Samples were prepared in EPA and degassed by five freeze-pump-thaw cycles with an oil diffusion pump in special thin-walled, quartz EPR tubes. These were then irradiated at 77°K with the same 2500 watt lamp as above focused on the sample in the cavity of the spectrometer, a Varian V4501A. After irradiation the spectrum was recorded. Finally the sample was warmed, recooled and the spectrum recorded again.

Flash Photolysis

Samples for flash-kinetic analysis were prepared as described previously[34,37] in cells 21 cm in length with quartz windows on the end. The degassing was carried out in a manner similar to that for the EPR experiments. The measurements were then made with the apparatus described by Herkstroeter,[37] but no transients whatsoever were seen at any wavelength checked (3488Å, 3660Å, 4358Å, 5000Å, and 5500Å).

Spectral Data

All UV spectra were recorded on a Cary Model 14 or a Beckman DU Spectrophotometer.

The NMR were done on a Varian A-60A or an HR-220. The IR spectra reported were measured on a Perkin-Elmer 257 Grating Infrared Spectrophotometer.

Isolation and Identification of Photoproducts

All of the preparative irradiations were carried out with a Hanovia 450 watt, medium pressure mercury lamp with a pyrex filter sleeve around the lamp. In some cases, test tubes of N-methyl-2-pyridone were taped to the cooling jacket and irradiated for a week. Every day the tube was removed and the solid dimer scraped from the walls. Irradiations of more dilute samples in ethanol were carried out in reactor vessels into which the cooling jacket fit. In these cases nitrogen gas was bubbled through the solution during irradiation.

The solid dimer was filtered off the solutions and recrystallized from ethyl acetate. This proved to be the 1,4-1,4 dimer, D; and its NMR, IR and UV spectra were identical to those previously reported.[1,3,4] It gave a wide melting range and reverted to monomer on melting as reported.

The bicyclic monomeric photoproduct, P, was isolated by column chromatography of the reaction mixture from which the solvent had been removed. The brown liquid was put on a silica gel column and on elution with 50% ether in ligroin, the product came off. The spectral data are consistent with those previously reported.[7]

The other two products were isolated by preparative TLC on silica gel using 20% methanol in ether as the developer. It was necessary to be very careful about overloading the plate because of a very poor separation. However finally a satisfactory separation was achieved and the bands were scraped off under UV light. The silica gel was then washed with methanol or acetone and the products obtained.

Dimer M showed the following NMR peaks ($CDCl_3$, TMS standard): 2.93 ppm and 3.00 ppm (singlets, 3 protons each); 3.42 ppm (multiplet, 1 proton); 3.52 ppm (multiplet, 2 protons); 4.45 ppm (triplet (broad), J = 8.5 cps, 1 proton); 4.80 ppm (doublet of doublets, J = 8.0 cps, J = 5.0 cps, 1 proton); 5.82 ppm (doublet (broad), J = 10 cps, 1 proton); 6.07 ppm (doublet, J = 8.0 cps, 1 proton); 6.48 ppm (doublet of doublets, J = 10.0 cps, J = 3.25 cps, 1 proton). The spectrum on the HR-220 was not helpful in resolving the multiplets enough to analyze the couplings. The IR showed a rather broad carbonyl band at 1662 cm^{-1} and another strong band at 1610 cm^{-1}. The UV showed a λ_{max} at 265 nm with $\varepsilon = 3530$. Molecular weight by mass spectrometry showed only the monomeric peak at 109.

With dimer T only an NMR could be obtained because only 1 mg was isolated. The NMR peaks were ($CDCl_3$, TMS standard): 2.98 ppm (singlet); 3.50 ppm to 4.40 ppm (multiplet); 5.70 ppm to 6.60 ppm (multiplet). These peaks are quite similar to those due to dimer D, however, because of the poor quality of the spectrum it was not possible to analyze the splittings.

The NMR spectra of dimers M and T are shown in Figures 17 and 18.

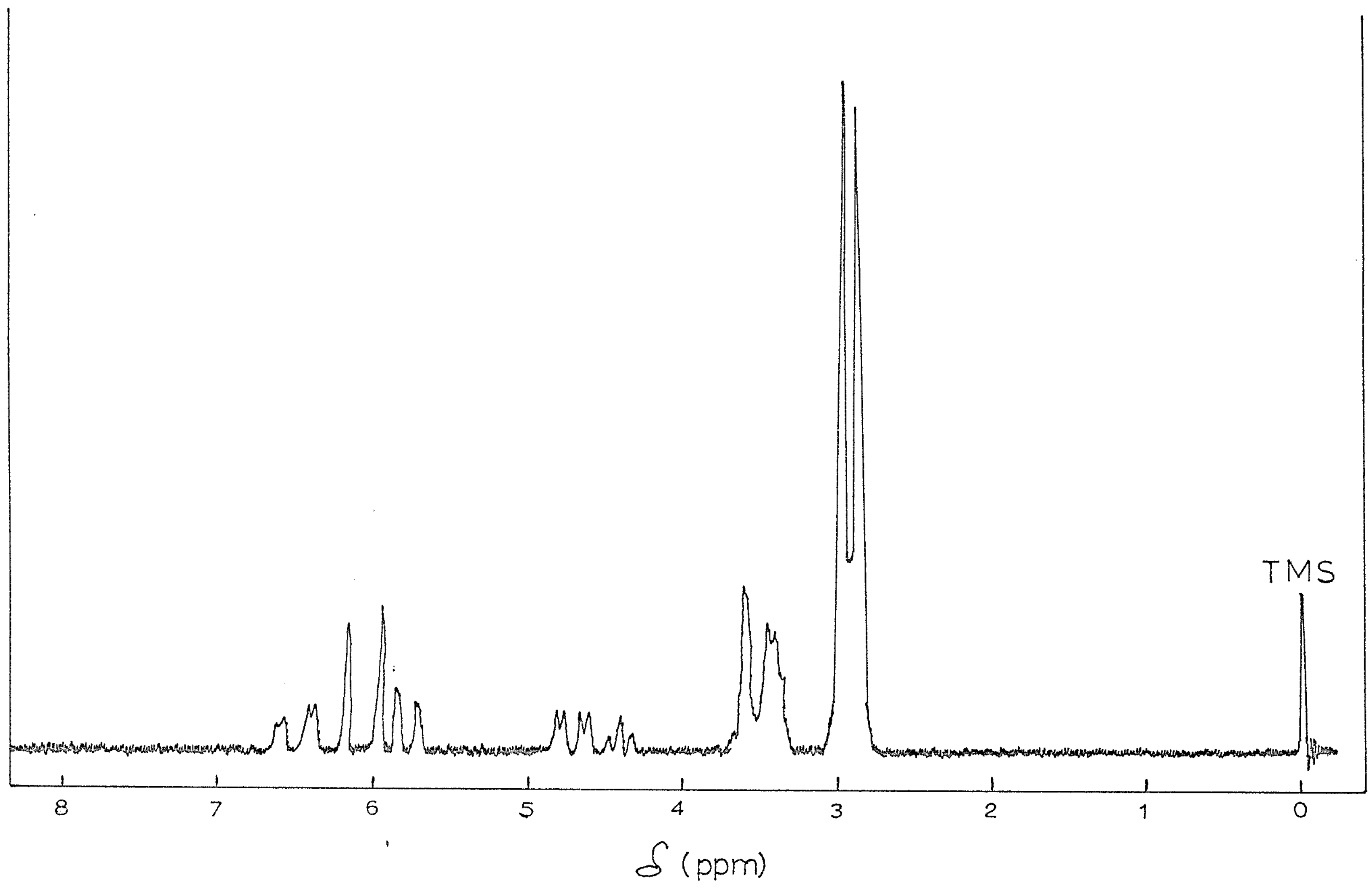


Figure 17. NMR Spectrum of Dimer M.

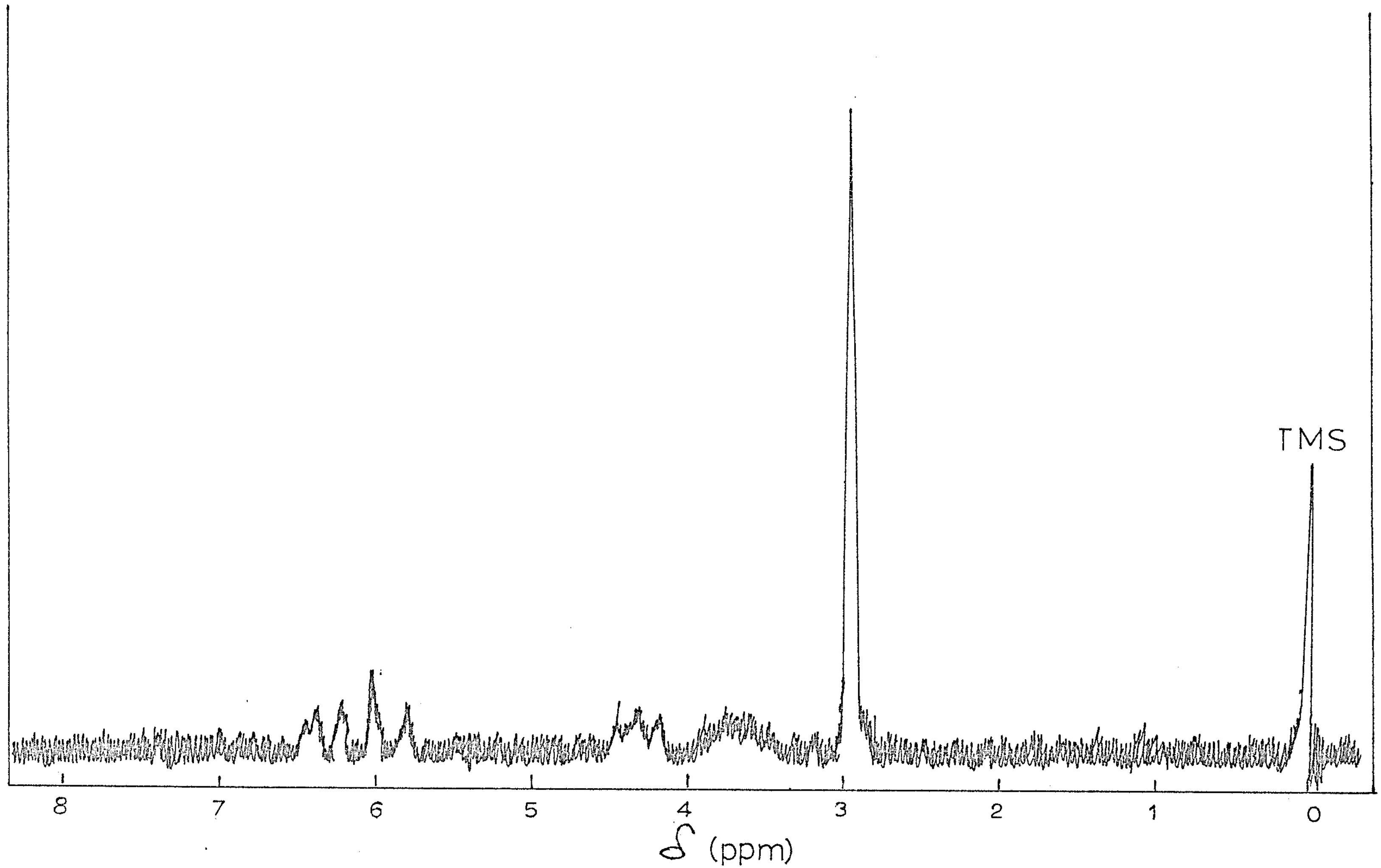


Figure 18. NMR Spectrum of Dimer T.

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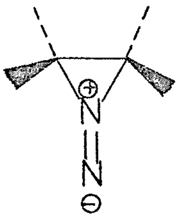
PROPOSITION I

It is proposed to prepare cis- and trans-1,2-diphenylethylene sulfides in order to study the stereospecificity of the thermal desulfurization as predicted by Woodward-Hoffmann Theory.

All of the common three-membered heterocyclic systems undergo reactions leading to cleavage of one of the carbon to hetero atom bonds, but only in the episulfides do both bonds cleave. (Now aziridines may be deaminated[1] using special reagents.) Many cases[2] of the thermal desulfurization of episulfides to give the corresponding olefin and elemental sulfur are known. These include styrene sulfide[2a], 3-acylthiopropylene sulfide[2b], 1-octene sulfide[2c], and many aryl substituted ethylene sulfides[2d]. Because of symmetric substitution, it was not possible to study the stereochemical course of the reaction.

One doubtful case of stereospecificity has been described. In a study of episulfide reactions, McGhie and co-workers[3] looked at the reduction of cis- and trans-epithiodicarboxylic acids with lithium aluminum hydride, and noted that only the carboxyl groups were reduced. However under more drastic conditions, the stereospecific cis and trans olefinic alcohols were obtained. Two possibilities exist: either the temperature increase caused the loss of sulfur or the reagents induced the loss of sulfur. This loss of sulfur due to nucleophilic attack has been observed in several cases.[3,4] The most well documented case[4] is the formation of olefins stereospecifically on treatment of cis- and trans-but-2-ene episulfide with phenyllithium or triethylphosphite. This has been shown not to occur through a two step loss of sulfur which proceeds faster than bond rotation. The exact nature of the intermediate has not been determined, but it is proposed to occur by attack on the sulfur with d-orbital participation.

Another feature of the proposed system is the chance to obtain more evidence concerning the predictability of the Woodward-Hoffmann rules for cycloadditions.[5] Recently it has been suggested[1] that perhaps they do not really apply to three-membered rings because of contradictory evidence. In studying the deamination of cis- and trans-2,3-butenimines with difluoramine, Freeman and Graham[1] noted that the stereochemistry was retained to the extent of 96% or more in both cases. Using the postulated intermediate (I), they predicted that the concerted elimination is not thermally allowed. In a similar study,[6] it was shown that the elimination of nitrous oxide from



(I)

N-nitrosoaziridines was stereoselective to better than 99% as predicted by the Woodward-Hoffmann Theory.

Two other examples are known, one which goes as predicted and one which does not. The elimination of sulfur dioxide from episulfones[7] is stereoselective and the elimination of [SO] from episulfoxides[8] leads to a mixture of olefins. Because of the apparent confusion more work needs to be done in this area. However in the systems where stereochemistry is preserved, it is possible to say that the elimination takes place in two steps which are faster than bond rotation leading to the observed products. Then the Woodward-Hoffmann rules would be redeemed because they only apply to concerted reactions.

In regard to predictions of episulfides, it is possible to do a Woodward-Hoffmann type calculation[5] and obtain the following correlation diagram (Figure 1). This would indicate that the concerted loss of sulfur should be forbidden thermally or that if the reaction goes thermally it will be a two step loss of sulfur leading to nonstereospecific olefins.

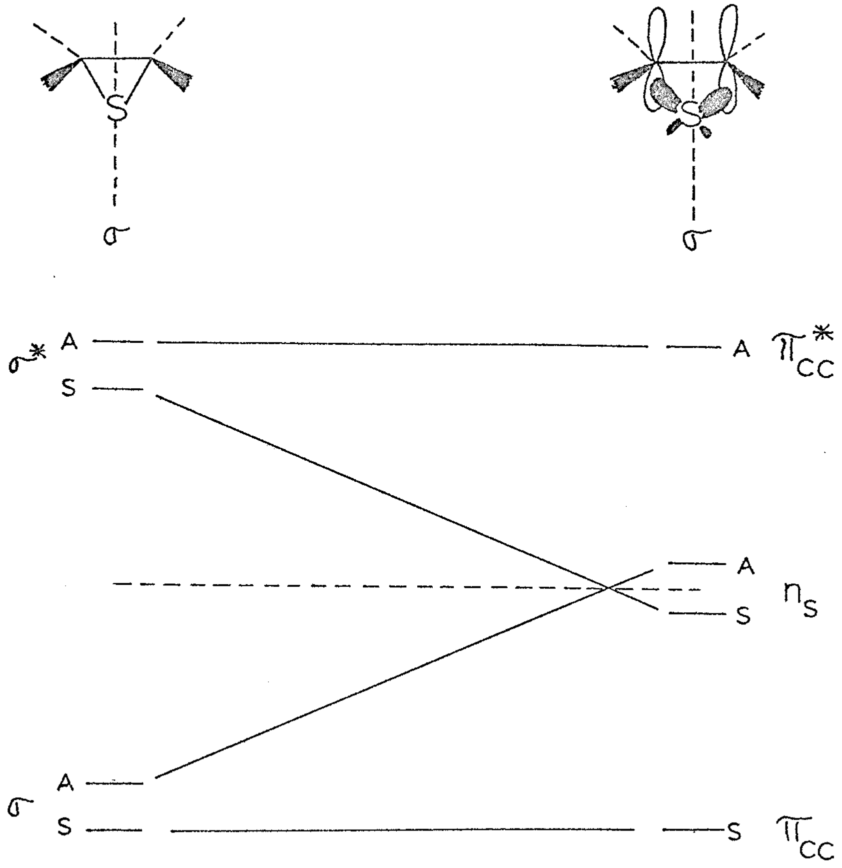
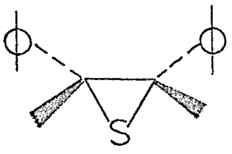


Figure 1

It is proposed that by synthesizing and studying the thermal decomposition of cis-(II) and trans-(III) 1,2-diphenylethylene sulfide, the mechanism of this



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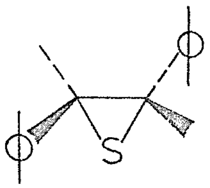
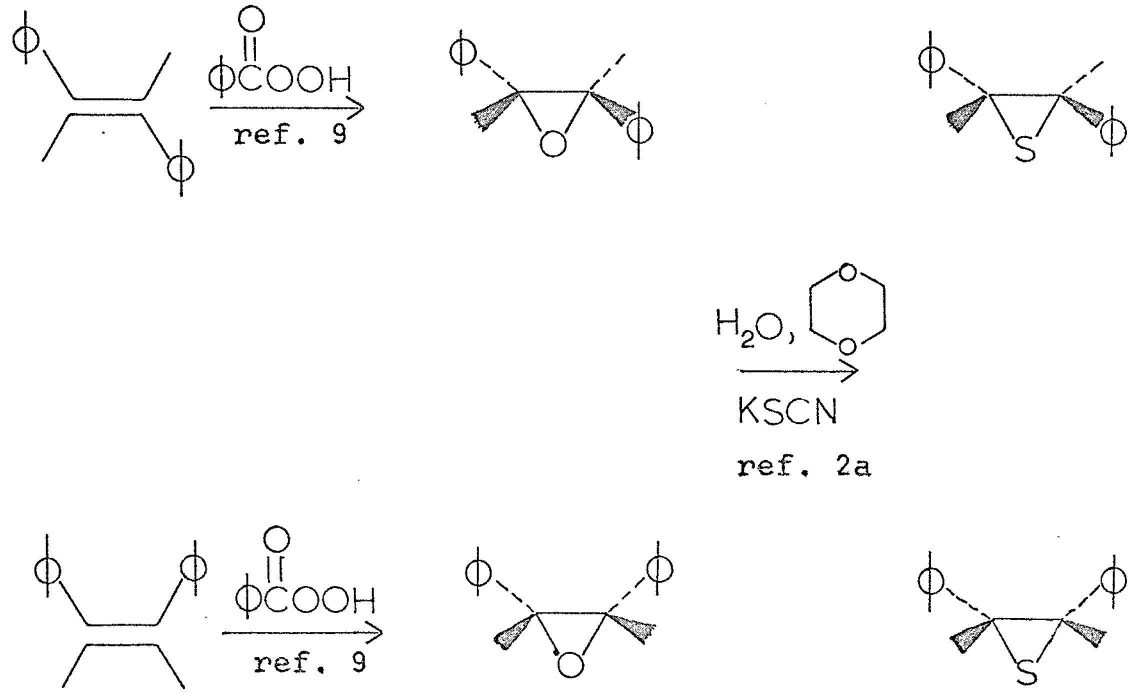


(III)

elimination can be elucidated. The preparation of these compounds can be effected by a series of reactions which have analogies in the literature. If a mixture of episulfides is obtained they should be easily separable by standard methods.



The thermal desulfurization can then be run by heating the compounds in clean glass tubes and analyzing the product olefins by vapor phase chromatography. It is necessary to stress clean because mineral acids and alkali seem to catalyze polymerization.[2d] However styrene has been obtained from styrene sulfide on distilling at 88°C (4mm);[2a] and, in this case, the stilbenes should be less susceptible to polymerization. The fact that a polymer (believed to be a sulfur containing chain) has been formed would tend to indicate a nonconcerted loss of sulfur has taken place to some extent. The temperature required for the desulfurization is hard to estimate, but it has been shown that aromatic ethylene sulfides part with their sulfur more readily than their aliphatic counterparts.[10]

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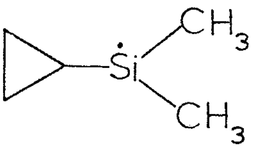
PROPOSITION II

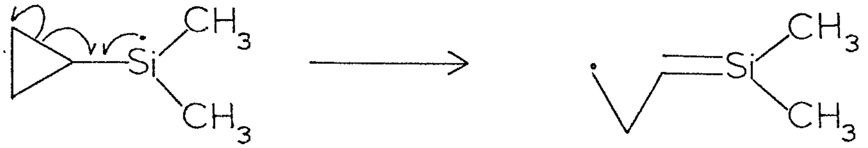
It is proposed that compounds of the type $Hg(Si(CH_3)_2CR_3)_2$ be prepared for an investigation of 1,2-migrations to silicon radicals from carbon.

In the past several years there has been an increasing interest in the reactions of silicon free radicals. However these consisted mainly of the bimolecular reactions of relatively simple radicals such as triphenylsilyl or trimethylsilyl. Several systems capable of 1,2-migrations have been reported, even though in these cases rearrangement would be improbable. Sakurai and co-workers,[1] in a study of the reactions of cyclopropyldimethylsilyl radicals, noted that the cyclopropyl group remained intact throughout the reaction. However this is not surprising since the radical formed (I) is the



(I)

silicon analog of the cyclopropylcarbinyl radical in which the cyclopropyl group undergoes ring opening but not ring expansion.[2] Ring opening in this case would require formation of a double bond to silicon to give an intermediate whose existence has been postulated but not proven. Also since silicon radicals are notoriously reactive toward oxygen-containing compounds,[3] they should react well with the di-t-butylperoxide initiator. Evidence for this is seen in the large amount of t-butoxy- and isopropoxycyclopropyldimethylsilane formed.



Two other reports[4] give an indication that silyl radicals are very reactive. On formation of the silyl radical from an optically active silane in the presence of carbontetrachloride, optically pure silylchloride of the same configuration was produced. This was best explained as due to the high reactivity of the silyl radical in abstracting a chlorine.

In a study of free radical disproportionation of aryl silanes, Nelson et al.[5] commented that no aryl migration was seen on treatment of benzyldimethylsilane with di-t-butylperoxide in the liquid phase at 160°C. Lack of migration can be due to the increased reactivity of the alkylsilyl radicals in fluid solution.

Other silyl radicals produced in various investigations[6] did not rearrange due to facile reaction paths available or perhaps due to hydrogen abstraction from the surroundings. Included are some gas phase investigations[6a,b] in which the possibility of migration was masked by the products obtained.

The stability of the carbon radical expected on migration is indicated by the work of Wilt and Kolewe.[7] In a search for migration from silicon to carbon radical in fluid solution, they explained the lack of rearrangement as due to an increase in stabilization of the carbon radical by the adjacent silicon or a lack of the "push-pull" effect present in ionic rearrangement from silicon to carbon. Another possibility would be increased strain in the transition state for rearrangement. In any case the α-silyl carbon radical does not show the same proclivity to rearrange as the corresponding carbon system.

Some migrations in related systems[8] are known and these only seem to occur at high temperatures under specific conditions. Recently a novel migration of phenyl from carbon to silicon was found to occur[9] on thermolysis of benzyldimethylsilane at 450°C. These appear to be the proper conditions for the production of silyl radicals but added hydrosilanes had no effect whatsoever on the reaction. This would tend to rule out a radical mechanism and one must imagine a concerted rearrangement of some sort. In this same investigation, 1,4-migrations of phenyl groups were also observed to occur at high temperatures, whereas previously the same compounds were inert to rearrangement in fluid solution in the presence of peroxides. This might indicate a large activation energy necessary for rearrangement.

The proposed compounds should help clear the confusion surrounding 1,2-migrations to silicon radicals from carbon. Recently the disilylmercury compounds[10] have been synthesized and shown to be a source of free radicals through photolysis.[10b,11] The proposed compounds should be obtainable through a series of reactions which have analogies in the literature.[10,12]

SYNTHESIS

$$\phi_3CBr \xrightarrow[\text{ether}]{\text{Mg}} \phi_3CMgBr \xrightarrow[(CH_3)_2SiClH]{}$$

$$(CH_3)_2SiHC\phi_3 \xrightarrow{(\phi CH_2)_2Hg} Hg(Si(CH_3)_2C\phi_3)_2$$

$$\phi_3CMgBr + (CH_3)_2SiCl_2 \longrightarrow$$

$$(CH_3)_2SiClC\phi_3 \xrightarrow{\text{Na/Hg}} Hg(Si(CH_3)_2C\phi_3)_2$$

A similar sequence can be used for the t-butyl derivative simply by starting with the corresponding Grignard.

The decomposition of these compounds can be effected in several ways.[9] In the gas phase or in solution they are decomposed both by light and by heat. There is some question as to the actual value of the thermal reaction due to an increased bimolecular reaction not going through radicals.[13] However photolysis seems to avoid this problem and leads almost exclusively to radical derived products.

It is convenient that similar silylmercury compounds can be sublimed[10a] at relatively low temperatures in vacuo, making a gas phase decomposition possible. From previous experimental evidence, a high temperature gas phase decomposition would appear to be the most advantageous because of decreased bimolecular encounters and an increase in higher activation processes. This can be accomplished using flow systems in which a carrier gas blows over the sample, through the reaction vessel and into a source of abstractable hydrogen, or perhaps just by irradiating the mercury compound in the gas phase in sealed tubes. Two possible schemes of reaction are shown in Figure 1. Some care must be taken in interpreting the results. Silicon radicals are known to abstract aryl groups[5] and the appearance of a phenyl attached to a

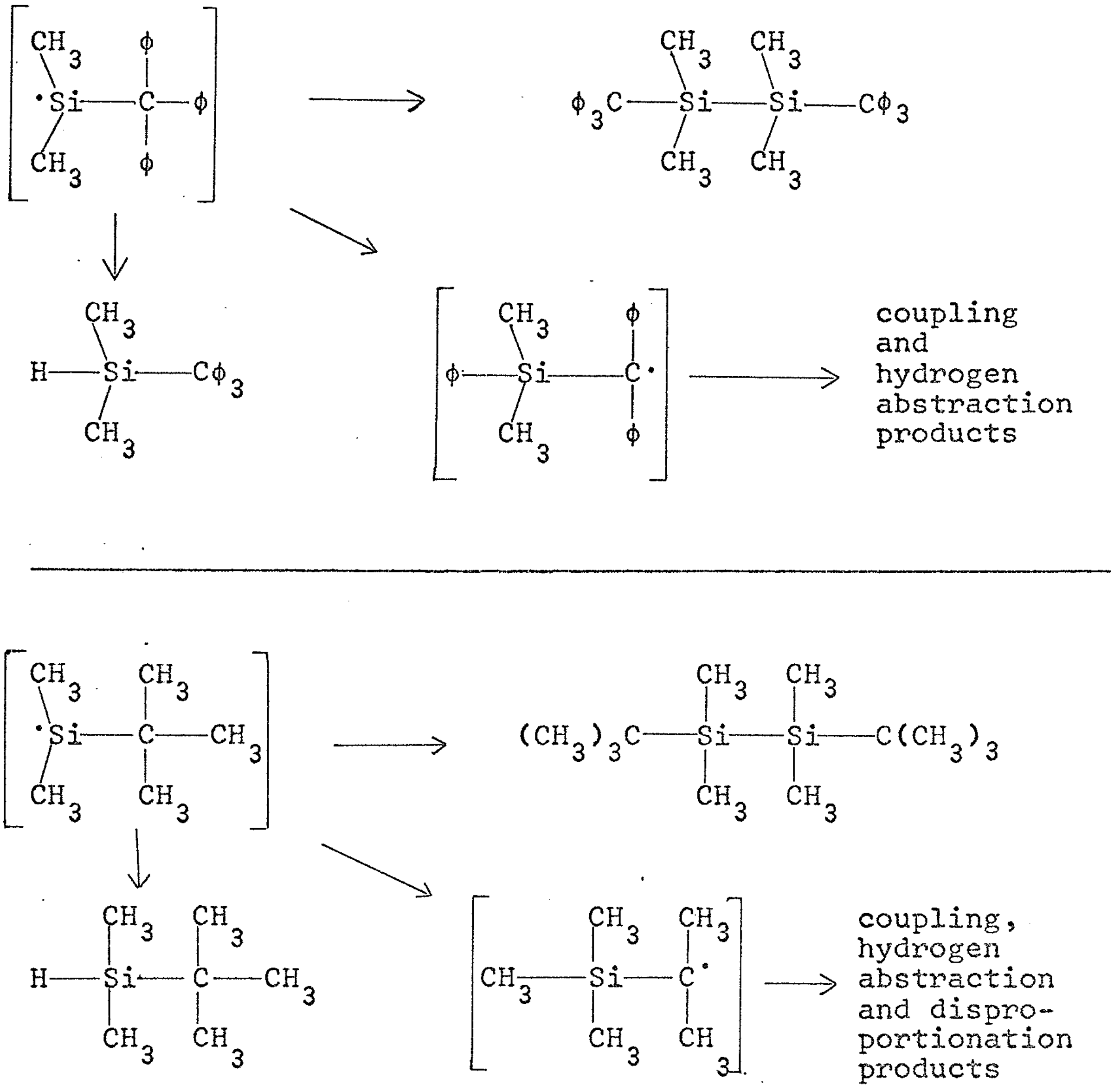


Figure 1

silicon could arise in this manner. This product would be expected to be pressure dependent though, and a detailed study may be necessary to confirm the migration step. With the alkylsilyl radical system this problem is considerably alleviated because silyl radicals apparently do not abstract alkyl groups. The parent radical is not expected to decompose to the unsaturated silicon compound and triphenylmethyl radical so this removes one of the obvious reactions present in the carbon systems. It would also be interesting to try this reaction in the liquid phase although here complications due to increased interactions may obscure the desired products.

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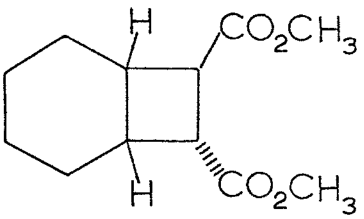
PROPOSITION III

It is proposed that the photosensitized isomerization of diethylfumarate and diethylmaleate be reinvestigated in an effort to elucidate the complex mechanism.

In the detailed study of photochemical cis-trans isomerization, Hammond et al.[1] investigated the photosensitized isomerization of the maleate-fumarate system. In general, this was explainable in a manner similar to the stilbenes and α-methylstilbenes. There seemed to be some nonvertical energy transfer from the sensitizers which had spectroscopic triplets lower than the olefin spectroscopic triplets. Two things, however, appeared to be different. First, there was no "high energy" group of sensitizers which would transfer triplet energy equally efficiently to either isomer, thus resulting in a $[\text{cis}]_{ss}/[\text{trans}]_{ss}$ independent of triplet energy. Second, sensitizers with triplet energies below 59 kcal/mole did not effect isomerization at appreciable rates. The first was explained in that the estimated spectroscopic triplet energy of maleate was between 72 and 77 kcal, and, from previous work,[1] it had been seen that the "high energy" ratio was only obtained by sensitizers with triplet energies 4 to 5 kcal above the highest spectroscopic triplet of the olefins. Since xanthone (E_T = 74.2 kcal/mole) was the highest energy sensitizer used, the 4 to 5 kcal excess was probably not achieved. Although it was not explicitly stated, the second could be explained in that the rate of isomerization goes down with decreasing triplet energy[2]; and it might be that in this case the energy had decreased to such a point to make the isomerization proceed very slowly.

With these data and the explanations in hand, it was quite interesting to note the work of de Mayo.[3] In an effort to elucidate the mechanism of the maleate-cyclohexene cycloaddition, the use of photosensitizers was employed to effect a triplet reaction. The photosensitizers ranged in triplet energy from 84 kcal to 40 kcal; and the addition process proceeded with approximately the same rate in each case. By looking at the ratios of the products formed (I, II, III, IV) no change whatsoever appeared with the different sensitizers.



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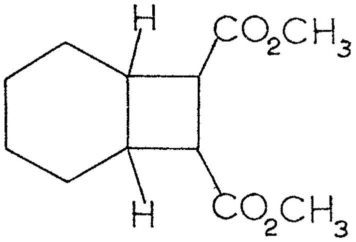

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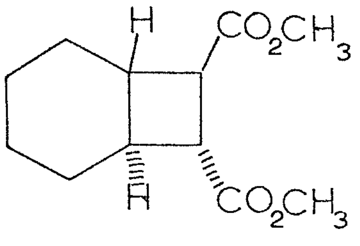

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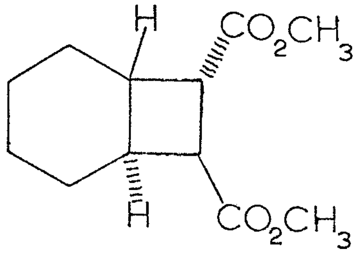

(IV)

In an effort to reconcile the existing data, Sahyun[4] proceeded with a study of the maleate-fumarate photoisomerization emphasizing the effects of low energy sensitizers. Table I lists the sensitizers used and their triplet energies along with quantum yields measured. In retrospect however some of the sensitizers used seem to be of dubious character. It has been shown[5] that 1,2-diketones, halogenated aromatics and quinones are poor sensitizers to use because of possible radical formation on excitation and consequent interaction with the surroundings producing false photostationary states. Neglecting these sensitizers it is still possible to see that for the low energy sensitizers a measurable Φ_{t-c} is obtained under certain conditions. Several other problems come from Sahyun's data. There appears to be an anomalous oxygen effect; in some cases the quantum yields are enhanced by oxygen and in others they are diminished. A wavelength dependence is present (though

TABLE I

Sensitizer	E_T (kcal/mole)	Φ_{t-c} (sen.)
Anthraquinone	61	0.42 (3660 Å)
		0.24 (3130 Å)
Naphthoquinone	57	0.02 (3660 Å)
		0.04 (3130 Å)
Fluorenone	53	0.00 (3660 Å)
		0.02 (3130 Å)
Duroquinone	51	0.00 (3660 Å)
		0.30 (3130 Å)
Pyrene	48	0.016 (3660 Å)
		0.02 (3130 Å)
Benzanthrone	46	0.00 (3660 Å)
		0.01 (3130 Å)

there is some question as to the validity of corrections made for direct isomerization at 3130 Å). Also pyrene fluorescence and pyrene excimer fluorescence were quenched by the olefins.

In a recent investigation of the formation of oxetanes between acetone and dimethylmaleate or dimethylfumarate, Albone[6] commented that, while the maleate to fumarate isomerization could be sensitized by acetone, the reverse could not be sensitized.

The basis of the proposed study will be to separate the isomerizations into their various energetic pathways; that is, instead of looking at the quantum yields of isomerization and the photostationary state ratios, looking at the triplet energy transfer and the singlet sensitization separately in an effort to deduce something about the mechanism.

Perhaps the first investigation should be for the presence of complex formation between the olefins and the sensitizers, both in the ground state and in the excited state. Charge transfer complexes of maleic anhydride and maleic or fumaric nitrile have been observed[7] although a complex with dimethylmaleate has not. Similarly a complex between diethylfumarate and cyclohexene was seen in another case.[3] These complexes usually appear in the UV spectrum as a broad or intense band at wavelengths longer than the absorption of either species. Cases of charge transfer complexes with the sensitizers are not known for this system, but it could cause some unusual photochemical results. Likewise, complexes formed in the excited state (so-called exciplexes) could play havoc with the photochemical system. They also are usually seen as shifted or new emission bands.

With these possibilities, it is necessary to scrutinize the absorption and emission spectra of mixtures of the olefins and sensitizers in an effort to detect the presence of complex formation. Another possible means of detection would be through the use of emission decay curves. If the complexes cause only a slight change in the uncomplexed spectra, it may be difficult to say anything about their presence. The decay curves may be used in an effort to detect nonexponential decay attributable to some complex of a different radiative lifetime.

Herkstroeter developed flash spectroscopic techniques[2] as a means of studying the photosensitized isomerization of the stilbenes and α-methylstilbenes. By looking at the decay of the triplet states of the sensitizers, it was possible to measure the rate constant for quenching of the triplet sensitizers by the olefins. This method is extremely useful because triplet quenching can be observed irregardless (a detectable concentration of triplets must be produced) of quenching in the singlet state of the sensitizer. A k_q (rate constant for quenching of sensitizer triplets) near to diffusion controlled is expected for sensitizers with triplet energy 4 or 5 kcal above the olefin. Then as the sensitizer energy drops there should be a simultaneous drop in k_q until quenching by the olefin becomes no longer competitive with other modes of deactivation of the sensitizer. This is one good method of separating the energy transfer processes.

A detailed look at the quenching of sensitizer singlet states is available by observing the quenching of sensitizer fluorescence by the olefins or by looking at the decrease in fluorescence lifetimes with increasing olefin concentration. Since many of the sensitizers used in the previous studies did fluoresce and fluorescence quenching by dienes[9] was relatively unknown at that time, this was neglected. Now however some cases of reactions taking place by "nonclassical" singlet sensitization are known[10] and this could be an important contribution to the maleate-fumarate interconversion.

It should be possible to measure the quantum yields of interconversion and the photostationary state ratios under conditions where either the triplet sensitization or singlet sensitization is dominant and have some confidence in ascribing meaning to these numbers. The analytical procedures in measuring the olefin concentrations should be essentially the same as in reference 1.

Sahyun's study brought out several important features which will have to be investigated in the light of the aforementioned experiments. Both a wavelength dependence and a sensitizer concentration dependence are present. The wavelength dependence and the fact that in many cases 3660 Å light did not effect isomerization could explain Lamola's claim.[1] An interesting possibility would be increased intersystem crossing from the higher excited singlet states of the sensitizers. However, before much speculation Sahyun's numbers should be rechecked because of the rather large uncertainties. A sensitizer concentration dependence in the stilbenes was attributed to reverse energy transfer which might also be operative in this case.

The maleate-fumarate conversion process is very complex and much work will be required to resolve the existing confusion.

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PROPOSITION IV

It is proposed that the high energy radiation chemistry of Cr(III) complexes be investigated in an effort to observe ligand substitution reactions.

Although extensive work[1] has been carried out on the photochemistry of transition metal complexes, very little is known of their reactions on excitation with high energy radiation in the liquid phase. Co(III) complexes have been most often studied[2] and appear to undergo redox reactions yielding Co(II) and the oxidized ligand. These reactions can be summarized below:

$$[\mathrm{Co\ en_2\ F_2}]\ \mathrm{NO_2} \xrightarrow{\gamma} \mathrm{Co(II)} + \mathrm{NH_3} + \mathrm{CO_2}$$

$$[\mathrm{Co\ en_3}]\ \mathrm{Cl_3} \xrightarrow{\gamma} \mathrm{Co(II)} + \text{fragmentation products}$$

$$\mathrm{Co(III)\text{-}EDTA} \xrightarrow{\gamma} \mathrm{Co(II)\text{-}EDTA'}$$

EDTA' = degraded EDTA

The photoreactions of Co(III) complexes are similar to this and thus might be proceeding through the same intermediates. It is now known that in organic systems a correlation[3] between photochemical and radiation chemical transformations can be observed and the same situation might be occurring in the inorganic systems. However in most of these cases it has not been possible to rule out radical induced redox reactions which might yield similar products, but be distinctly different from the photoreactions. In fact in the case of the Co(III)-EDTA complex,[2c] the mechanism is proposed as proceeding by way of H· or ·OH attack on the EDTA.

A few obscure reports of ligand substitution reactions on γ-irradiation are known. Two groups[4] reported the aquation of ferrocyanide ion. However ferricyanide ion yielded only reduced products under the same conditions. Likewise the γ-irradiation of sodium nitroprusside[5] proceeded to aqueous ferric ions presumably through interaction with excited water molecules.

One group[6] also reported on the γ-irradiation of halopentaammine Co(III) complexes in which the halide is replaced by H_2O. They report that this is similar to the photoreactions of the same compounds which can also be photoreduced on ultraviolet irradiation.[1]

Chromium(III) complexes seem to be the most suitable for several reasons. They appear to give almost exclusively ligand substitution products on photoexcitation;[1] they are easily obtained; and they are reasonably stable to thermal reactions.[1b] Both $Cr(NH_3)_6^{+3}$ and $Cr(CN)_6^{-3}$ appear to be quite labile to aquation on irradiation in any of the ligand field bands. These could be irradiated in aqueous solution similar to the photosystems and the reaction followed spectrophotometrically or chemically as done before.[1a]

It might also be interesting to examine the reactions of $Cr(CO)_6$ which also undergoes photosubstitution reactions.[1c] However in this case, nonaqueous solvents must be used. The reaction can be carried out in pyridine to yield $Cr(CO)_5(py)$ complexes or it could be carried out in nonbasic solvents with bases added as solutes. In this way it will be possible to know the G of excited state formation in the solvent and then get some idea of possible energy transfer to the complex.

The aqueous systems might be useful in obtaining values for $G(H_2O^*)$, which has only been estimated before. By using the proper quenchers for radical and ionic species, it might be shown that the reactions of the complexes are due to interaction with excited water molecules. Some Cr(III) complexes[1b] are known to quench triplet states but whether this is due to energy transfer is not certain.

All of the experimental procedures would be similar to those for the photochemical investigations and need not be elaborated here. Other possibilities for investigation include the use of less energetic radiation and the observation of redox reactions of Cr(III) complexes which are rare in their photochemistry.

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PROPOSITION V

It is proposed that through the use of a nanosecond flash photolysis apparatus the nature of excimers may be more completely studied.

Although excimers and exciplexes now seem to play an important role[1] in many photochemical and photobiological systems, the only direct evidence for them is their fluorescence. In many systems because of a lack of emission, their existence can only be postulated. Likewise very little is known of their higher excited states and their modes of decay.

The development of new flash spectroscopic techniques employing lasers has enabled Windsor[2] to investigate species existing for only nanoseconds. A complete description of the apparatus is available in reference 2, but a more condensed version is given below. The light source is a Q switched ruby laser of wavelength 694 nm. The beam is passed through a KH_2PO_4 crystal frequency doubler and the beam split by a prism. The 347 nm line is used as the primary excitation beam, with the 694 nm line being focused on a gas cell. By selecting the proper type of gas, a spark is produced which serves as the second, analyzing flash. The duration of the spark and the time delay are dependent on the type of gas employed.

After the beams have passed through the samples they enter a spectrograph or in the case of flash kinetics a TRW image converter camera. Using these techniques Windsor was able to measure $S_1 \longrightarrow S_n$ absorption spectra and to observe intersystem crossing. With newer techniques it should be possible to observe species in the picosecond range.

This then might prove to be a powerful tool in studying excimers in solution. Heretofore the intermediacy of excimers could only be postulated in many systems. It should now be possible to observe them directly by use of their $S_1 \longrightarrow S_n$ absorption. This would become as valuable for excimers as standard flash photolysis is for triplet states and radical species. Some reactions with proposed excimers which could be investigated are: a) the dimerization of thymine;[3] b) the photodimerization of acenaphthylene;[4] and c) the photodimerization of 2-alkoxynaphthalenes.[5]

However before one can undertake this, a more detailed investigation into $S_1 \longrightarrow S_n$ absorption in simple excimers must be carried out. Ferguson[6] and Chandross[7] prepared "sandwich dimers" of aromatic hydrocarbons in rigid matrices by controlled heating and recooling[6] or by photosplitting anthracene dimers.[7] The species produced then exhibited an excimer type emission, although not in every case identical with that reported in solution.

The absorption spectra were also measured showing the existence of two bands. These were then used[7] to distinguish two different theories. However this method suffered in that a geometry was forced on the two molecules, and it is not certain that this is the same as expected of excimers in fluid solution. Another group,[8] in attempting to measure the fluorescence decay times of dimers produced in the same manner, observed a strange fluorescence excitation spectrum which was ascribed to absorption into a higher excited state.

In many of the theoretical treatments of excimers,[1,9] energy levels for higher excited states of excimers were calculated although the papers dealt with explaining the luminescence. The most successful explanations appear to come from a configuration interaction of charge-transfer states with molecular exciton states derived from the ^1L_b or ^1L_a states of the aromatic hydrocarbon. However calculations[10] employing the exciton states derived from the ^1B_b states have also been shown to predict bound excimer states for some aromatic hydrocarbons.

In studying the nanosecond pulse radiolysis of liquid benzene and toluene, Cooper and Thomas[11] observed a fluorescence and transient absorption which was assigned as $S_1 \rightarrow S_n$ of monomer benzene. In a second paper, Birks[12] proposed that this was not absorption due to monomer benzene but actually excimer benzene. This was because of the short lifetime of the transient and because the emission was observed in the excimer region. Recently, a new investigation[13] employing nanosecond flash photolysis techniques observed the same transient but at a concentration of 0.1 M where benzene shows little or no excimer emission. The absorption corresponds closely to what would be expected for the $^1E_{1u} \leftarrow {}^1B_{2u}$ absorption in benzene. Since the data seem to fit each assignment equally well, it is possible that each group is observing different species. However before a conclusive assignment can be made a more detailed investigation must be carried out to determine the nature of the absorbing species.

With the apparent $S_1 \rightarrow S_n$ absorption observed and the theoretical calculations,[9,10] a thorough investigation for higher excited states of excimers by flash photolysis seems likely to yield more data concerning this elusive species. The advantage of this method over the low temperature approach is that excimers can be studied in fluid solution in which all conditions would be "natural". Development of the techniques using fluorescent excimers would aid in investigations involving nonfluorescent excimers which were proposed earlier.

These techniques, along with standard flash spectroscopy, could also help in dealing with the question of triplet excimers[1] and intersystem crossing in excimers.

Very little data are available on triplet excimers, perhaps because of their fast radiationless decay at room temperature. In any case it might be possible to observe T—T absorption in fluid solution due to excimers. Chandross[7b] reported a very marked heavy atom effect on the ratio of monomer to excimer fluorescence indicating an induced intersystem crossing. Likewise O_2 quenching of excimer emission in solution has been reported.[14] It should be possible to study intersystem crossing by observing a decrease in singlet excimer and an increase in triplet excimer using the fast time scale of the flash apparatus.

The experimental difficulties may be quite great. It may be very difficult to pick out excimer absorptions from among those due to monomer as in the benzene case so concentration studies will have to be undertaken. In most cases the lifetimes of excimer emissions[8] are greater than the corresponding monomer emissions, so short lifetimes should not present a problem. It is very difficult to predict the outcome of these investigations because of the many variables present.

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