STUDIES OF PHOTOCHEMICAL AND PHOTOPHYSICAL PROCESSES

I. THE PHOTOCHEMISTRY OF 3-METHYL-1-PHENOXYBUT-2-ENE

II. THE ROLE OF CHARGE TRANSFER INTERACTIONS IN THE QUENCHING OF 1,4-DIMETHOXYBENZENE FLUORESCENCE

III. A NEW METHOD FOR THE DETERMINATION OF INTERSYSTEM CROSSING QUANTUM YIELDS

Thesis by

Felix Alvin Carroll, Jr.

In Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

1973

(Submitted August 3, 1972)

ACKNOWLEDGMENTS

I express sincere appreciation to Professor George S. Hammond for guidance and encouragement throughout the course of this work. He has been more than a research director alone. The atmosphere of independent, and interdependent, investigation which has characterized the Hammond group is a direct result of his unique approach to research. It has been a real pleasure to be associated with him and with the many people who have been a part of this group during the past three years.

Dr. M. T. McCall, Dr. R. G. Weiss, and Mr. F. H. Quina deserve special thanks for invaluable assistance, suggestions, and constructive criticism at many stages of the studies reported in this thesis. Much of the work in Part II was done in collaboration with McCall, and Quina made direct and vital contributions to the work described in Part III. I also thank Quina and Dr. D. J. MacGregor for constructive criticism of the manuscript of this thesis.

I acknowledge the National Science Foundation (Predoctoral Fellowship) and the California Institute of Technology (Supplementary Teaching Assistantships) for financial support.

TABLE OF CONTENTS

PART I.

PART II.

PART III.

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

PART I

The photochemical reactions 3-methyl-1-phenoxybut-2-ene (8) have been investigated in solution and in the gas phase. Irradiation of 8 results in the formation of phenol (9), 3-methyl-3-phenoxybutene (10), 1-(2-hydroxyphenyl)-3-methylbut-2-ene (11), 1-(4-hydroxyphenyl)-3-methylbut-2-ene (12), 3-(2-hydroxyphenyl)-3-methylbutene (13), and 3-(4-hydroxyphenyl)-3-methylbutene (14). Formation of 10-14 in the gas phase is efficiently quenched by nitric oxide. The results suggest that all products are formed by a dissociation-radical recombination mechanism and that none are formed by concerted processes. The absorption spectrum of 8 and its quantum yields of photochemical reaction and fluorescence are used to estimate the rates of the processes which deactivate its lowest-lying excited singlet state. The results suggest that O-C bond homolysis need not occur *via* intersystem crossing from an $S_1(\pi,\pi^*)$ to a $^3\sigma$(C-O) state. Fragmentation to radicals, and perhaps nonradiative decay without chemical reaction, probably involves excitation to high vibrational levels of the C-O bond. Weak electronic interaction between the aromatic and olefinic chromophores may also be important.

PART II

The fluorescence of 1,4-dimethoxybenzene (DMB) in acetonitrile is quenched by a number of organic compounds having lowest-lying excited singlets higher in energy than that of DMB. The rate constants show a structure-reactivity pattern which implicates charge transfer as an integral process, but they do not agree qualitatively with rate constants predicted from a kinetic formulation involving the intermediacy of radical ion pairs. The results suggest that charge transfer provides the binding energy of the exciplex, while the internal conversion of electronic excitation involves a vibronic mechanism which depends primarily on the type of quencher (organic chloride, acetate, or mesylate) and not on its reduction potential.

PART III

A method is described for the determination of intersystem crossing quantum yields which is especially useful for benzene derivatives. The experimental procedure involves measurement of relative fluorescence intensities of the aromatic compound and relative yields of isomerization of a "triplet counter" in solutions with varying concentrations of a heavy atom fluorescence quencher such as xenon. Intersystem crossing quantum yields for anisole, mesitylene, and toluene in isooctane solution are 0.74, 0.60, and 0.52, respectively.

ABSTRACTS OF PROPOSITIONS

Proposition I

It is proposed that a study of the quenching of naphthalene fluorescence by stereochemically labelled bicyclobutanes could give insight into the radiationless decay processes in fluorescence quenching interactions.

Proposition II

It is proposed that trialkylboranes could quench the fluorescence of electronically excited aromatic hydrocarbons by a charge transfer interaction in which the electronically excited aromatic molecule is the electron donor and the trialkylborane is the electron acceptor.

Proposition III

Experiments are proposed to elucidate the pathways of phenyl ester decomposition reactions.

Proposition IV

A set of experiments is proposed to elucidate the structures of the products obtained by reduction of porphyrins with metal ions in aqueous solution.

Proposition V

It is proposed that the ring-contracted intermediate suggested for photochemical rearrangements of 2-arylthiophenes could be trapped with alkyl Grignard reagents.

PART I

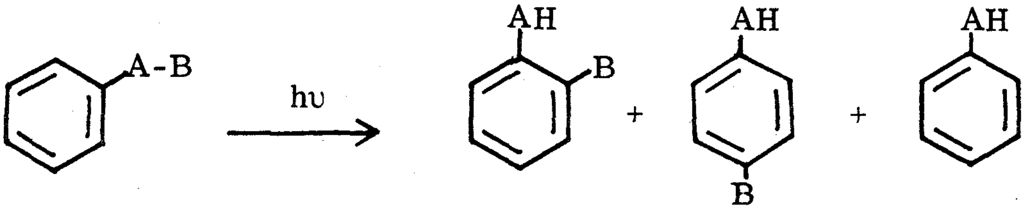
The Photochemistry of

3-Methyl-1-phenoxybut-2-ene

INTRODUCTION

The first reports of the photochemical rearrangement of aryl esters to *o*- and *p*-hydroxyarylphenones by Kobsa (1) and by Anderson and Reese (2) introduced an active area of photochemical research. Reactions formally analogous to that of phenyl acetate have since been observed upon irradiation of acetanilide (3), phenoxyacetic acids (4), allyl aryl ethers (4-6), diaryl ethers (7), aryloxyacetones (8), alkyl benzyl ketones (9), acetylsalicylic acid (10), benzyl enol ethers (11), benzhydryl- and benzylamines (12), α-benzyloxystyrenes (13), alkyl phenyl carbonates (14), and arenesulfonanilides (15). The reactions may all be illustrated by the generalized reaction scheme below:

Scheme I



1 **2** **3** **4**

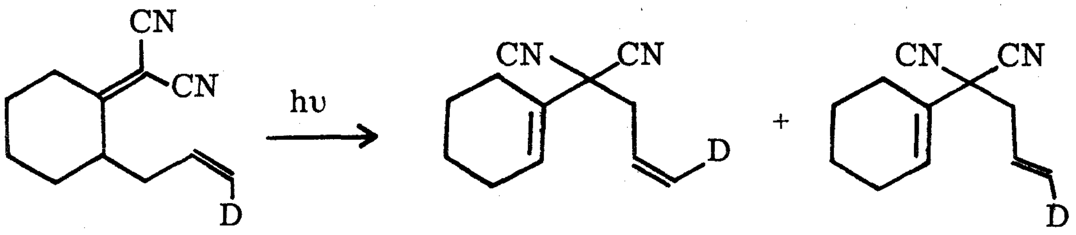
The observation that **4** (*e.g.*, phenol when the reactant is phenyl acetate) is usually a reaction product suggests that at least some electronically excited molecules decay through pathways involving A-B bond dissociation. The nature of the steps leading to the formation of **2** and **3** has been the subject of controversy for almost a decade.

Kobsa (1) suggested that a bond homolysis--radical recombination mechanism was sufficient to account for all of the observed products. Anderson and Reese, however, preferred bridged biradicals as intermediates (16). Because of the steric requirements of such species, Trecker and coworkers (17) discounted this model and suggested concerted photochemical sigmatropic rearrangements for the formation of the ortho and para products. Such pathways are "allowed" by the "Woodward-Hoffmann rules" (17).

To determine which mechanism operates, Meyer and Hammond investigated the photochemical reactions of phenyl acetate in a gas phase flow system (18). They found essentially no _o_- or _p_-hydroxyacetophenones; products isolated from the photolysis were attributable to recombination reactions of phenoxy and methyl radicals--the latter being formed by decarbonylation of the acyl radical. These results suggested that the bond dissociation pathway was the only one operating in the gas phase and strongly implicated it as the predominant pathway in solution.

The reactions analogous to phenyl acetate listed above have been less exhaustively investigated. While bond dissociation--radical recombination pathways have been suggested for many of them, there is _a priori_ no reason why concerted sigmatropic rearrangements could not be operating, either wholly or in part, for some of these reactions.

The existence of concerted photochemical rearrangements in some systems has been established. Woodward and Hoffmann have discussed numerous examples in their papers on orbital symmetry control of reaction pathways (19). One pertinent example is the series of photochemical [1, 7]-sigmatropic hydrogen shifts seen among the isomers of 1, 4-di(cycloheptatrienyl)-benzene (20). A concerted [1, 3]-sigmatropic rearrangement has also been seen in the rearrangement of 5 to 6 and 7 (21).



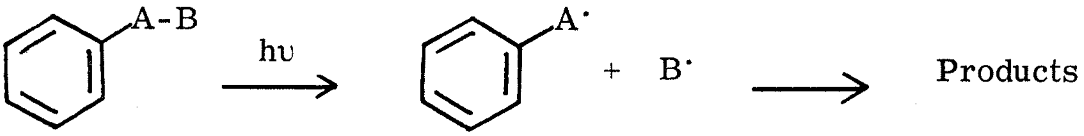
5 6 7

In spite of the cis, trans isomerization about the deuterium-substituted olefin function, the total lack of inversion of the migrating deuterioallyl group indicated strongly that bond cleavage to allyl radicals, followed by recombination, was not the course of the reaction. This reaction suggests that other concerted photochemical reactions might occur.

The question as to whether the photochemical analog of the Claisen rearrangement (the thermal rearrangement of allyl phenyl ethers to o-allylphenols) proceeds in part by concerted pathways had not previously been conclusively resolved. The first report of the photochemical reaction of phenyl allyl ether indicated only phenol and p-allylphenol as products (22). Subsequently, Schmid and Schmid found that 3-^{14}C-prop-2-enyl 2,6-dimethylphenyl ether rearranged photochemically to give roughly equal yields of 4-(1-^{14}C-prop-2-enyl)- and 4-(3-^{14}C-prop-2-enyl)-2,6-dimethylphenol (23). Although Woodward and Hoffmann have cited this work as evidence of a [3,5]-photochemical sigmatropic rearrangement (24), these results suggest a bond dissociation--radical recombination mechanism for the formation of p-allylphenol. Later reports have indicated that o-allylphenol is also formed in the photolysis of allyl phenyl ether (5,25). Product ratios from preparative irradiations, which generally showed slightly more ortho than para isomer and two to three times as much of each as of phenol, support the view that a radical mechanism operates in the formation of ortho products, but do not conclusively establish it as the only source of ortho product. It is conceivable that concerted [1,3]-sigmatropic suprafacial rearrangements could give rise to some or all of the ortho product. A [3,3]-sigmatropic rearrangement antarafacial with respect to the allyl group is formally allowed by orbital symmetry and would give rise to ortho product with inversion of the allyl group, but the transition state for such a pathway seems sterically unfeasable.

Another reason for interest in the allyl phenyl ether system was its potential utility as a probe into the pathways of photochemical σ bond dissociation reactions. Although the absence of concerted photochemical product formation has been conclusively demonstrated only for phenyl esters, the reactions mentioned above are all related in the sense that the products are consistent with a bond homolysis--radical recombination mechanism:

Scheme II



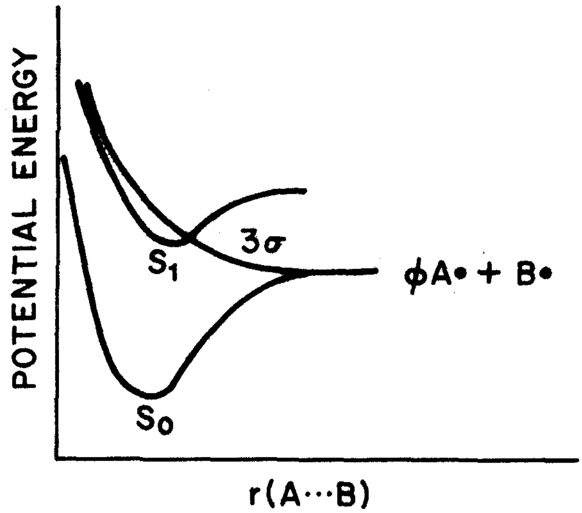
A fundamental question applicable to this formulation is the following: how is the energy of the electronically excited aromatic chromophore converted into the relative translational energy of the two fragments released when a bond is broken?

Shizuka _et al_. (3,26,27) have proposed that acetanilide and phenyl acetate dissociate _via_ predissociative σ^* triplet states of the N-C (acyl) or O-C (acyl) bonds which arise by intersystem crossing from the aromatic S_1 (π,π^*) states. Figure 1 illustrates the energy levels of the states involved as a function of the A-B bond distance, as proposed by Shizuka. A similar mechanism had earlier been advanced by Porter (28,29) to explain the formation of benzyl radicals in the photolysis of toluene. Even though such a transition is spin-forbidden, Porter concluded that the quantum yield was sufficiently low (_ca_. 10^{-2}) to be in qualitative agreement with known rates of intersystem crossing. In applying this same model to their studies, Shizuka _et al_. have concluded that the considerably larger quantum yields for photodissociation of acetanilide and phenyl acetate (0.25 and 0.61, respectively) result from enhanced intersystem crossing due to

Figure 1

Predissociative Triplet Model

for σ Bond Dissociation



H. SHIZUKA, *BULL. CHEM. SOC. JAP.*, **42**, 52 (1969) vibronic coupling of the aromatic S_1 (π,π^*) and carbonyl T_1 (n,π^*) states.

Of the compounds which give photochemical reactions analogous to that of phenyl acetate, the allyl phenyl ethers are of interest since there is no obvious basis for expecting interchromophoric coupling to enhance the rate of intersystem crossing to excited triplets.

The purpose of this study was to investigate qualitatively and quantitatively the photochemistry of 3-methyl-1-phenoxybut-2-ene (γ,γ-dimethylallyl phenyl ether), $\underset{\frown}{8}$. This particular compound was chosen because the two methyl groups provided markers to show whether the allylic group was inverted during the photochemical reaction. If, as seemed highly probable, all products arose from radical recombination pathways, product ratios would be of interest since products from dimethylallyl radical recombination reactions have not been previously reported (30).

Comparison of the reactivity of $\underset{\frown}{8}$ with that of phenyl acetate and acetanilide, the only systems for which quantum yield measurements are available, was expected to provide insight into the steps in σ bond dissociation.

RESULTS

Preparative Irradiations and Product Isolation

Irradiation at 254 nm of a solution of 1 ml of 8 in 100 ml of cyclohexane or isopropyl alcohol led to the disappearance of 8 and to the appearance of six photoproducts as determined by vapor phase chromatography (vpc). The solvent was removed from the isopropyl alcohol solution and the residual oil was chromatographed on silica gel. Products 9, 11, and 13 were isolated by this technique. Products 12 and 14 were obtained as a mixture and were separated by preparative vpc. For the isolation of 10, a solution of 1 ml of 8 in 100 ml of cyclohexane was irradiated to less than 10% conversion. Removal of the solvent left 1 ml of brown oil. This procedure was carried out eight times and the combined residues were distilled under vacuum through a spinning band column. The first 0.25 ml of distillate was found by vpc to contain one major component, the retention time of which matched that of product 10. Pure 10 was isolated from this distillate by preparative vpc.

Identification of Products

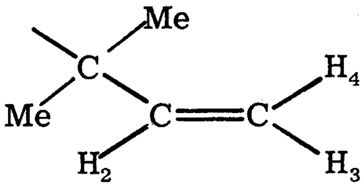
Product 9 was found to be phenol by comparison of its vpc retention time and pmr and ir spectra with those of an authentic sample (commercial material).

Products 11 and 12 were identified on the basis of their pmr and ir spectra as 1-(2-hydroxyphenyl)-3-methylbut-2-ene and 1-(4-hydroxyphenyl)-3-methylbut-2-ene, respectively. They had been previously reported from the photolysis of 8, and the spectra of the products obtained here agree with those in the literature (25).

Products 10, 13, and 14 were identified on the basis of their pmr and ir spectra. In addition, mass spectral and elemental analyses were used to confirm the identity of 10.

Both 13 and 14 show peaks in the ir at frequencies characteristic of O-H stretching vibrations. In carbon tetrachloride solution, 14 shows a free O-H stretch at 3620 cm^{-1} and a broad peak at *ca.* 3400 cm^{-1} for intermolecularly hydrogen bonded O-H stretch. In carbon tetrachloride solution 13 also shows a small free O-H stretch at 3620 cm^{-1}. A much larger peak appears at 3500 cm^{-1}, however, and is somewhat less broad that the intermolecularly hydrogen bonded O-H stretching peak seen for 14. Such absorptions are characteristic of intramolecularly hydrogen bonded hydroxy compounds and commonly appear at 3600-3450 cm^{-1} when an OH group is situated near a proton acceptor function such as a heteroatom or a double bond (31). The ir spectrum of 10 shows no O-H stretch absorption. It does, however, have a strong absorption at 1280 cm^{-1} which suggests aryl-O-C stretching.

The pmr spectra of 10, 13, and 14 each show the characteristic pattern of a monosubstituted ethylene function. The spectra of these systems have been discussed in detail by Pople, Schneider, and Bernstein (32), and the chemical shifts and apparent coupling constants seen for the vinyl protons of 10, 13, and 14 are consistent with the published values. The numbering of the protons is indicated below:



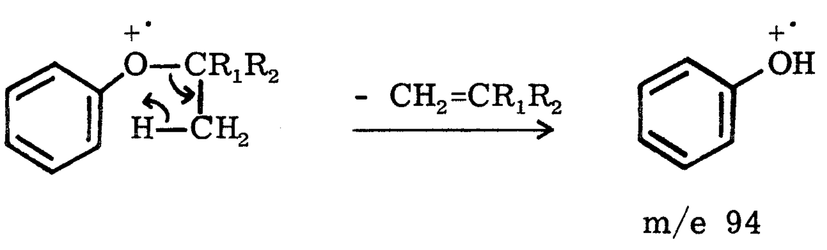
The pmr spectrum of 10 shows aromatic absorption at δ 7.0 (m, 5H) and aliphatic absorption at 1.40 (s, 6H) ppm in addition to the vinyl protons at 6.10 (H_2), 5.08 (H_3), and 5.12 (H_4) ppm (J_{23} = 10 cps, J_{24} = 19 cps, J_{34} = 1.5 cps). This spectrum and the appearance of a C-O-C absorption in the ir spectrum suggested that 10 was 3-methyl-3-phenoxybut-2-ene.

The pmr spectrum of 13 displays aromatic absorption at δ 7.0 (m, 4H) and aliphatic absorption at 1.44 (s, 6H) ppm in addition to the vinyl proton absorption at 6.20 (H_2), 5.25 (H_3), and 5.28 (H_4) ppm (J_{24} = 19 cps, J_{23} = 10.4 cps, J_{34} = 1.5 cps). With the ir spectrum, the data suggested that 13 is 3-(2-hydroxyphenyl)-3-methylbutene.

The pmr spectrum of 14 exhibits aromatic absorption at δ 7.0 (m, 4H) and aliphatic absorption at 1.35 (s, 6H) ppm in addition to vinyl proton absorption at 6.05 (H_2), 5.10 (H_3), and 5.10 (H_4) ppm (J_{23} = 10 cps, J_{24} = 18 cps, J_{34} = 1.8 cps). This spectrum and the ir data suggested that 14 was 3-(4-hydroxyphenyl)-3-methylbutene.

The products from the photochemical reaction of 8 are shown in Scheme III.

In order to confirm the structure assignment of 10, an elemental analysis and a mass spectrum were obtained. The elemental analysis found 81.51% C and 8.68% H, in good agreement with the 81.44% C and 8.70% H required for $C_{11}H_{14}O$. The mass spectrum of 10, shown in Figure 2, is distinctly different from that of 8, which is shown in Figure 3 for comparison. Both compounds show a parent peak at m/e 162. The base peak in the spectrum of 10 is m/e 94, corresponding to the fragment $(C_6H_5OH)^{+\cdot}$. Alkyl aryl ethers commonly show this peak, which is thought to arise from the fragmentation shown below (33a):



In the case of 10, CH_2=CR_1R_2 is isoprene, so the elimination is especially facile (33b).

Scheme III

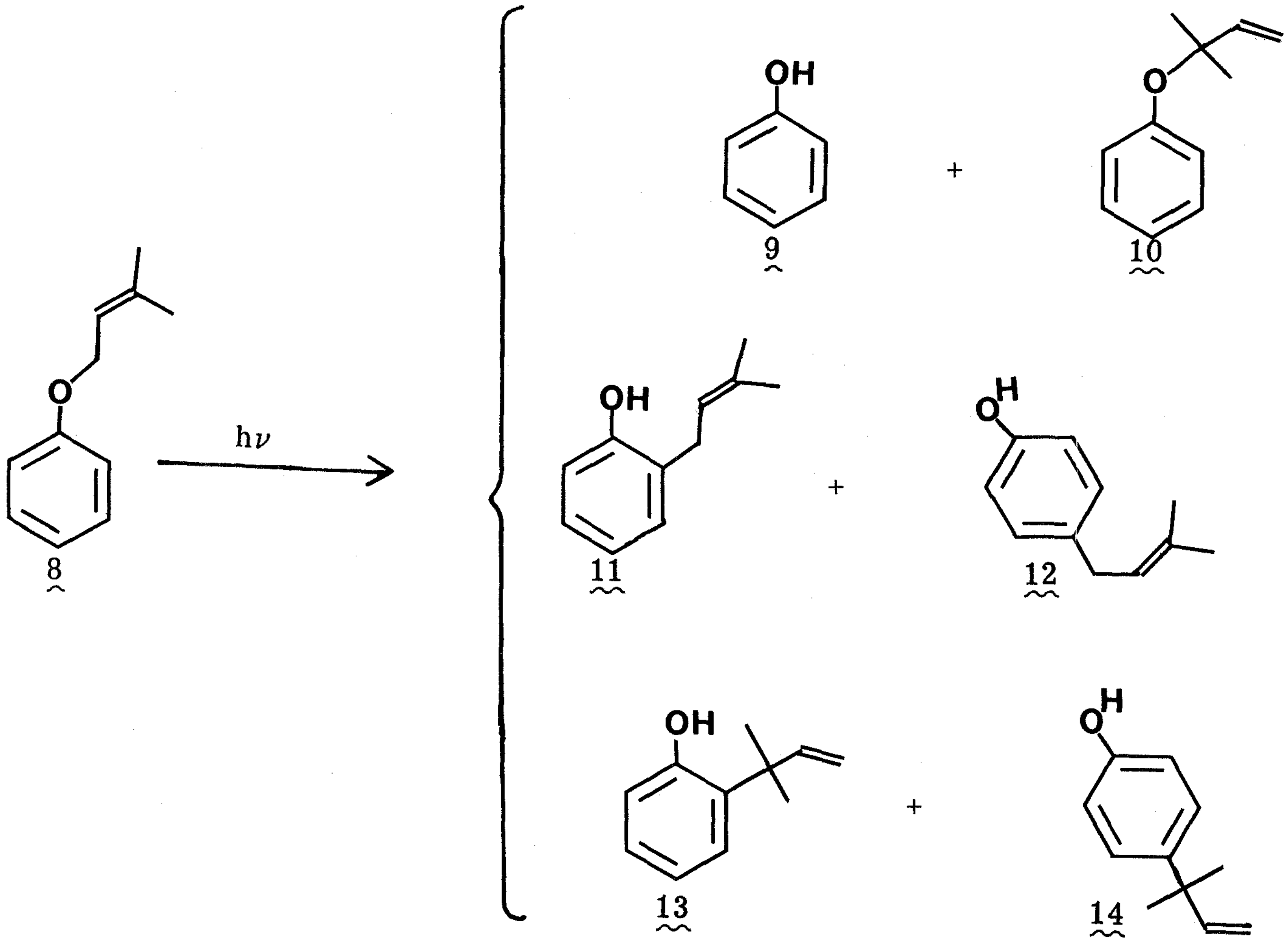


Figure 2

Mass Spectrum of $\underset{\sim}{10}$

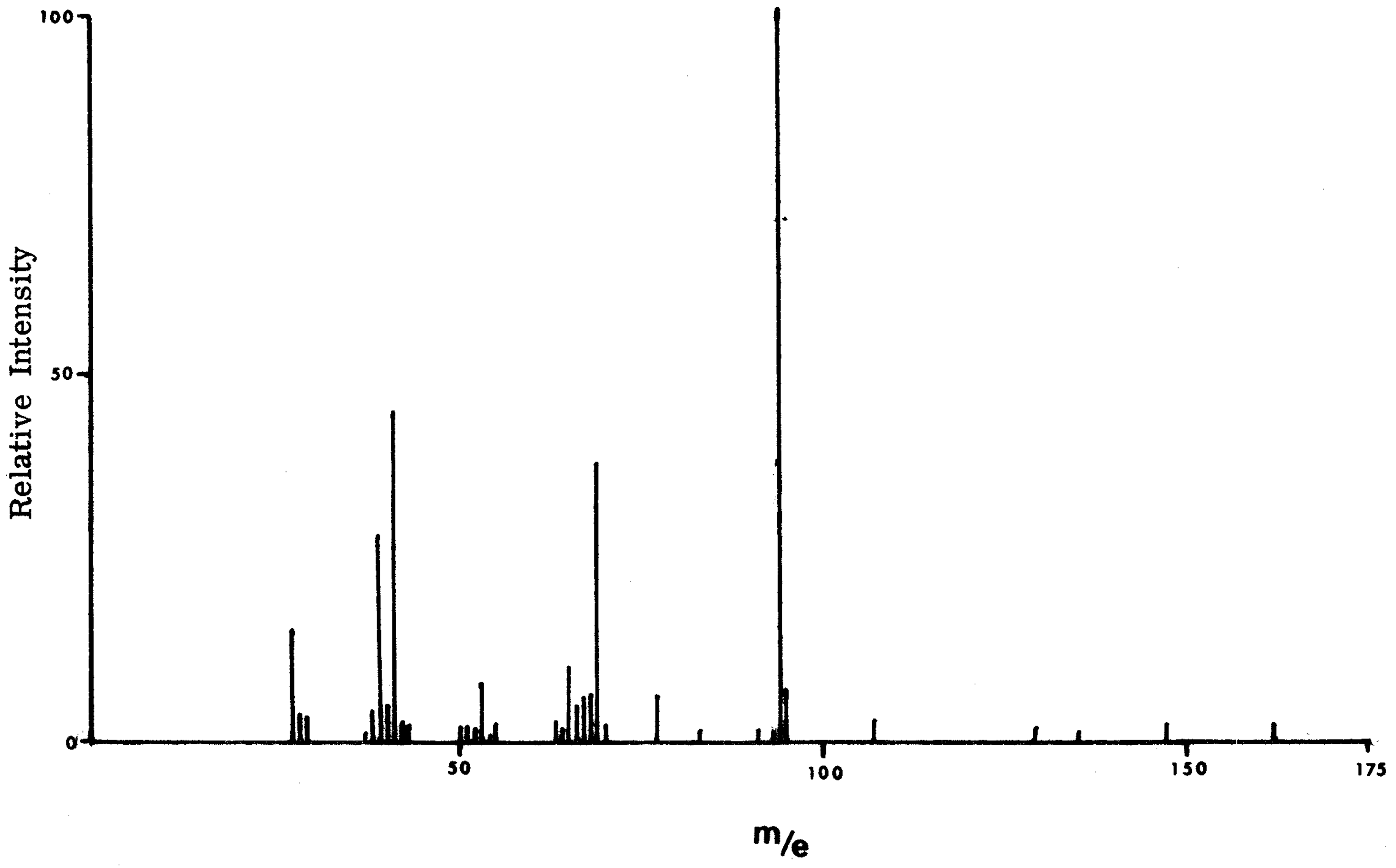
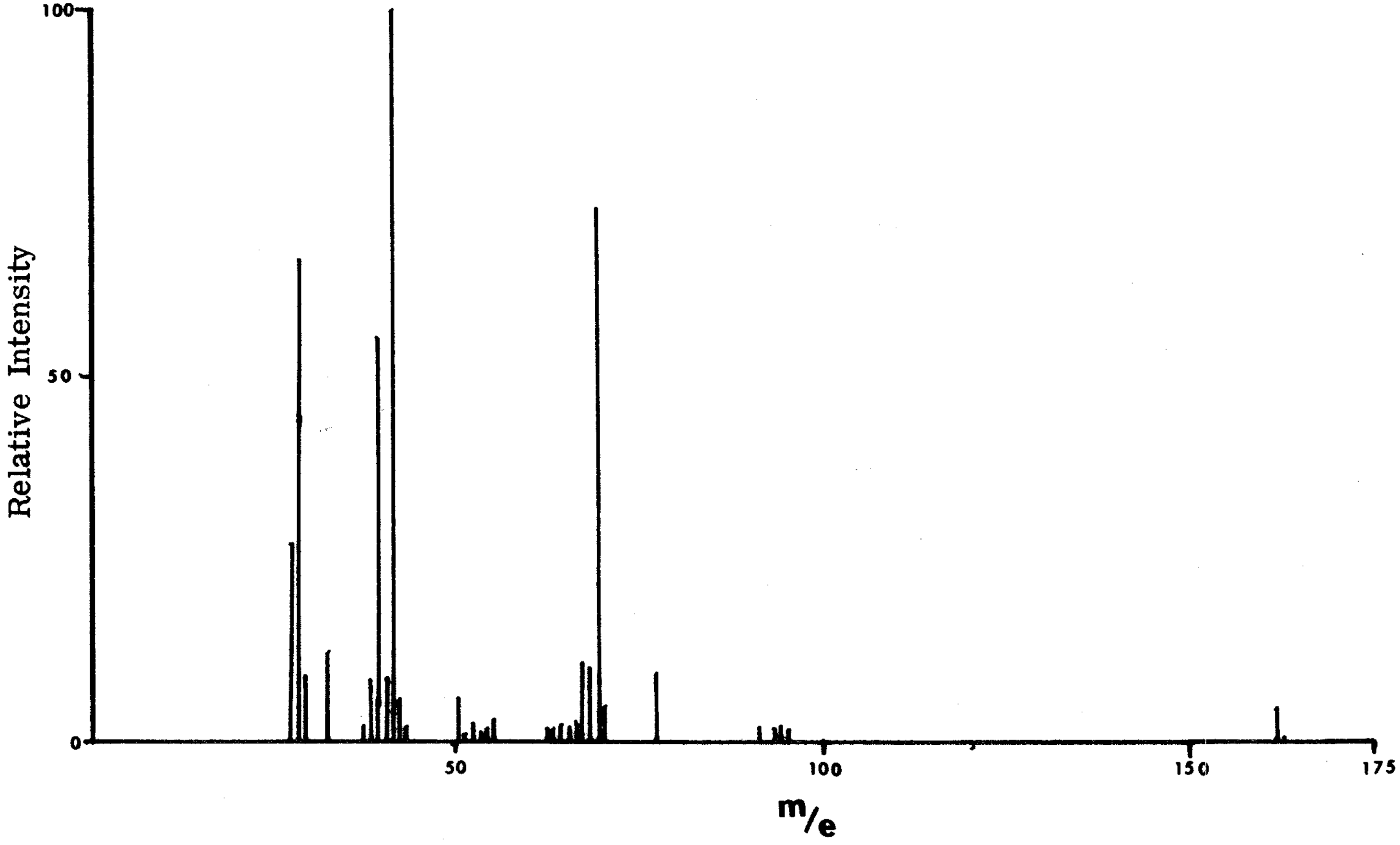
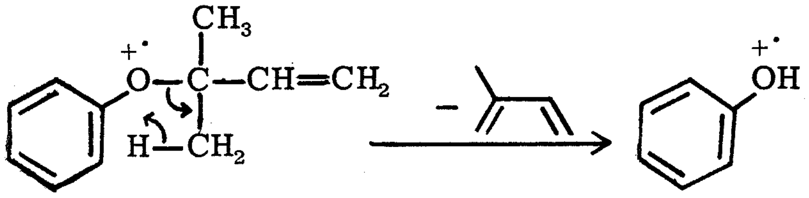


Figure 3

Mass Spectrum of 8





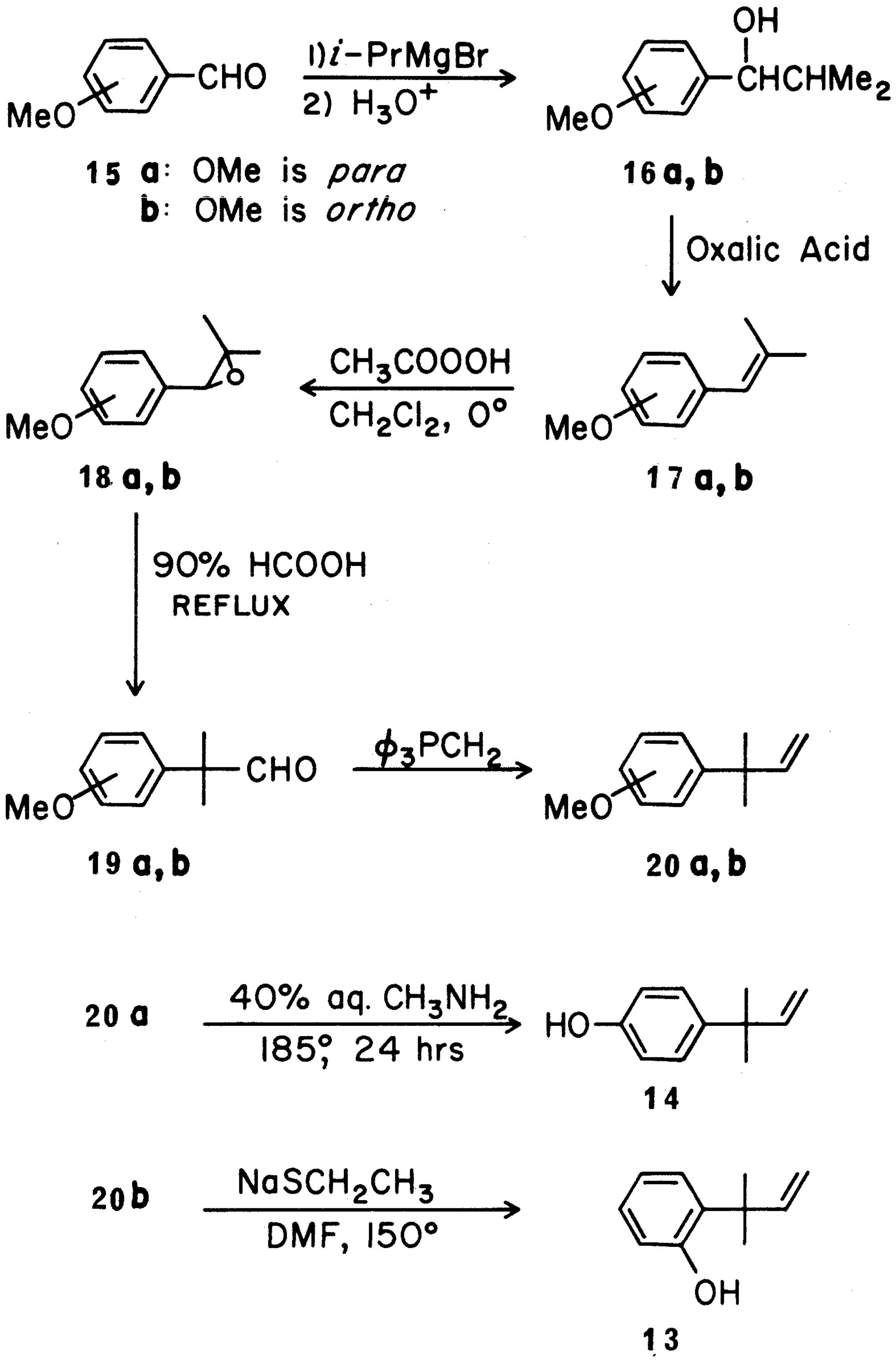
m/e 94

With 8, $CH_2CR_1R_2$ is an allene, and the neutral fragment is much less stable than the fragment released from the radical cation of 10. As a consequence m/e 94 is almost absent in the mass spectrum of 8.

Syntheses of 13 and 14

In order to confirm the structural assignments made to 13 and 14, they were synthesized by unambigous routes as shown in Scheme IV. Treatment of *p*-anisaldehyde, 15a, with *i*-propylmagnesium bromide gave 1-(4-methoxyphenyl)-2-methylpropanol (16a) in high yield. Dehydration of 16a to 1-(4-methoxyphenyl)-2-methylpropene (17a) was carried out by heating the neat alcohol with oxalic acid and distilling off the water, a procedure which had been described by Conant and Blatt (34). Epoxidation of the olefin with peracetic acid gave 1-(4-methoxyphenyl)-2-methylpropene oxide (18a) in fair yield. The acid catalyzed rearrangement of 18a to 2,2-dimethyl-2-(4-methoxyphenyl)-acetaldehyde (19a) went in high yield in refluxing 90% formic acid (35). This procedure was found to give a better yield than that described by

Scheme IV



MeO
CHO
1) i-PrMgBr
2) H_3O^+
OH
$CHCHMe_2$
15 a: OMe is *para*
b: OMe is *ortho*
16 a, b
Oxalic Acid
CH_3COOOH
CH_2Cl_2, 0°
O
18 a, b
17 a, b
90% HCOOH
REFLUX
CHO
ϕ_3PCH_2
19 a, b
20 a, b
20 a
40% aq. CH_3NH_2
185°, 24 hrs
HO
14
20 b
$NaSCH_2CH_3$
DMF, 150°
OH
13

Reif and House (36), who used boron trifluoride-etherate as the acid catalyst. A Wittig reaction with the ylid derived from methyltriphenylphosphonium iodide and 19a gave 3-(4-methoxyphenyl)-3-methylbutene (20a).

Several attempts were made to cleave the methyl phenyl ether 20a by standard techniques. Use of HI solution or BBr_3 (37) gave products in which the monosubstituted ethylene function was lost, as determined by pmr. Apparently acid catalysis moved the double bond into conjugation with the phenyl ring. It was therefore necessary to carry out the cleavage under basic conditions. Use of 40% aqueous methylamine in a sealed tube reaction, as described by Lockhart and Webb (38), gave sufficient synthetic 3-(4-hydroxyphenyl)-3-methylbutene for comparison with 14 isolated from the photochemical reaction. The two samples had identical pmr and ir spectra. Furthermore, they had the same retention time under analytical vpc conditions; a coinjection of the two gave only one peak with no apparent broadening.

The set of reactions detailed for the conversion of 15a to 20a was also carried out on 15b. All reactions proceeded generally as above, except the dehydration of 16b to 17b, which went in relatively poor yield. The methylamine cleavage of 20b was unsuccessful. The method used for this cleavage was the reaction of the ether with sodium ethylmercaptide in N,N-dimethylformamide, a procedure recently reported by Feutrill and Mirrington (39). The product, 3-(2-hydroxyphenyl)-3-methylbutene, was isolated by preparative vpc. The pmr and ir spectra and vpc retention time of the synthetic material were identical, respectively, with those of 13 isolated from the photolysis.

Quantum Yield Determinations

The quantum yields for the photochemical reactions of 8 were determined in both cyclohexane and isopropyl alcohol solutions. A 6×10^{-3} M solution of 8, containing tetradecane as an internal vpc standard, was prepared and 4.0 ml was pipetted into each of seven quartz tubes (13 mm o.d.). In the case of isopropyl alcohol solution, four of the tubes were degassed by the freeze-pump-thaw technique and were sealed under a pressure of $< 5 \times 10^{-4}$ Torr. The cyclohexane solutions were not degassed. The tubes were irradiated for different lengths of time, the longest irradiation causing ca. 10% conversion, at 254 nm in a merry-go-round apparatus (40). The contents of the tubes were analyzed by vpc. The disappearance of 8 and the appearance of photoproducts, relative to tetradecane, were plotted versus irradiation time. Straight lines were obtained and slopes were calculated by the least squares method. Quantum yields for degassed and nondegassed isopropyl alcohol solutions were found to be identical within experimental error. This result was not surprising, since the singlet lifetime of 8 is so short that oxygen quenching is not a serious problem (vide infra). The experimental uncertainty in the measured quantum yields is estimated to be ± 10%, due primarily to uncertainty in the analytical method. Table I summarizes the results obtained. The difference between the disappearance quantum yield and the sum of the appearance quantum yields is probably due to polymerization of **8**.

Gas Phase Irradiations

The photolysis of **8** was also carried out in a gas phase flow system which has been previously described (18a, c). Approximately 1 g of **8** was swept through the flow system each twenty-four hours; 1000 cc/min of nitrogen was used as the carrier gas. Isobutylene (32 cc/min) was added to the flow system to trap any unstable radicals, but no such trapping products were observed. Photolysis products and unreacted **8** were trapped in a Dry Ice-cooled, glass helices-packed column and were extracted with ether. The ether solutions were analyzed by vpc and the results are shown in Table II. Control experiments confirmed that passing **8** through the flow system in the dark did not cause chemical change.

When the trap was removed from the Dry Ice after each photolysis, it was noticed that the first few centimeters of glass helices were colored bright red. As the trap warmed to room remperature, the color faded. It did not reappear upon cooling. A similar observation had been made in the gas phase photolysis

TABLE I. Quantum Yields for Photoreactions of 3-Methyl-3-phenoxybut-2-ene

Solvent	Φ_{diss}	Φ_{app}:	9	10	11	12	13	14
Cyclohexane	0.55		0.10	0.05	0.06	0.05	0.02	0.03
2-Propanol	0.75		0.11	0.03	0.18	0.15	0.05	0.07

TABLE II. Relative Product Yields from Photochemical Reaction of **8**

Conditions	Products: **9**	**10**	**11**	**12**	**13**	**14**
2-Propanol Solution	1.0	0.31	1.64	1.36	0.51	0.82
Gas Phase	1.0	0.43	1.27	1.18	0.10	0.29
Gas Phase with 25 Torr Nitric Oxide	1.0	<.01	<.01	<.01	<.01	<.01

of phenyl acetate in the same flow system (18a).

The gas phase irradiation of 8 was also carried out in the same apparatus with 30 cc/min of nitric oxide, instead of isobutylene, as a trapping agent. Photolysis products and unreacted 8 were trapped, extracted with ether, and analyzed by vpc as above. As shown in Table II, the addition of nitric oxide efficiently quenched the formation of products 10-14. Some phenol and several new products were detected by vpc; the new products were not characterized. Control experiments confirmed that passing 8 and nitric oxide through the flow system in the absence of light did not give rise to the new products.

Attempt to Sensitize the Photorearrangement of 8

In an attempt to sensitize the photorearrangement of 8, acetone and 8 were dissolved in isopropyl alcohol and the solution was deoxygenated by purging with nitrogen. As determined by vpc, even prolonged irradiation through Pyrex at 305 nm did not cause any observable chemical reaction of 8.

Irradiation of 10

Some of the 3-methyl-3-phenoxybutene, 10, isolated from the photolysis of 8 was dissolved in cyclohexane and irradiated at 254 nm. Appearance of 8, 9, and 11-14 was determined by vpc. Because of impurities having retention times similar to those of products **11**, **12**, and **14**, it was not possible to determine accurately the relative yields of these products. At approximately 10% conversion of **10**, the ratio of **8** : **9** : **13** was seen to be 1 : 2.5 : 1.5.

Comparison of Absorption Spectra of **8** and of Anisole

The absorption spectra of **8** and of anisole were taken under identical conditions in cyclohexane solution. The spectra obtained are shown in Figure 4. The position, shape, and intensity of the ^1L_b band in both compounds are essentially identical. The ^1L_a band of **8** is slightly more intense than that of anisole.

Determination of the Fluorescence Quantum Yield of **8**

The fluorescence spectra of anisole and of **8** were obtained in dilute degassed cyclohexane solution are are shown in Figure 5. The band shapes and positions of emission are identical, respectively, for the two compounds. The excitation spectra of the fluorescence of the two were also identical and roughly (on an uncorrected instrument) showed the structure of the ^1L_b band of anisole. Under the condition that a 1.0 cm path length of solutions of **8** and of anisole had equal optical densities, two separate determinations indicated that the intensity of anisole

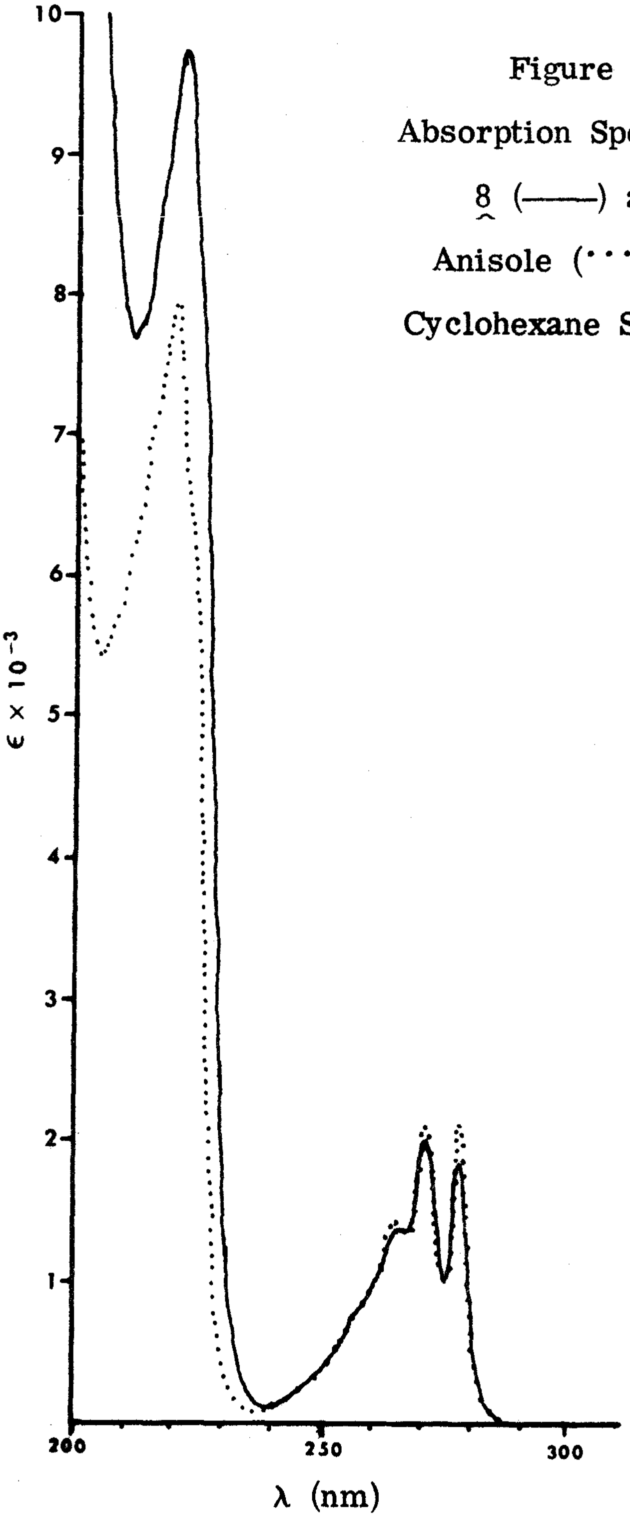


Figure 4
Absorption Spectra of
8 (——) and
Anisole (····) in
Cyclohexane Solution

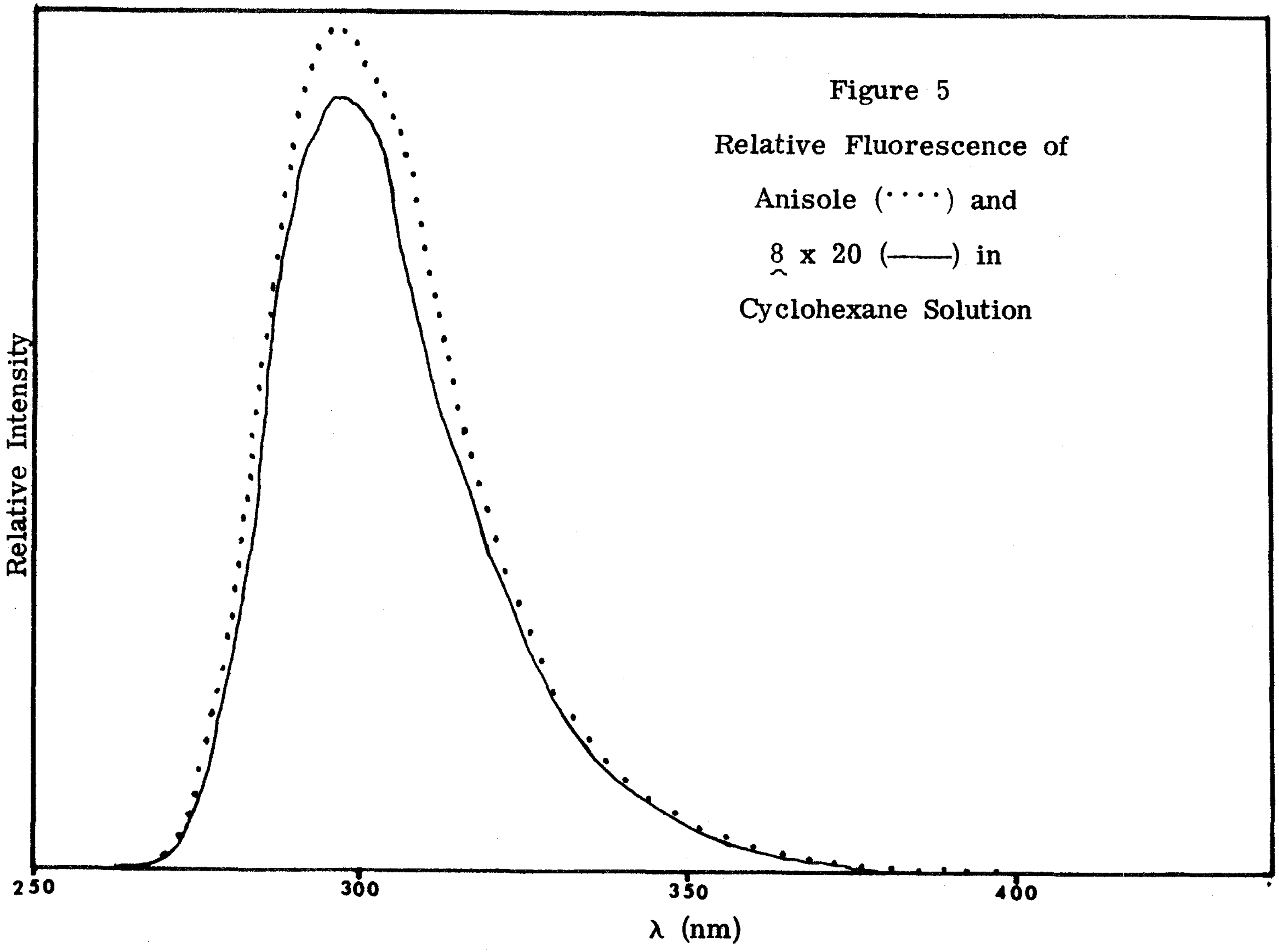


Figure 5

Relative Fluorescence of Anisole (····) and **8** x 20 (——) in Cyclohexane Solution fluorescence was 22 times greater than that of 8. The fluorescence quantum yield of anisole has been reported to be 0.24 (41). The fluorescence quantum yield of 8, therefore, is $\phi_f = 1.1 \times 10^{-2}$.

Attempt to See Phosphorescence from 8

Strong phosphorescence was observed from anisole in an EPA glass at 77° K. Under identical conditions, no emission from 8 was detected. It was estimated that the quantum yield of phosphorescence of 8 must by ca. 10^{-3} that of anisole, or less.

DISCUSSION

Mechanism of the Photochemical Reaction

The results obtained both in solution and in the gas phase suggest very strongly that the photochemical reaction of 8 involves scission to phenoxy and dimethylallyl radicals which recombine to give all possible simple coupling products--the isomeric ether, 10, and four dienones which can give 11-14 by tautomerization.

The isolation of the isomeric ether 10 provides especially satisfying evidence for radical processes. Products analogous to 10 have not been previously reported from the photolysis of allyl phenyl ethers or related systems.

The gas phase irradiations provide strong evidence that radical pathways are the only significant route to products. In the gas phase irradiation of phenyl acetate, decarbonylation of the acyl radical provided a clear differentiation between concerted and radical processes. The dimethylallyl radical generated in the present study was considerably more stable and underwent extensive recombination reactions with phenoxy radicals in the gas phase. However, nitric oxide effectively quenched the formation of all such coupling products. The reactions of nitric oxide with alkyl radicals have recently been reviewed by Heicklen and Cohen (42). While the total scope of mechanisms involved in the reaction of nitric oxide with the radicals generated in the present study is probably complex, the scavenging of dimethylallyl radicals by nitric oxide is in accord with known reactions.

There could, of course, be some concerted reactions occurring in parallel with radical processes in solution, but there is no evidence for such reactions from comparison of the relative product yields in the two phases. The relative yields of ortho to para products for the possible coupling positions of the dimethylallyl radical are about the same in solution as in the gas phase. Furthermore the ratio of 11 to 12, both in the gas phase and in solution, is very close to the ratio of ortho to para products formed in the photorearrangement of phenyl acetate (18, 26) and in the coupling of phenoxy and methyl radicals (43), suggesting that all the processes have a common mechanism.

Recombination Reactions of the Dimethylallyl Radical

The conclusion that products 10-14 arise from radical recombinations prompts some discussion of radical recombination processes. Mulcahy and Williams noted that, in combination reactions with the methyl radical, the reactivity of the ortho and para positions of the phenoxy radical closely parallels the relative free electron density at these positions ($\rho_{para} = 1$, $\rho_{ortho} = 0.63$) (43). Such correspondence may well be fortuitous. The activation enthalpy of radical recombination reactions is usually very small. It seems equally reasonable that the variation from statistical product distribution (twice as much 11 as 12) is due primarily to slightly greater steric hindrance at the ortho position. Evidence for this argument is seen in the slightly greater yield of 14 than 13; intuition suggests that coupling of allylic radicals at a primary center will be faster than competitive coupling at a tertiary center. The ratios 11 : 12 and 13 : 14 show little variation in the two solvents studied.

The difference in temperature between the solution and gas phase reactions (see Experimental section) precludes quantitative comparison, but the relatively greater ratio of (11 + 12) : (13 + 14) in the gas phase may be in part a result of the nature of solvation of the dimethylallyl radical. There is in fact a small difference in this ratio in the two solvents isopropyl alcohol and cyclohexane.

Comparison of Absorption Spectra

Comparison of the absorption spectra of 8 and of anisole shows a close correspondence between the ^1L_b bands of the two compounds, suggesting that in 8 this transition is much like that of anisole. The compounds should, therefore, have the same fluorescent lifetime (τ_s^o), 3.4×10^{-8} sec (41), and rate constant for fluorescence (k_f), 2.9×10^7 sec^{-1} (44). The slightly greater intensity of the ^1L_a band of 8 over that of anisole may indicate some interaction of the two chromophores in this transition. Similar coupling has been previously seen in some bichromophoric molecules (45).

Comparison of Fluorescence Spectra

The spectra in Figure 5 show that the fluorescence of 8 is identical in band shape and position to that of anisole. This result suggests that the lowest-lying excited singlet of 8 cannot have geometry greatly different from that of anisole. However, the greatly diminished intensity of the emission indicates that the lifetime of the fluorescent state of 8 is shortened. For anisole, the observed fluorescence lifetime, τ_s, is 8.3×10^{-9} sec (46). For 8, $\tau_s = \Phi_f/k_f = 3.7 \times 10^{-10}$ sec.

Discussion of Lack of Phosphorescence from 8

There are two primary reasons for decreased phosphorescence yield from 8: 1) the short lifetime of the lowest-lying singlet of 8 means that the quantum yield of triplet formation will be reduced correspondingly, and 2) any triplets which do form will likely be quenched by the olefinic portion of the molecule at a rate much faster than the rate of phosphorescence.

The lifetime of anisole is the inverse of the sum of the rate constants for processes which deactivate it: $1/\tau_s = k_f + k_{isc} + k_d = 1.2 \times 10^8 \text{ sec}^{-1}$, where k_d is the rate constant for radiationless decay. Since k_f is 2.9×10^7 $\sec^{-1}$ (*vide supra*), the sum of ($k_{isc} + k_d$) is estimated to be 9×10^7 $\sec^{-1}$. The recent finding that Φ_{isc} for anisole is 0.74 ± 0.05 (47) suggests that intersystem crossing in anisole must account for nearly all the S_1 states that do not fluoresce. Radiationless decay, if it occurs, must do so with a quantum yield of 0.02 or less. Therefore, k_{isc} for anisole is about 9×10^7 $\sec^{-1}$. The maximum quantum yield for intersystem crossing in **8** is $\Phi_{isc} = k_{isc} \times \tau_s = 0.03$, which is more than an order of magnitude smaller than the upper limit for Φ_{isc} for anisole.

The triplet energy of anisole is *ca*. 81 kcal/mole (48). The triplet energies of simple olefins are not known with certainty, but are estimated to be from 70-83 kcal/mole (49). Acetone, which has an 80 kcal/mole triplet, has recently been shown to sensitize the isomerization of cis-2-pentene (50). Thus, the olefinic portion of **8** could act as a triplet quencher for the aromatic moiety with a rate constant orders of magnitude faster than the rate constant for phosphorescence.

Discussion of Acetone Sensitization Experiment

The lack of photochemical reaction in the case of acetone sensitization can be easily rationalized. The triplet energy of acetone is 80 kcal/mole, which is almost 2 kcal/mole less than that of anisole. Acetone would not be expected to efficiently transfer triplet energy endothermically to 8. Triplet sensitization of the olefinic group could occur, but it is likely to do so by a Schenck mechanism (50). Sensitization of the $^3\sigma$ (O-C) state should give rise to the photochemical reaction observed on direct irradiation if the dissociation model proposed by Shizuka is correct, but failure to observe such reaction may only mean that the efficiency of the transfer is low compared to that of other processes which destroy acetone triplets.

Discussion of σ Bond Homolysis Mechanisms

Anisole does not give a photochemical reaction analogous to that of 8 upon irradiation at 254 nm (51). Thus, substitution of either a dimethylallyl or an acyl function for the methyl group in anisole produces a photoreactive species. The quantum yield for product formation from phenyl acetate in cyclohexane is 0.38 (26), which is not much greater than the quantum yield for product formation from 8 in cyclohexane, 0.31. Since there is no evidence for enhancement of intersystem crossing by olefins, which themselves undergo intersystem crossing very inefficiently (52), these results suggest that the photochemical reactivity of 8 is inconsistent with a general model in which *enhancement* of intersystem crossing is a prerequisite for photochemical dissociation. There must be other features common to 8 and phenyl acetate which lead to photochemical reactivity.

In discussing the formation of benzyl radicals in the photolysis of toluene, Porter suggested that in a representation of potential energy curves as a function of CH_2-H bond distance (Figure 1) the $^3\sigma$ (C-H) predissociative curve should intersect the S_1 (π,π^*) curve near its minimum to facilitate intersystem crossing from one state to the other. The rates of intersystem crossing are fast enough to account for the rates of product formation observed in the present study *if* there should be a close correspondence of the potential energy curves of the two states.

It would be quite fortuitous, however, if the $^3\sigma$ energy levels of the diverse compounds mentioned in the introduction showed such correspondence. Furthermore, the utility of drawing potential energy curves for π,π^* states as a function of C-H bond distance is highly questionable, since the C-H bond distance is only one coordinate of the multidimensional energy surface needed to describe the molecular excited state.

For a further discussion of the dissociation reaction, it is helpful to consider all the processes which deactivate excited **8**. At least some of the processes which depopulate the S_1 state of **8** are quite similar to those of anisole. The values of k_f have been shown to be identical. There is little *a priori* reason to expect the rate constant for intersystem crossing to increase upon substitution of a dimethylallyl group for the methyl group (*vide supra*).

An additional deactivation process is the obvious path of chemical reaction (including the "trivial" but perhaps significant back reaction--cleavage into two radicals which recombine to give 8). The rate constant for product formation, k_r, can be calculated from the quantum yield and knowledge of the lifetime of the excited state involved.

The quantum yield for the appearance of products from photolysis of 8 was 0.31 in cyclohexane and 0.6 in isopropyl alcohol. The extent of the back reaction is not known. Consideration of the data in Table I suggests that in cyclohexane the radicals recombine to give 10 roughly twice as often as to give 13 or 14. If the same ratio holds for the relative formation of 8 to 11 or 12, the quantum yield for the back reaction in cyclohexane might be *ca.* 0.10. The observation that photolysis of 10 leads to a ratio of 8 : 9 : 13 of 1 : 2.5 : 1.5 in cyclohexane suggests that the quantum yield of the back reaction may be between 0.03 and 0.04. The product distributions from photolysis of 8 and 10 need not be necessarily the same, since extensive recombination might occur before complete vibrational and rotational equilibrium of the radical pair in the solvent cage occurs. Thus, these values of Φ_{back} are only a very rough estimate. Furthermore, there is a real semantic problem in differentiating between back reaction and radiationless decay through the vibrational modes of the O-C (allyl) bond. For the purposes of this discussion, it will be sufficient to consider in k_r only the steps which lead to formation of products 9-14. In cyclohexane solution, the rate constant for product formation is thus calculated:

$$k_r = \Phi_r/\tau_s = 8.6 \times 10^8 \text{ sec}^{-1}$$

The processes of back reaction and radiationless decay must account for the deactivation of the remainder of the S_1 states of 8. If Φ_{back} is no larger than 0.10, then the rate constants for these processes may be calculated:

$$k_{back} = \Phi_{back}/\tau_s = 2.7 \times 10^8 \text{ sec}^{-1}$$

$$k_d = 1/\tau_s - k_{isc} - k_r - k_{back} = 1.5 \times 10^9 \text{sec}^{-1}$$

The conclusion to be drawn from these calculations is that nonchemical, nonradiative decay and chemical reaction are both markedly accelerated in 8, relative to anisole.

The two accelerated nonradiative decay processes may be closely related. Several authors have recently pointed out that anharmonicity in a bond vibration can increase the Franck-Condon overlap between initial and final states and thus can make that bond a better acceptor of energy in an internal conversion process (53-55). Stretching of the allyl ether O-C (allyl) bond must become highly anharmonic in the energy region near the dissociation energy in the ground state. The transfer of charge from oxygen into the aromatic ring which accompanies the excitation (56) should increase the anharmonicity of the vibration and perhaps weaken the O-C (allyl) bond. The presence of this very weak bond could enhance the radiationless decay rate of the excited singlet state even when the process does not lead to dissociation, perhaps because the vibrational energy is less than the dissociation energy or because internal vibrational relaxation occurs in the dissociative mode before separation occurs.

Another deactivation path, available in 8 but not in anisole, would invoke weak electronic interaction between the olefinic and excited aromatic groups, thus allowing decay by way of vibronic mechanisms similar to those that lead to rapid nonradiative decay of simple alkenes. Such a mechanism has recently been proposed by Morrison to account for the short fluorescent lifetime of 6-phenylhex-2-ene (57), and the quenching of anisole singlets by olefins, with bimolecular rate constants of *ca.* 10^8 l. m^{-1} sec^{-1}, has recently been demonstrated (58).

Bond homolysis also could occur as a radiationless transition from the initially populated excited singlet *via* vibronic interaction of the aromatic and olefinic chromophores. Recent theoretical treatments of dissociation reactions and other radiationless transitions have described the initially populated excited electronic state as being weakly coupled with an intermediate electronic state which is also strongly coupled with the vibrational continuum (59,60). The "exciplex" deexcitation mode proposed above would provide a convenient vehicle for coupling the aromatic excitation with the vibrational continuum. If this interaction leads to a lengthening of the O-C bond, then the excited state could partition to ground state 8 or to radicals. In the limiting case, as dissociation is approached, the multiplicity of the O-C bond electron pair would be of relatively little importance. While this description, like that of Shizuka, takes into consideration interaction of the two chromophores, it does not demand multiplicity change as an integral step in the dissociation.

Conclusion

The conclusion of this study is that the photochemical rearrangement of 3-methyl-3-phenoxybut-2-ene proceeds exclusively through phenoxy and dimethylallyl radicals and that no products are formed by concerted processes. Analysis of the decay rates of 8 indicates that enhanced intersystem crossing from an S_1 (π,π^*) state to a $^3\sigma$ (O-C) state is probably not involved in the dissociation. Photochemical reaction may occur as a result of radiationless decay of the S_1 (π,π^*) state through anharmonic vibrations of the O-C (allyl) bond. Intramolecular interaction of the aromatic and olefinic chromophores may also be a significant deactivation pathway.

EXPERIMENTAL

Instruments

Infrared spectra were recorded on a Perkin-Elmer Model 257 Grating Infrared Spectrophotometer, with either carbon tetrachloride solutions in a 0.1 mm path length cell or thin films of neat liquid between sodium chloride plates.

Pmr spectra were taken on a Varian A-60A Spectrometer. Deuterochloroform containing tetramethylsilane as internal standard was used as solvent.

Ultraviolet spectra were taken in 1.0 cm path length cells on a Cary 14 Recording Spectrophotometer or on a Beckman DU Spectrophotometer.

Fluorescence spectra were taken an an Aminco-Bowman Spectrophotofluorometer. The spectra are uncorrected for phototube response or instrumental wavelength error.

Phosphorescence spectra were obtained on the Aminco-Bowman Spectrophotofluorometer equipped with a phosphorescence accessory and are uncorrected.

Analytical vapor phase chromatography (vpc) was done on either a Hewlett-Packard Model 700 or a Hewlett-Packard Model 5750 Gas Chromatograph, both with flame ionization detectors and with nitrogen as carrier gas.

Preparative vapor phase chromatography was done with a Varian Aerograph Model 90-P Gas Chromatograph with thermal conductivity detection and with helium as carrier gas.

Mass spectra were obtained by Mr. Ron Klefbeck on a Consolidated Electrodynamics Corporation Model 21-103C Mass Spectrometer. All samples were run under the following conditions: electron beam current, 10 μa; electron beam voltage, 70 V; sample pressure, 5×10^{-7} Torr; sample temperature, 100°; magnet current, 360.2 ma.

Boiling points were measured with standard thermometers and are uncorrected. Pressures below 5 Torr were measured with a Scientific Glass Apparatus Company McCloud Gauge and are uncorrected. Elemental analyses were performed by the Spang Microanalytical Laboratory, Ann Arbor, Michigan.

Materials

Isopropyl Alcohol was Matheson, Coleman, and Bell Spectroquality.

Cyclohexane, unless otherwise specified, was Matheson, Coleman, and Bell Spectroquality.

Tetradecane was obtained from Calbiochem.

Acetone was Matheson, Coleman, and Bell Spectroquality.

1,2-Dimethoxyethane (DME) was received from Matheson, Coleman, and Bell. It was distilled from lithium aluminum hydride and stored over sodium hydride prior to use.

1-Chloro-3-methyl-2-butene was Eastman Practical Grade. Analysis by vpc showed one major (ca. 70%) and several minor components.

n-Hexane was obtained from Phillips Petroleum Company.

Isobutylene and nitric oxide were obtained from the Matheson Gas Company, Inc.

3-Methyl-1-phenoxybut-2-ene (8). Sodium methoxide (Matheson, Coleman, and Bell, 14 g, 0.25 mol) was dissolved in methanol (150 ml) under a nitrogen atmosphere. Phenol (Allied Chemical, 23.8 g, 0.25 mol) dissolved in methanol (50 ml) was added to this solution with stirring. The solution was cooled to 0° and 1-chloro-3-methyl-2-butene (26.1 g, 0.25 mol) was added. The solution was allowed to warm and a white precipitate appeared before the solution reached room temperature. The mixture was heated to reflux during one hour and was then refluxed for one hour. The solution was cooled and the solvent was removed by evaporation. The residue was extracted with ether and the ether layer was washed three times with 10% potassium hydroxide solution followed by two washings with saturated sodium chloride solution. The organic phase was dried over anhydrous magnesium sulfate and concentrated on the rotary evaporator. The yield of crude product was 22.5 g (ca. 50%). Vacuum distillation yielded two main fractions: 1 ml (bp $40\text{-}55^{\circ}$, 0.25 Torr) and 23 ml (bp $55\text{-}60^{\circ}$, 0.25 Torr). The product was passed through silica gel and bulb-to-bulb vacuum distilled prior to use. The material used for preparative irradiations was greater than 99% pure. The mass spectrum of 8 showed the following m/e ratios: 41 (100), 69 (73), 67 (11), 68 (10), 77 (10), and 162 (5) as shown in Figure 3. Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.26; H, 8.76.

Preparative Photolysis in Solution

Compound 8 (1.0 ml) was dissolved in isopropyl alcohol (50 ml). The solution was placed in a quartz tube and was purged with dry nitrogen for 10 min. It was then irradiated at 254 nm with an Ultraviolet Products PCQ-XI lamp. Samples were withdrawn at intervals for analysis by vpc on a 16 in x $\frac{1}{8}$ in column of 10% Carbowax 20M (on 60/80 mesh Chromosorb G, AW, DMCS treated). Disappearance of 8 and appearance of several products was seen. After ca. 100 hrs irradiation, less than 1% of 8 remained.

The solvent was removed from the solution above and the residue was chromatographed on silica gel (25 g) using benzene: methanol (99 : 1). Fractions were analyzed by vpc. Products 9, 11, and 13 were isolated in pure form. Products 12 and 14 were obtained as a mixture. They were separated by preparatave vpc on a 4 ft x $\frac{3}{8}$ in column of 10% Carbowax 20M (on 60/80 mesh Chromosorb G, AW, DMCS treated) at 183°. The pmr and ir spectra of **9** were identical with those of an authentic sample. The pmr spectra of **11** and **12** were identical with those previously reported (25).

For the isolation of **10**, **8** (1 ml) was dissolved in cyclohexane (100 ml). The solution was purged with nitrogen and irradiated, as above, to less than 10% conversion. The solvent was removed to leave a brown oil (1 ml).

This procedure was carried out eight times and the combined residue was distilled through a 50 cm spinning band column (pot temperature, 80°). The first 0.25 ml of distillate at 0.5 Torr was found by vpc to contain one major and several minor components. The major component, **10**, was isolated by preparative vpc on a 3 ft x $\frac{3}{8}$ in column of 5% Castorwax (on 60/80 mesh Chromosorb G, AW, DMCS treated) at 80°.

The pmr spectrum of **10** shows the following peaks: δ 7.0 (m, 5 H); 6.1 (d of d [J = 19 cps, J = 10.0 cps], 1 H); 5.08 (d of d [J = 10.0 cps, J = 1.5 cps], 1H); 5.12 (d of d [J = 19 cps, J = 1.5 cps], 1H); 1.4 (s, 6H) ppm. The ir spectrum of **10** (neat) exhibits the following strong absorptions: s 995, 1600, 1495, 1230 (broad), 1130 (broad), and 690 cm^{-1}.

The mass spectrum of **10** (Figure 2) shows the following m/e ratios: 94 (100), 41 (45), 69 (38), 65 (11), 53 (8), 77 (7), and 162 (6). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.51; H, 8.68.

The pmr spectrum of 13 shows the following peaks: δ 7.0 (m, 4H), 6.2 (d of d [J = 19 cps, J = 10.4 cps], 1H); 5.25 (d of d [J = 10.4 cps, J = 1.5 cps], 1H); 5.28 (d of d [J = 19 cps, J = 1.5 cps], 1H); 1.44 (s, 6H) ppm. The ir spectrum of 13 (carbon tetrachloride solution) has strong absorptions at 3480 (broad), 2980, 1490, and 1190 (broad) cm^{-1}.

The pmr spectrum of 14 shows peaks at δ 7.0 (m, 4H); 6.05 (d of d [J = 10 cps, J = 18 cps], 1H); 5.10 (d of d [J = 10 cps, J = 1.8 cps], 1H); 5.10 (d of d [J = 18 cps, J = 1.8 cps], 1H); 1.35 (s, 6H) ppm. The ir spectrum of 14 (carbon tetrachloride solution) exhibits strong absorption at 3600, 3400 (very broad), 2980, 1510, and 1170 (broad) cm^{-1}.

Synthesis of 3-(4-hydroxyphenyl)-3-methylbutene (14)

1-(4-methoxyphenyl)-2-methylpropanol (16a). Magnesium (40.2 g, 1.68 mol) was placed in ether (500 ml). 2-Bromopropane (Matheson, Coleman, and Bell, 206.2 g, 1.68 mol) dissolved in ether (300 ml) was added dropwise over 1 hr. *p*-Anisaldehyde (Matheson, Coleman, and Bell, 228 g, 1.68 mol) dissolved in ether (100 ml) was added dropwise over 2 hr. The mixture turned white and solidified. It was allowed to sit for 2 hr, then sufficient cold dilute hydrochloric acid was added to break up the mass. The layers were separated and the aqueous phase was washed with ether. The combined ether layers were dried over anhydrous magnesium sulfate. Removal of the ether left 320 g of crude product. (Theoretical yield: 302 g. The crude product contained some residual ether. Actual yield, *ca*. 95%) The pmr spectrum shows peaks at δ 7.0 (m, 4H); 4.18 (d [J = 7 cps], 1H); 3.65 (s, 3H); 1.82 (d [J = 7 cps] of q [J = 6.5 cps], 1H); 0.95 (d [J = 6.5 cps], 3H); 0.71 (d [J = 6.5 cps], 3H) ppm. The ir spectrum (neat) shows strong absorption at 3400 (very broad), 2950, 1610, 1510, 1250, 1070, and 840 cm^{-1}.

1-(4-methoxyphenyl)-2-methylpropene (**17a**). Crude **16a** from the previous reaction (100 g) was added to oxalic acid dihydrate (25 g) and heated. Approximately 10 ml of a clear distillate was obtained at *ca*. 100°. The mixture was cooled and ether and water were added. The organic layer was dried over anhydrous magnesium sulfate and the ether was removed. The yield was 85 g (94%). The pmr spectrum shows peaks at δ 7.0 (m, 4H); 6.2 (s, broad, 1H); 3.7 (s, 3H); 1.8 (s, 6H) ppm. The ir spectrum (film) shows strong absorption at 2960, 1610, 1510, 1250, and 1070 cm^{-1}.

1-(4-methoxyphenyl)-2-methylpropene oxide (**18a**). Compound **17a** (32.4 g, 0.2 mol) was dissolved in dichloromethane (220 ml). The solution was chilled to 0° and a chilled slurry of powdered sodium acetate trihydrate (10 g) in 70% peracetic acid (FMC Corporation, 42 ml) was added dropwise over 15 min. The reaction temperature rose to 2.5° during the addition. After the addition was complete, the mixture was stirred at 0° for 10 min;

it was then allowed to rise to room temperature during 10 min. The solution was washed several times with water and then with aqueous 5% potassium carbonate until no more carbon dioxide was evolved. It was then washed with saturated aqueous sodium chloride and dried over anhydrous magnesium sulfate. Removal of the solvent left a yellow oil (23 g) which was vacuum distilled. The fraction distilling from 76-78° at 0.10 Torr (10 g) was used in the next step. The pmr spectrum shows peaks at δ 7.05 (m, 4H); 3.75 (m, 4H); 1.3 (s, 3H); 1.05 (s, 3H) ppm. The ir spectrum (film) shows strong absorption at 2950, 1610, 1510, 1250, 1040, and 800 cm^{-1}.

2,2-dimethyl-2-(4-methoxyphenyl)-acetaldehyde (**19a**). Compound **18a**(10 g) was dissolved in 90% formic acid (100 ml). There was a very slight exotherm and a light orange color appeared. Nitrogen was bubbled through the solution for 5 min and the solution was refluxed for 1 hr, during which time it turned red. A nitrogen blanket was maintained while the flask was cooled. Water and ether were added. The ethereal layer was washed several times with water, with saturated aqueous potassium carbonate until no more carbon dioxide was evolved, and then with saturated aqueous sodium chloride. It was then dried over anhydrous magnesium sulfate. Removal of the solvent left a cloudy yellow liquid (10.2 g) which was 90% pure by vpc. (Analysis was on a 16 in x $\frac{1}{8}$ in column of 10% Carbowax 20M on 60/80 mesh Chromosorb G, AW, DMCS treated, with temperature programming from 100^o to 210^o at 10^o/min.) Distillation yielded two fractions: 4.6 ml (bp 74-87^o, 0.04 Torr) and 3.0 ml (bp 86-87^o, 0.05 Torr). The pmr spectrum of the second fraction shows absorption at δ 9.35 (s, 1H); 6.95 (m, 4H); 3.7 (s, 3H); and 1.35 (s, 6H) ppm. The ir spectrum (film) shows the following strong absorptions: 2970, 1720, 1510, 1250 (broad), 1070, 840 cm^{-1}.

3-(4-methoxyphenyl)-3-methylbutene (20a). The apparatus for the reaction was baked dry with hot air from a "heat gun" while dry nitrogen flowed through the system. Methyltriphenylphosphonium bromide (Aldrich, 10.0 g, 0.028 mol) was suspended in benzene (55 ml). Phenyl lithium (Alfa Inorganics, 16 ml of a 2 M solution in 70 : 30 benzene : ether, 0.032 mol) was added via syringe. Some orange color appeared but not all the salt dissolved. The mixture was refluxed 1 hr. An additional 4 ml of the phenyl lithium solution was added and an immediate darkening of the orange color was seen. The mixture was refluxed another ½ hr and allowed to cool. Compound 19a (4.6 g, 0.026 mol) was added dropwise; a white precipitate appeared and the orange color of the solution became much less intense. The mixture was refluxed for ½ hr, then the solution was cooled and the benzene was removed. The residue was extracted with petroleum ether (30-60^o), and the petroleum ether was dried over anhydrous magnesium sulfate. Removal of the solvent left ca. 10 ml of yellow liquid. Distillation of the residue gave two fractions:

2.5 g (bp 51-58° at 0.05 Torr) and 1.7 g (bp 58-80° at 0.05 Torr). Vpc analysis (as in **19a**) showed the first fraction to be *ca.* 75% of one component with several impurities. The second fraction was about 90% pure. The pmr spectrum of the second fraction shows the following patterns: δ 7.0 (m, 4H); 6.0 (d of d [J = 18 cps, J = 10 cps], 1H); 4.94 (d of d [J = 10 cps, J = 1.5 cps], 1H); 4.96 (d of d [J = 18 cps, J = 1.5 cps], 1H); 3.65 (s, 3H); 1.35 (s, 6H) ppm. The ir spectrum (film) shows strong absorption at 2960, 1510, 1250, 1080, and 840 cm^{-1}.

3-(4-hydroxyphenyl)-3-methylbutene (**14**). Crude **20a** (second fraction from the distillation above, 0.4 ml) was placed in a heavy-walled (3 mm) Pyrex test tube. Aqueous methylamine (2.0 ml, 40%) was added. The mixture was degassed by the freeze-pump-thaw technique (two cycles) and sealed under a pressure of 5 x 10^{-4} Torr. The tube was heated at 185° for 24 hrs. After it had cooled, the tube was opened and the contents were extracted with ether and water. The ether layer was washed with 10% aqueous hydrochloric acid. It was then extracted with 10% aqueous sodium hydroxide. The sodium hydroxide solution was acidified and extracted with ether. The organic layer was dried over anhydrous magnesium sulfate and concentrated on the rotary evaporator. The residue was taken up in deuterochloroform. The pmr and ir spectra were identical to those of **14** isolated from the photolysis. Its vpc retention time under analytical conditions (as in quantum yield determinations, *vide* *infra*) was also identical to that of 14 isolated from the photolysis. A coinjection of the two gave only one peak; no broadening was seen.

Synthesis of 3-(2-hydroxyphenyl)-3-methylbutene (13)

1-(2-methoxyphenyl)-2-methylpropanol (16b). Magnesium turnings (24 g, 1 mol) were added to ether (250 ml). 2-Bromopropane (Matheson, Coleman, and Bell, 123 g, 1 mol), which had been freshly passed through grade I alumina, was dissolved in ether (250 ml) and added over $\frac{1}{2}$ hr. The mixture was stirred at reflux for 1 hr, then cooled to 0°. *o*-Anisaldehyde (Matheson, Coleman, and Bell, 136 g, 1 mol, freshly distilled--bp 60.5° at 0.01 Torr) in ether (50 ml) was added dropwise. The contents of the flask solidified during the addition. After the addition was complete, the reaction mixture was broken up and added to 250 ml of cold dilute aqueous hydrochloric acid. More ether was added and the two phase system was stirred until all solids had dissolved. The ether layer was washed with 10% aqueous sodium hydroxide and with saturated aqueous sodium chloride. It was dried over anhydrous magnesium sulfate and concentrated on the rotary evaporator to yield an orange-yellow oil (166 g). The pmr spectrum shows peaks at δ 7.0 (m, 4H); 4.6 (t [J = 7 cps], 1H); 3.8 (s, 1H); 2.9 (d [J = 7 cps], 1 H); 1.93 (d [J = 7 cps], 1H); 1.0 (d [J = 7 cps], 3H); 0.85 (d [J = 7 cps], 3H) ppm, as well as peaks for ether and residual aldehyde.

1-(2-methoxyphenyl)-2-methylpropene (**17b**). The crude **16b** from the reaction above was added to oxalic acid dihydrate (19g). The mixture was heated and *ca.* 30 ml of volatile material was distilled below 60^{o}. Then 19 ml of distillate was collected (at *ca.* 100^{o}). The pot residue turned dark and syrupy. It was cooled and water and ether were added. The ether layer was washed with dilute aqueous sodium hydroxide and with saturated aqueous sodium chloride. The organic phase was dried over anhydrous magnesium sulfate and concentrated to yield a syrupy orange oil (140 g). Distillation of the material yielded 20 g (bp $60\text{-}67^{o}$ at 0.5 Torr). Analysis of the pmr spectrum indicated the product was *ca.*75% **17b** and *ca.* 25% **16b**. The pmr peaks attributable to **17b** are at δ 7.0 (m); 6.4 (s, broad, 1H); 3.70 (s, 1H); 1.9 (s, 1H); and 1.75 (s, 1H) ppm.

1-(2-methoxyphenyl)-2-methylpropene oxide (**18b**). The crude **17b** from the previous step was treated as in the synthesis of **18a**. The reaction workup was also the same and yielded a cloudy product (6.4 g) which was used in the next step. The pmr spectrum shows peaks at δ 7.0 (m); 3.75 (m); 1.5 (s, 3H); 1.05 (s, 3H) ppm.

2,2-dimethyl-2-(2-methoxyphenyl)-acetaldehyde (**19b**). The crude **18b** from the previous step was treated exactly as was **18a** in the previous synthesis of **19a**. The yield was 6 g of cloudy liquid. The pmr indicates an aliphatic aldehyde proton at δ9.6

ppm and an aromatic proton at δ 10.6 ppm in the ratio of 3 : 1. Pmr peaks due to 19b are at δ 9.6 (s, 1H); 7.0 (m); 3.8 (s); and 1.43 (s, 3H) ppm.

Methyltriphenylphosphonium iodide. Triphenylphosphine (Matheson, Coleman, and Bell, 26.2 g, 0.10 mol) was dissolved in benzene (100 ml). Methyl iodide (Matheson, Coleman, and Bell, 21.3 g, 0.15 mol), which had been passed through a plug of grade I alumina, was added to the solution. A white precipitate began forming within one minute. After 1 hr, the precipitate was collected on a coarse fritted glass filter and washed with benzene and with ether. After drying in a dark cupboard, the yield was 40 g (95%).

3-(2-methoxyphenyl)-3-methylbutene (20b). Methyltriphenylphosphonium iodide from the synthesis above (15 g, 0.037 mol) was suspended in 1,2-dimethoxyethane (DME, 100 ml). Phenyl lithium solution (16.8 ml of a 2.2 M solution in 30 : 70 benzene : ether, 0.037 mol) was added *via* syringe. A light orange solution formed over some remaining solid. The solution was refluxed for ½ hr. An additional 1 ml of phenyl lithium solution was added and the solution was refluxed for another ½ hr, by which time all the solid had dissolved. The solution was cooled to 0^{o}. Compound 19b (6 g , 0.034 mol) in DME (50 ml) was added dropwise over 15 min and a precipitate appeared. The mixture was allowed to warm to room temperature during ½ hr and was refluxed for 15 min. The reaction was worked up as in the synthesis of 20a to yield 5.2 g (87%) of yellow oil. The pmr spectrum shows peaks for 20b at δ 7.0 (m); 6.28 (d of d [J = 18 cps, J = 10 cps], 1H); 5.0 (m, 2H); 3.80 (s, 3H); and 1.45 (s, 3H) ppm, but impurities were present in about equal integral count.

3-(2-hydroxyphenyl)-3-methylbutene (13). Ethanethiol (Eastman Organic Chemicals, 1 ml) was added to a suspension of sodium hydride (Alfa Inorganics, 0.67 g of a 57% dispersion) in N,N-dimethylformamide (DMF, 40 ml). Crude 20b from the previous reaction (1 ml, *ca.* 50% pure) was added to the solution. The solution was heated to 150° during $\frac{1}{2}$ hr and held at that temperature for another $\frac{1}{2}$ hr. The solution became yellow and some precipitate was seen. The reaction mixture was cooled and was poured into cold aqueous 5% ammonium chloride. The solution was extracted several times with ether. The combined ether washings were dried over anhydrous magnesium sulfate and concentrated to leave a yellow oil (1 ml). Vpc analysis (as in the synthesis of 19a) showed one major and several minor components. The major compound was isolated by preparative vpc (column as in photoproduct isolation) at 142°. Its pmr and ir spectra and vpc retention time under analytical conditions were identical with those of 13 isolated from the photolysis.

Determination of Quantum Yields

Tetradecane (0.06 g) and **8** (0.05 g) were dissolved in isopropyl alcohol or cyclohexane (50.0 ml) A 4.0 ml aliquot of the solution was pipetted into each of seven quartz tubes (13 mm o. d.). In the case of isopropyl alcohol solutions, four of the tubes were degassed by the freeze-pump-thaw technique (3 cycles) and were sealed under a pressure of $< 5 \times 10^{-4}$ Torr. The cyclohexane solutions were not degassed. The optical density of a 1.0 cm path length of each solution was seen to be > 2 at 254 nm on a Beckman DU Spectrophotometer. The tubes were irradiated for different lengths of time (the longest irradiation causing *ca.* 10% conversion) at 254 nm in a merry-go-round apparatus (39). The light intensity was measured by potassium ferric oxalate actinometry (60).

The contents of the tubes were analyzed by vpc. The column used was a 3 ft x $\frac{1}{8}$ in column packed with 6.65% Carbowax 20M, 1.63% Castorwax (on 60/80 mesh Chromosorb G, AW, DMCS treated) with temperature programming from 90 to 190° at 6°/min. The detector response of **9** was found to be 61% of that of **8**. The disappearance of **8** and the appearance of photoproducts, relative to tetradecane, were plotted *vs.* irradiation time. Straight lines were obtained and slopes were calculated by the least squares method. Quantum yields for degassed and nondegassed isopropyl alcohol solutions were found to be identical within experimental error.

Irradiation of 10

Product 10 (ca. 0.01 g) was dissolved in 10 ml of cyclohexane. A 5 ml aliquot of this solution was irradiated through quartz at 254 nm with an Ultraviolet Products PCQ-XI lamp. Samples were withdrawn at intervals for analysis by vpc (as in quantum yield determinations).

Gas Phase Irradiations

Gas phase irradiations were carried out in an apparatus previously described (18a). Approximately 1 g of 8 was swept through the flow system every 24 hrs. In the irradiation of 8 alone, nitrogen (1000 cc/min) was used as the carrier gas, and 32 cc/min isobutylene was added to the flow system. To keep the starting material in the gas phase during the photolysis, the quartz irradiation tube was heated to 80°. In some experiments the isobutylene was replaced with 30 cc/min of nitric oxide. Irradiation at 254 nm was with a battery of Ultraviolet Products PCQ-XI lamps. In some experiments the procedure was repeated exactly as in the irradiations except that the lights were not turned on. Products of the photolysis were trapped in a Dry Ice-cooled glass helices-packed column and were extracted with ether. The ether extracts were analyzed by vpc as in the quantum yield determinations.

Attempt to Sensitize the Reaction of **8** with Acetone

A 2×10^{-3} *M* solution of **8** was prepared by diluting **8** (0.0086 g) and acetone (10.0 ml) to 25.0 ml with isopropyl alcohol. A 5.0 ml aliquot of this solution was placed in a Pyrex test tube and deoxygenated by bubbling in nitrogen. It was irradiated at 305 nm with a UV Products circular lamp. Analysis by vpc (column as in preparative photolysis) showed no decrease in the height of the peak corresponding to **8** and none of the products of photolysis of **8** appeared, even after irradiation overnight.

Comparison of Absorption Spectra of **8** and of Anisole

All glassware used in these determinations had been cleaned with soap and water. Immediately before use the glassware was rinsed several times with distilled water and then with methanol; it was then dried at 120°. Compound **8** was purified by preparative vpc on a 10 ft x $\frac{1}{4}$ in column of 20% Carbowax 20M (on 60/80 mesh Chromosorb W, AW) at 162°, followed by bulb-to-bulb vacuum distillation from lithium aluminum hydride. The anisole had been doubly distilled by Dr. M. T. McCall. Samples were prepared by diluting weighed amounts of anisole or **8** with cyclohexane until the concentrations were in the range needed for uv spectra (Cary 14 Spectrophotometer).

Determination of Relative Fluorescence Intensities of 8 and of Anisole

Anisole and 8 were purified by preparative vpc and bulb-to-bulb vacuum distillation from lithium aluminum hydride, as described above. Both were greater than 99.9% pure by analytical vpc (conditions as in quantum yield measurements). Solutions of anisole and of 8 in cyclohexane (purified by the method of Murray and Keller (62)) were prepared by dilution until a 1.0 cm path length of each had equal O D (0.095). Three quartz tubes (1.0 cm i.d.) fitted with grease seals and ground glass joints were filled with solutions of 8 or of anisole. They were degassed by the freeze-pump-thaw technique and sealed under a final pressure of $< 10^{-4}$ Torr. The fluorescence spectra and excitation spectra of both compounds were identical in band shape and position. The intensity of the emission from anisole was 22 times that of 8.

Attempt to See Phosphorescence from 8

Anisole (1 drop) was added to EPA (1 ml) and the solution was added to a phosphorescence tube which was then immersed in liquid nitrogen in the phosphorescence accessory of the Aminco-Bowman Spectrophotofluorometer. Strong emission with onset at *ca.* 350 nm was seen. The procedure was repeated with 8 but only very weak long wavelength emission was seen. The excitation spectrum of this weak emission did not match that of anisole.

REFERENCES

1. H. Kobsa, *J. Org. Chem.*, **27**, 2293 (1961).
2. J. C. Anderson and C. B. Reese, *Proc. Chem. Soc.*, 217 (1960).
3. H. Shizuka and I. Tanaka, *Bull. Chem. Soc. Jap.*, **42**, 909 (1969) and references therein.
4. D. P. Kelly, J. T. Pinhey, and R. Rigby, *Aust. J. Chem.*, **22**, 977 (1969) and references therein.
5. G. Koga, N. Kikuchi, and N. Koga, *Bull. Chem. Soc. Jap.*, **41**, 745 (1968).
6. F. L. Bach and J. C. Barclay, *Abstracts,* 150th National Meeting of the American Chemical Society, Atlantic City, New Jersey, Sept. 1965, p. 9s.
7. H. J. Hageman, H. L. Louwerse, and W. J. Mijs, *Tetrahedron,* **26**, 2045 (1970).
8. M. K. M. Dirania and J. Hill, *J. Chem. Soc.*, **C**, 1311 (1968).
9. H. J. Hageman, *Chem. Commun.*, 401 (1968).
10. Y. Ogata, K. Tagaki, and Y. Izawa, *Tetrahedron,* **24**, 1617 (1968).
11. J. T. Pinhey and K. Schnaffner, *Aust. J. Chem.*, **21**, 2265 (1968).
12. M. Fischer, *Chem. Ber.*, **101**, 731 (1968).

13. Y. Izawa and Y. Ogata, *J. Org. Chem.*, **35**, 3192 (1970).

14. C. Pac and S. Tsutsumi, *Bull. Chem. Soc. Jap.*, **37**, 1392 (1964).

15. H. Nozaki, T. Okada, R. Noyori, and M. Kawanisi, *Tetrahedron*, **22**, 2177 (1966).

16. J. C. Anderson and C. B. Reese, *J. Chem. Soc.*, 1781 (1963).

17. M. R. Sandner, E. Hedaya, and D. J. Trecker, *J. Amer. Chem. Soc.*, **90**, 7249 (1968).

18. (a) J. W. Meyer, Ph.D. Thesis, California Institute of Technology, Pasadena, California, 1971.

    (b) J. W. Meyer and G. S. Hammond, *J. Amer. Chem. Soc.*, **92**, 2187 (1970).

    (c) J. W. Meyer and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 2219 (1972).

19. R. B. Woodward and R. Hoffmann, *Angewandte Chemie Int. Ed.*, **8**, 781 (1969).

20. R. W. Murray and M. L. Kaplan, *J. Amer. Chem. Soc.*, **88**, 3527 (1966).

21. R. F. C. Brown, R. C. Cookson, and J. Hudel, *Tetrahedron*, **24**, 3955 (1968).

22. M. S. Kharasch, G. Stampa, and W. Nudenberg, *Science*, **116**, 309 (1952).

23. K. Schmid and H. Schmid, *Helv. Chim. Acta*, **36**, 687 (1953).

24. R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 2511 (1965).

25. D. P. Kelly, J. T. Pinhey, and R. D. G. Rigby, *Aust. J. Chem.*, **22**, 977 (1969).

26. H. Shizuka, T. Morita, Y. Mori, and I. Tanaka, *Bull. Chem. Soc. Jap.*, **42**, 1831 (1969).

27. H. Shizuka, *Bull. Chem. Soc. Jap.*, **42**, 52 (1969).

28. G. Porter in "Reactions of Free Radicals in the Gas Phase," Special Publication No. 9, The Chemical Society (London), 1957, pp. 139-149.

29. G. Porter and E. Strachan, *Trans. Faraday Soc.*, **54**, 1595 (1958).

30. Kelly *et al*. (25) investigated the photochemistry of **8** but identified only **9**, **11**, and **15** as reaction products. Furthermore, their study lacked the quantitative character needed here.

31. R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, 1967, p. 84.

32. J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, New York, 1959, p. 238.

33. (a) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., New York, 1967, p. 241.

(b) Ibid., p. 24.

34. J. H. Conant and A. H. Blatt, J. Amer. Chem. Soc., **50**, 551, (1928).

35. H. Kristinsson and G. S. Hammond, J. Amer. Chem. Soc., **89**, 5968 (1967).

36. D. Reif and H. O. House, Org. Syn., Coll. Vol. IV, p. 860.

37. (a) F. L. Benton and T. E. Dillon, J. Amer. Chem. Soc., **64**, 1128 (1942).

(b) J. F. W. McOmie, M. L. Watts, and D. E. West, Tetrahedron, **24**, 2289 (1968).

38. I. M. Lockhart and N. Webb, Chem. and Ind., 1230 (1970).

39. G. I. Feutrill and R. N. Mirrington, Tetrahedron Letters, 1327 (1970).

40. F. G. Moses, R. S. H. Liu, and B. M. Monroe, Mol. Photochem., **1**, 245 (1969).

41. (a) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, London, 1970, pp. 103-106.

(b) Ibid., p. 122.

42. J. Heicklen and N. Cohen, Adv. Photochem., **5**, 157 (1968).

43. M. F. R. Mulcahy and D. J. Williams, Nature, **199**, 761 (1963).

44. The relationships used in these calculations are discussed in N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, 1967, and have been similarly used in two previous publications: J. C. Dalton and N. J.

Turro, *J. Amer. Chem. Soc.*, **93**, 3569 (1971); H. E. Zimmerman and A. A. Baum, *J. Amer. Chem. Soc.*, **93**, 3646 (1971).

45. E. C. Sanford and G. S. Hammond, *J. Amer. Chem. Soc.*, **92**, 3497 (1970) and references therein.

46. I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, 1965 , p. 65.

47. F. A. Carroll, this dissertation, p. 111.

48. P. S. Engel and B. M. Monroe, *Adv. Photochem.*, **8**, 245 (1971).

49. H. Morrison and R. Pfeiffer, *J. Amer. Chem. Soc.*, **90**, 3428 (1968).

50. J. Saltiel, K. R. Neuberger, and M. Wrighton, *J. Amer. Chem. Soc.*, **91**, 3658 (1969).

51. J. J. Houser and M.-C. Chen, *Chem. Commun.*, 1447, (1970).

52. P. J. Wagner and G. S. Hammond, *Adv. Photochem.*, **5**, 21 (1968).

53. W. Siebrand and D. F. Williams, *J. Chem. Phys.*, **49**, 1860 (1968).

54. G. S. Hammond, *Adv. Photochem.*, **7**, 369 (1969).

55. A. Heller, *Mol. Photochem.*, **1**, 257 (1969).

56. H. Baba, *Bull. Chem. Soc. Jap.*, **34**, 76 (1963).

57. W. Ferree, Jr., J. B. Grutzner, and H. Morrison, *J. Amer. Chem. Soc.*, **93**, 5502 (1971).

58. F. A. Carroll, L. Lorenc, and G. S. Hammond, unpublished results.

59. J. Jortner, S. A. Rice, and R. M. Hochstrasser, *Adv. Photochem.*, **7**, 149 (1969).

60. B. R. Henry and M. Kasha, *Ann. Rev. Phys. Chem.*, **19**, 161 (1968).

61. The basic procedure was that used in Ref. 18(a). The quantum yield for the ferric oxalate reaction was taken to be 1.25 at 254 nm.

62. E. C. Murray and R. N. Keller, *J. Org. Chem.*, **34**, 2234 (1969).

PART II

The Role of Charge Transfer Interactions in the Quenching of 1,4-Dimethoxybenzene Fluorescence

INTRODUCTION

One active area of photochemical research in recent years has been study of the quenching of the fluorescence of electronically excited molecules by compounds having lowest-lying excited singlet states higher in energy than those of the quenchees.

A particularly active field of study has been the quenching of excited singlets of naphthalene derivatives by conjugated dienes. The problem had its origin in a method devised by Lamola and Hammond (1) for measuring the intersystem crossing yields of aromatic hydrocarbons. The energy of the lowest-lying singlet of conjugated dienes, though not known with certainty, is thought to be about 120 kcal/mole, considerably higher than that of naphthalene (ca. 91 kcal/mole) (2). However, the diene triplet, about 57 kcal/mole higher in energy than its ground state, is lower than the energy of the naphthalene triplet, 61 kcal/mole (2). Thus when naphthalene is irradiated, decay of its S_1 states should not be influenced by the presence of diene molecules; the excited naphthalene should show the same quantum yields of fluorescence, intersystem crossing, and radiationless decay as in the absence of diene. The naphthalene triplets, however, should be rapidly quenched by the diene to give the naphthalene ground state and the diene triplet, which would then undergo a characteristic reaction such as cis-trans isomerization or dimerization. By measuring the amount of diene reaction, the number of naphthalene triplets which had been formed could be determined. Dividing this number by the number of naphthalene molecules which had been excited gave a measure of the efficiency of naphthalene intersystem crossing (Φ_{isc}). Lamola and Hammond used this technique to measure Φ_{isc} for a number of aromatic compounds (1).

A surprising observation in these studies was that the intersystem crossing yield determined by this method was a function of diene concentration (2). Above a certain level which was required to quench all the naphthalene triplets, the value of Φ_{isc} determined by the method of Lamola and Hammond decreased with increasing diene concentration.

The problem was studied in detail by Stephenson, Whitten, Vesley, and Hammond (2-5), who found that the intensity of naphthalene fluorescence was decreased by the addition of diene. This result suggested that diene molecules could interact with excited naphthalene singlets in a process leading to decay of the energy of electronic excitation. The kinetic data were consistent with a very simple bimolecular mechanism (eq 1):

$$A^* + Q \xrightarrow{k_q} A + Q \qquad (1)$$

The rate constant k_q is determined from the Stern-Volmer kinetic formulation (eq 2) in which I_f and I_f^o are the fluorescence intensities in the presence and absence of quencher, τ_s is the singlet lifetime of the quenchee, and [Q] is the quencher concentration.

$$I_f^{o}/I_f \quad = \quad 1 \quad + \quad k_q \tau_s[Q] \qquad (2)$$

Stephenson (2) proposed three general models to explain the quenching phenomenon. The first was chemical quenching which considered that an adduct between the excited naphthalene and the diene might decay to the ground states of both molecules. While there was no firm evidence against this model, the extremely low quantum yield for naphthalene disappearance ($\Phi_{diss} < 0.01$ when 90% of S_1 states are quenched) suggested that any intermediate could not lie too far in the direction of chemical adduct along a reaction coordinate.

The second model considered was a charge transfer interaction. Stephenson studied a large number of substituted dienes and found that in general substitution of methyl groups on the basic diene skeleton produced several changes: a lowering of the diene S_1 energy, a lowering of the diene ionization potential, an increasing of the electronic polarizability, and an increasing of steric repulsion. Since molecular properties are so closely related, correlating quenching rate constants with ionization potentials for a simple charge transfer model (eq 3) gave fair correlations, but not much better than correlations of quenching with other molecular parameters, such as boiling points (2).

$$A^{*(1)} \quad + \quad D \quad \xrightarrow{k_q} \quad (A^{-}D^{+})^{*} \quad \xrightarrow{\text{fast}} \quad A \quad + \quad D \qquad (3)$$

The third model proposed by Stephenson was the exciton delocalization model (eq 4):

$$A^{*(1)} + Q \longrightarrow (A^{*}\cdot\cdot Q \longleftrightarrow A\cdot\cdot Q^{*}) \longrightarrow A + Q \qquad (4)$$

This model predicts that correlations between singlet excitation energies and quenching rates should appear. The first excited singlet energy level of dienes are not accurately known (2), but the best available estimates gave structure-reactivity correlations which were about as good as those obtained from the charge transfer model.

The theoretical advantage of this last model is that it considered the excitation energy of the naphthalene to have access to the rapid non-radiative decay modes of the dienes (Conjugated dienes typically show no fluorescence). That some of the energy of the electronic excitation can be dissipated through the quencher is evidenced by the rearrangement of quadricyclene to norbornadiene (6) and the racemization of optically active sulfoxides (7) when naphthalene fluorescence is quenched by quadricyclene and aryl alkyl sulfoxides, respectively.

This specific description of the singlet quenching interaction has provided the basis for a more general model of quenching phenomena (8): quenching is thought to proceed through the reversible formation of an exciplex (eqs 5 and 6) which can decay to the ground electronic states of both quencher and quenchee by dissipating energy through the vibrational modes of each.

$$A^* + Q \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{exciplex}}{(AQ)^*} \qquad (5)$$

$$\begin{tikzcd}
(AQ)^* \arrow[r, "k_2"] & A^{*(vib)} \arrow[d] & + & Q^{*(vib)} \arrow[d] & (6) \\
& A & & Q \text{ or other products} &
\end{tikzcd}$$

The binding energy of the exciplex is seen to arise from many factors, including exciton delocalization and charge transfer interactions (eq 7), but binding interactions (eq 5) may be distinct from radiationless decay processes (eq 6).

$$(AQ)^* \equiv A^*Q \longleftrightarrow AQ^* \longleftrightarrow A^+Q^- \longleftrightarrow A^-Q^+ \qquad (7)$$

While this model was being developed, however, work being done in related areas was advancing a quite different viewpoint about the nature of singlet quenching. Weller (9), Van (10), and others had been studying the reactions of excited molecules and had observed quenching of the fluorescence of aromatic hydrocarbons by aliphatic and aromatic amines. They had shown that in many cases the quenching is accompanied by broad, structureless emission to the red of normal fluorescence. The results suggested a charge transfer interaction in which the amine was thought to donate a nonbonding electron to the excited molecule to form an exciplex which could emit exciplex fluorescence or separate into ion radicals (eq 8):

$$\begin{tikzcd}
A^* \arrow[r, "NR_3"] \arrow[d, "h\upsilon"] & (\overset{-}{\dot{A}}\ \overset{+}{\dot{N}}R_3) \arrow[r] \arrow[d, "h\upsilon"] & \overset{-}{\dot{A}} + \overset{+}{\dot{N}}R_3 & (8) \\
A & A + NR_3 & &
\end{tikzcd}$$

The separated radical ions have been identified by flash spectroscopy in some cases. When these radical ions are generated independently and are allowed to diffuse together, emission is seen which is identical to that seen from the exciplex formed from NR_3 quenching of A*. As solvent polarity increases, two effects on the exciplex emission are noted: (1) the polar exciplex is stabilized, so the emission moves to longer wavelength and (2) the stability of the radical ions also increases; more exciplexes separate and the exciplex emission becomes less intense (9,10).

Since that time Weller and coworkers have begun to apply this type of charge transfer description to an increasing number of quenching processes. In 1969 Solomon, Steel, and Weller (11) wrote the change in free energy for formation of a charge transfer exciplex as eq 9, in which A and D represent an acceptor and donor in an electron transfer process and $^1\Delta E_A$ is the singlet excitation energy of A, IP_D is the ionization potential of D, EA_A is the electron affinity of A, and C is the Coulombic energy gained by bringing A^- and D^+ from infinity to a distance X apart in solution.

$$\Delta F \cong -{}^1\Delta E_A + IP_D - EA_A - C \qquad (9)$$

Even though electron affinities are not accurately known, they may be estimated from polarographic reduction potentials, $E_{\frac{1}{2}}$, by eq 10 in which ΔF_{sg} is the change in free energy for the reaction $A_{solution} + A^-_{gas} \longrightarrow A^-_{solution} + A_{gas}$.

$$EA_A = E_{\frac{1}{2}} + \Delta F_{sg} + \text{constant} \qquad (10)$$

Solomon, Steel, and Weller concluded that for a series of acceptors, a constant donor, and the same solvent, eq 11 should hold.

$$\Delta F = \text{constant} - [{}^{1}\Delta E_A + E_{\frac{1}{2}}] \qquad (11)$$

These workers obtained a good correlation between log k_q and the right side of eq 11 for quadricyclene quenching singlets of a large number of naphthalene compounds and concluded that the stabilization of the exciplex was largely charge transfer (eq 12):

$$(AD)^* \equiv (A^*D) \longleftrightarrow (A^-D^+) \qquad (12)$$

Since piperylene showed a similar structure-reactivity pattern (eq 11) with selected naphthalenes, they concluded that charge transfer stabilization might be significant in that case also. They also suggested as an explanation for the observed naphthalene-sensitized rearrangement of quadricyclene to norbornadiene that the quadricyclene radical cation involved in the exciplex could, in accepting an electron through radiationless decay of the exciplex, relax either to quadricyclene or norbornadiene.

Subsequently, Evans (12) contrived another kinetic formulation for analysis of singlet quenching processes. In this model the concept of a "proximity pair" (A^*/Q) is introduced and irreversible radical ion pair formation is seen to occur at rate k_q' (eqs 13 and 14).

$$A^{*(1)} \quad + \quad Q \quad \underset{k_{-q}}{\overset{k_{\text{diff}}}{\rightleftharpoons}} \quad (A^*/Q) \quad \xrightarrow{k_r} \quad (A^-Q^+) \qquad (13)$$

$$I_o/I \quad = \quad 1 \quad + \quad k_q'\tau_s[Q] \qquad (14)$$

The term k_{diff} is the rate constant for diffusion of A^* and Q together, k_{-q} is the rate constant for diffusion out of the solvent cavity, and k_r is the rate constant for the irreversible quenching step. In this formulation k_q' is given by eq 15:

$$k_q' \quad = \quad \frac{k_{\text{diff}}\ k_r}{k_{-q} + k_r} \qquad (15)$$

With this kinetic scheme, Evans arrived at the relation of eq 16, where IP is the ionization potential of the donor and C is the Coulombic term again.

$$\ln \frac{k_q'}{k_{\text{diff}} - k_q'} \quad \propto \quad IP \quad + \quad C \qquad (16)$$

The real difference between this model and that of Solomon, Steel, and Weller (eq 11) is that this formulation straightens the curvature in plots of log k_q vs. ionization potential which appear as the quenching rate approaches the rate of diffusion. For reactions in which $k_r \ll k_{\text{diff}}$ in eq 14, the encounter complex need not appear in the simplest kinetic formulation for the system (13).

Using eq 16 and published quenching rate constants, Evans was able to obtain a linear correlation for quenching of acridine fluorescence by a series of amines. He then applied the same equation to the quenching of naphthalene fluorescence by a series of dienes, quadricyclene, and norbornadiene. The fit for the dienes was fair--the linear correlation coefficient was 0.939. Interestingly, however, quadricyclene and norbornadiene showed great deviation from the diene line. This behavior was puzzling in view of Solomon, Steel, and Weller's assertion that quadricyclene quenched by a charge transfer interaction also (11).

Rehm and Weller (14) have since developed a more detailed kinetic model which they have applied to a number of charge transfer interactions. This description is based on the premise that electronic excitation, in raising an electron from a filled orbital to an unfilled one, both decreases the ionization potential and increases the electron affinity of the excited state over the ground state. This property might then give rise to electron transfer reactions between excited aromatic molecules and either donor or acceptor molecules in solution. Rehm and Weller's kinetic formulation (eq 17), like that of Evans, includes terms for diffusion together (k_{12}) and apart (k_{21}) of the quencher and quenchee.

$$\begin{tikzcd}
F^* \arrow[d, "1/\tau"] & + & Q \arrow[r, shift left, "k_{12}"] & F^* \cdots Q \arrow[l, shift left, "k_{21}"] \arrow[r, shift left, "k_{23}"] & {}^2F^{\dot{\mp}} \cdots {}^2Q^{\dot{\pm}} \arrow[l, shift left, "k_{32}"] \arrow[d, "k_{30}"] & (17) \\
F & & & & F + Q &
\end{tikzcd}$$

The rate constant k_{30} measures all possible paths for disappearance of the radical ion pair, such as diffusion apart or back transfer of the electron to give triplet or ground states. The rate constant k_{23} is the rate of the actual electron transfer which forms the exciplex and k_{32} is the rate constant for the reverse step.

By applying the steady state approximation to the transient species involved, Rehm and Weller were able to derive an expression (eq 18) for the experimental k_q measured in a typical Stern-Volmer plot.

$$k_q = \frac{k_{12}}{1 + \frac{k_{21}}{k_{23}} + \frac{k_{21}}{k_{30}} \cdot \frac{1}{K_{23}}} \qquad (18)$$

The last fraction in the denominator has the significance given in eq 19, where ΔG_{23} is the free enthalpy change for the actual electron transfer in going from the encounter complex to the ion pair.

$$K_{23} = k_{23}/k_{32} = \exp(-\Delta G_{23}/RT) \qquad (19)$$

This value can be calculated from eq 20 in which $E[D/D^+]$ represents the oxidation potential of the electron donor, $E[A^-/A]$ is the reduction potential of the acceptor, $e_o^2/\epsilon x$ is the change in free enthalpy for bringing the two radical ions to encounter distance x in a solvent of dielectric constant ϵ, and $\Delta E_{o,o}$ is the energy of electronic excitation.

$$\Delta G_{23} \;=\; 23.06(E[D/D^{+}] \;-\; E[A^{-}/A] \;-\; e_{o}^{2}/\epsilon x) \;-\; \Delta E_{o,o} \qquad (19)$$

Through arguments about solvent properties, approximations concerning the relative shape and size of reactants, and by fitting the activation free enthalpy to the experimental data for an isoenthalpic electron transfer, Rehm and Weller concluded that in acetonitrile experimental k_q values for all charge transfer quenching processes would be given by eq 21:

$$k_q \;=\; \frac{2 \times 10^{10}\ \underline{M}\,\mathrm{sec}^{-1}}{1 \;+\; 0.25(\exp(\Delta G_{23}^{\ddagger}/RT) \;+\; \exp(\Delta G_{23}/RT))} \qquad (21)$$

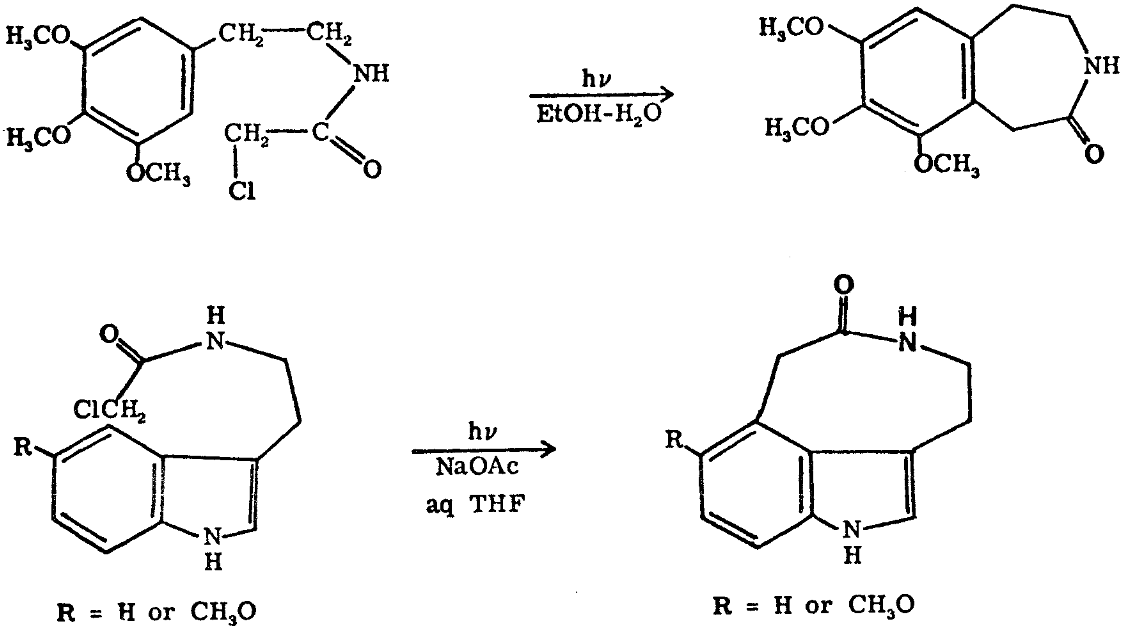
where

$$\Delta G_{23}^{\ddagger} \;=\; [\,(\Delta G_{23}/2)^{2} \;+\; (2.4\ \mathrm{kcal/mole})^{2}] \;+\; \Delta G_{23}/2 \qquad (22)$$

It should be emphasized that eq 22 is an empirical formula chosen to fit the experimental data. Nevertheless, Rehm and Weller claim that eq 21 should predict within a factor of 2 the rate constants for all quenching processes in acetonitrile which proceed by a charge transfer mechanism. Using this equation they report predicting from spectroscopic and electrochemical data the rate constants for quenching in more than 60 donor-acceptor systems with k_q values ranging from 10^{6} to 2×10^{10} $\underline{M}^{-1}\mathrm{sec}^{-1}$. Rehm and Weller did not consider the quenching of naphthalene fluorescence by strained hydrocarbons or by conjugated dienes. They did report the quenching of naphthalene fluorescence by tetracyanoethylene, 1,4-dicyanobenzene, and benzonitrile (in order of decreasing rate constants)--interactions in which the excited singlet was thought to act as the electron donor.

It was the prospect of investigating such quenchee to quencher charge transfer interactions which gave rise to the present study. The direct impetus for the present investigation was a series of reports by Witkop and coworkers, who have been investigating photocyclizations. They have reported a number of reactions of this type, among them those in Scheme I (15).

Scheme I



Although the lower energy chromophore in each molecule is the aromatic function, the results indicate that the chloroacetamide function must interact with it. McCall, Hammond, et al. began a study of the intermolecular interactions of chromophores such as those in Scheme I and found that chloroacetamide and methyl chloroacetate were efficient quenchers of such "electron-rich" aromatic molecules as indole or 1,4-dimethoxybenzene (16). Table I summarizes the results of that study. The observation that k_q increases on going from naphthalene to 2-methoxynaphthalene to 2,6-dimethoxynaphthalene, and from benzene to anisole to 1,4-dimethoxybenzene, suggested that charge transfer from the aromatic molecule to the quencher might accompany the quenching process.

The purpose of the study reported in this section was to extend the investigation of McCall et al. by determining the structure-reactivity relationships for the quenching of 1,4-dimethoxybenzene fluorescence by other organic compounds and to use the results to evaluate various models for the quenching interaction.

TABLE I. Rate Constants for Quenching of Fluorescence by Methyl Chloroacetate[a,c] (l. sec^{-1} mol^{-1})

	Solvent		
Compound	Acetonitrile	Hexane	τ_o[b]
Indole	4.2×10^9	1.4×10^{10}	8.5
Anisole	1.1×10^9	1.5×10^9	9.5
1, 4-Dimethoxybenzene	5.5×10^9	1.2×10^{10}	2 ± 1
N, N-Diethylaniline	8.9×10^9		3 ± 0.5
Naphthalene	4.0×10^6		95
2-Methoxynaphthalene	2.4×10^7		17.5
2, 6-Dimethoxynaphthalene	5.6×10^7	1.8×10^7	11.5

[a] Emission spectra from degassed solutions were recorded by an Aminco Spectrophotofluorometer. [b] Lifetime in nanoseconds determined by a TRW Model 31A nanosecond spectral source coupled to a Tektronix Type 556 dual beam oscilloscope. [c] From M. T. McCall, G. S. Hammond, O. Yonemitsu, and B. Witkop, J. Amer. Chem. Soc. **92**, 6991 (1970).

RESULTS AND DISCUSSION

1,4-Dimethoxybenzene (DMB) was chosen for further study for several reasons. The fact that it is a solid at room temperature makes it easy to purify and store. Since it absorbs light at 310 nm, fluorescence studies can be carried out in Pyrex glassware. Finally, it is suitable for use as a quenchee for a study of this type because its fluorescence is quenched by a number of organic compounds.

Since the value determined experimentally from a Stern-Volmer plot of relative fluorescence intensity vs. quencher concentration is the slope, $k_q\tau_s$ (cf., eq 2), it is necessary to know τ_s in order to know k_q. McCall (16) used the value 2 ± 1 nsec, which he determined experimentally using a TRW nanosecond spectral source coupled with a Tektronix Type 556 Dual Beam Oscilloscope, as has been described (8). However, Berlman reports τ_s to be 2.9 nsec in cyclohexane and 2.7 nsec in ethanol (17). These values were determined by the single photon counting technique (18), which enables one to measure lifetimes of 1 nsec or less with an accuracy of ± 10%.

In order to determine more accurately the lifetime of DMB in acetonitrile, the absorption spectra and fluorescence spectra of DMB in ethanol and acetonitrile were compared. The absorption spectrum of DMB in acetonitrile was approximately 2% less intense and its absorption maximum was shifted 2 nm to the red compared to that measured in ethanol. The integrated absorption spectrum of DMB in the two solvents is the same, within experimental error (ca. ± 10%). Thus, the natural lifetime, τ_s^o, of DMB in the solvents is the same within the experimental uncertainty of ± 10% (19). The fluorescence spectra (corrected for phototube response) were also identical within experimental error, although the quantum yield of fluorescence in acetonitrile was 2% less than that in ethanol and the fluorescence maximum was also shifted 2 nm to the red (21). Since $\tau_s = \Phi_f \tau_s^o$, it must be concluded that the lifetime of DMB singlets in acetonitrile is also 2.7 ± 0.3 nsec. This value will be used below.

Early experiments demonstrated that the quenching of DMB fluorescence was not limited to chloroacetamide and methyl chloroacetate. A number of other organic chlorides were investigated, and the results are summarized in Table II. All quenching studies were conducted in degassed acetonitrile solutions. As evidenced by their absorption spectra, all the quenchers had lowest-lying excited singlets higher than that of DMB. The k_q values were calculated from the slopes of Stern-Volmer plots which are accurate to within ± 10%. In all cases the unquenched portion of the fluorescence had the same spectral distribution as that observed in the absence of quencher. No new emission was detected in either acetonitrile or benzene solution.

The k_q's for the para-substituted benzyl chlorides yield a linear Hammett correlation with σ_ρ as shown in Figure 1.

TABLE II. Rate Constants for the Quenching of 1,4-Dimethoxybenzene Fluorescence by Organic Chlorides

Quencher	k_q($\underline{M}^{-1}$sec^{-1})
Cl-CH_2CN	9.6×10^9
p-Cl$C_6H_4CH_2$-Cl	8.9×10^{9a}
p-F$C_6H_4CH_2$-Cl	6.2×10^{9a}
$C_6H_5CH_2$-Cl	5.6×10^{9a}
p-$CH_3C_6H_4CH_2$-Cl	4.1×10^{9a}
Cl-CH_2COOCH_3	4.1×10^{9a}
CH_2=$CHCH_2$-Cl	2.0×10^{9a}
Cl-CH_2CONH_2	8.9×10^{8a}
Cl-CH_2OCH_3	1.2×10^{8a}
Cl-$CH_2CH_2CH_3$	$< 10^{6b}$

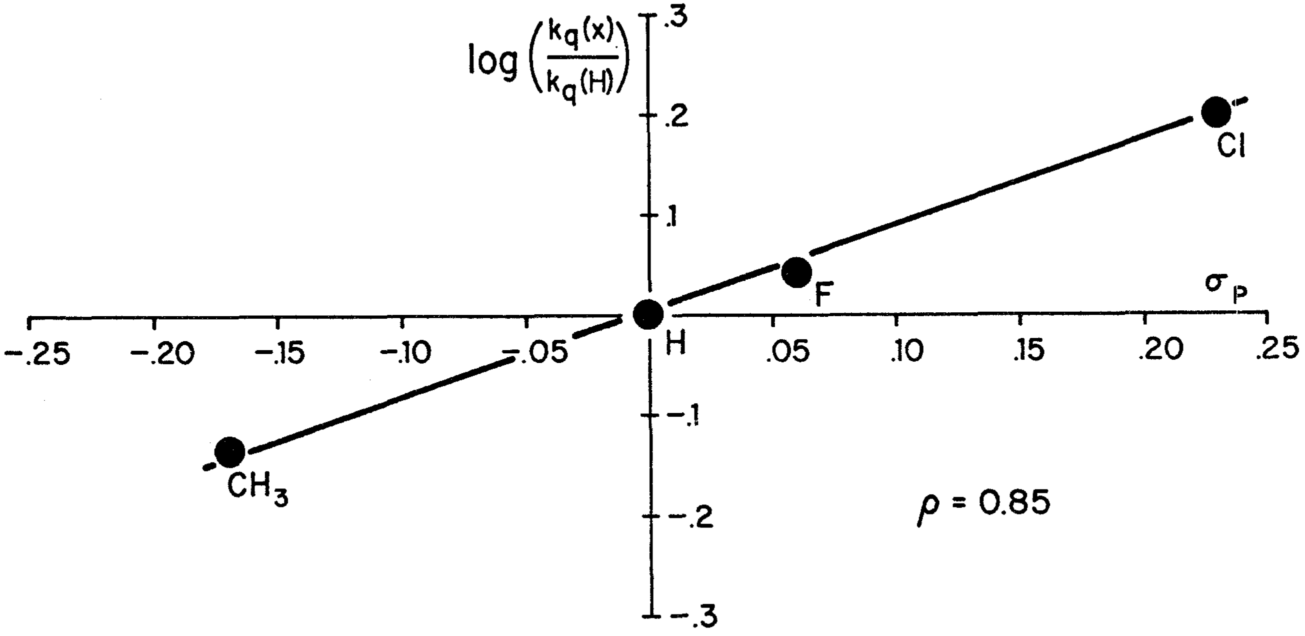
[a] Corrected from the data of McCall (23). [b] No fluorescence quenching was detected. This is an estimate of the upper limit of k_q.

Figure 1

Hammett Correlation in the

Quenching of 1, 4-Dimethoxybenzene

Fluorescence by p-X-$C_6H_4CH_2$-Y



The value of ρ calculated from this plot is 0.85.

It was also found that a carbon-chlorine bond is not a requirement for efficient quenching. Table III lists the rate constants for quenching DMB fluorescence by a number of additional compounds. The k_q values for the para-substituted benzyl acetates also show a linear Hammett correlation, with ρ equal to 5.2. Attempts to prepare para-substituted benzyl mesylates were successful only with p-chlorobenzyl mesylate and with benzyl mesylate itself. While there is no certainty that a linear Hammett plot would be obtained with the mesylates, the value of ρ determined from these two points is 0.14. The dependence of k_q on para-substitution for the three benzyl systems investigated here is summarized in Table IV.

These results suggest quite strongly that charge transfer from the excited molecule to the quencher occurs during the quenching process. A positive value of ρ in a Hammett plot is usually considered as evidence for some degree of negative charge at the transition state in the rate-determining step of the reaction under consideration. The relative values of the ρ's in Table IV do not, however, provide much insight into the precise nature of the quenching interaction.

As was pointed out in the Introduction (cf., eqs 5 and 6), in general quenching interactions structure-reactivity relationships may have an effect on either: (1) the binding energy of the exciplex, (2) the radiationless decay of the exciplex, or (3) both.

TABLE III. Rate Constants for the Quenching of 1,4-Dimethoxybenzene Fluorescence

Quencher	$k_q(\underline{M}^{-1}sec^{-1})$
$\underline{p}$-$ClC_6H_4CH_2$-OAc	4.1×10^9
$C_6H_5CH_2$-OAc	3.7×10^8
$\underline{p}$-$FC_6H_4CH_2$-OAc	5.2×10^8
$\underline{p}$-$CH_3C_6H_4CH_2$-OAc	3.0×10^7
CH_2=$CHCH_2$-OAc	1.0×10^7
$\underline{p}$-$ClC_6H_4CH_2$-OMs	6.2×10^9
$C_6H_5CH_2$-OMs	4.4×10^9
CH_2=$CHCH_2$-OMs	7.4×10^8
Trifluoroacetic Anhydride	1.0×10^{10}
Ethyl Trifluoroacetate	1.6×10^9
Acetic Anhydride	1.5×10^8

TABLE IV. Substituent Effects on Quenching by p-$XC_6H_4CH_2$-Y

$X = CH_3$, H, F, Cl

Y	ρ
OAc	5.2
Cl	0.85
OMs	0.14[a]

[a] Determined for X = H, Cl only.

These effects are related kinetically to the rate constants k_1 (and k_{-1}) and k_2, respectively, in eqs 5 and 6. In this formulation the experimental rate constant k_q has the significance shown in eq 23:

$$k_q = \frac{k_1 k_2}{k_{-1} + k_2} \tag{23}$$

If k_2 is much larger than k_{-1}, the relation for k_q reduces to the form shown in eq 24:

$$k_q \cong k_1 \tag{24}$$

In other words, the experimental k_q will be governed by factors which determine k_1, regardless of the nature of the radiationless decay step, k_2. On the other hand, if k_2 is slow relative to k_1 and k_{-1}, the relation for k_q reduces to the form shown in eq 25:

$$k_q = k_1 k_2 / k_{-1} = K k_2 \tag{25}$$

That is, the rate of radiationless decay of the excitation will be attenuated by the equilibrium constant K. If eq 24 holds, the effect of charge transfer on variations of k_q may be attributed to corresponding variations of k_1. This is the assumption made by Solomon, Steel, and Weller (11) and by Evans (12). If eq 25 holds, however, charge transfer effects might be observed on either or both K and k_2.

The use of the term "charge transfer interaction" in the present discussion should not be interpreted to mean, as do Solomon, Steel, and Weller (11) or Evans (12), the irreversible formation of a radical cation--radical anion pair. Such an interaction must necessarily give rise to the thermodynamic formulation of eq 9. For the quenching of one excited molecule by a series of quenchers which act as electron acceptors, eq 9 reduces to the form of eq 26; *i.e.*, there should emerge a linear correlation between log k_q and quencher reduction potential.

$$\log k_q = c_1 + c_2 E_{\frac{1}{2}} \tag{26}$$

This relationship is the analog of the linear correlation expected between log k_q and quencher ionization potential when one excited compound is quenched by a series of electron donors (11, 12). It follows directly from the equation for log k_q in the general charge transfer case (*cf.*, eqs 18, 19, 20, and references 11 and 12) if the Coulombic term is constant for the series of radical ion pairs. Rehm and Weller (14) have shown this to be true for charge transfer complexes which show ranges of molecular dimensions and charge transfer exothermicity at least as great as for those complexes which might be generated in the present study (The application of the more detailed eq 21 to the present study will be discussed below).

If charge transfer leads to irreversible formation of a radical ion pair in the quenching of DMB fluorescence, a correlation in the form of eq 26 would be predicted. However, it should be emphasized that although such a mechanism might predict the relationship shown in eq 26, the converse is not true. A similar correlation could arise from distinctly different interactions (vide infra).

To evaluate eq 26 for the quenching of DMB fluorescence, the reduction potentials of a number of quenchers used in this study were determined. The measurements were made at a carbon electrode in N,N-dimethylformamide (DMF) containing 0.01 M tetraethylammonium perchlorate as the supporting electrolyte. Control experiments in which reduction potentials of selected quenchers were determined at the carbon electrode in acetonitrile containing 0.01 M tetraethylammonium perchlorate as supporting electrolyte or at the dropping mercury electrode in DMF containing the same concentration of tetraethylammonium perchlorate ruled out significant solvent or electrode effects as important factors in determining relative values of the reduction potentials.

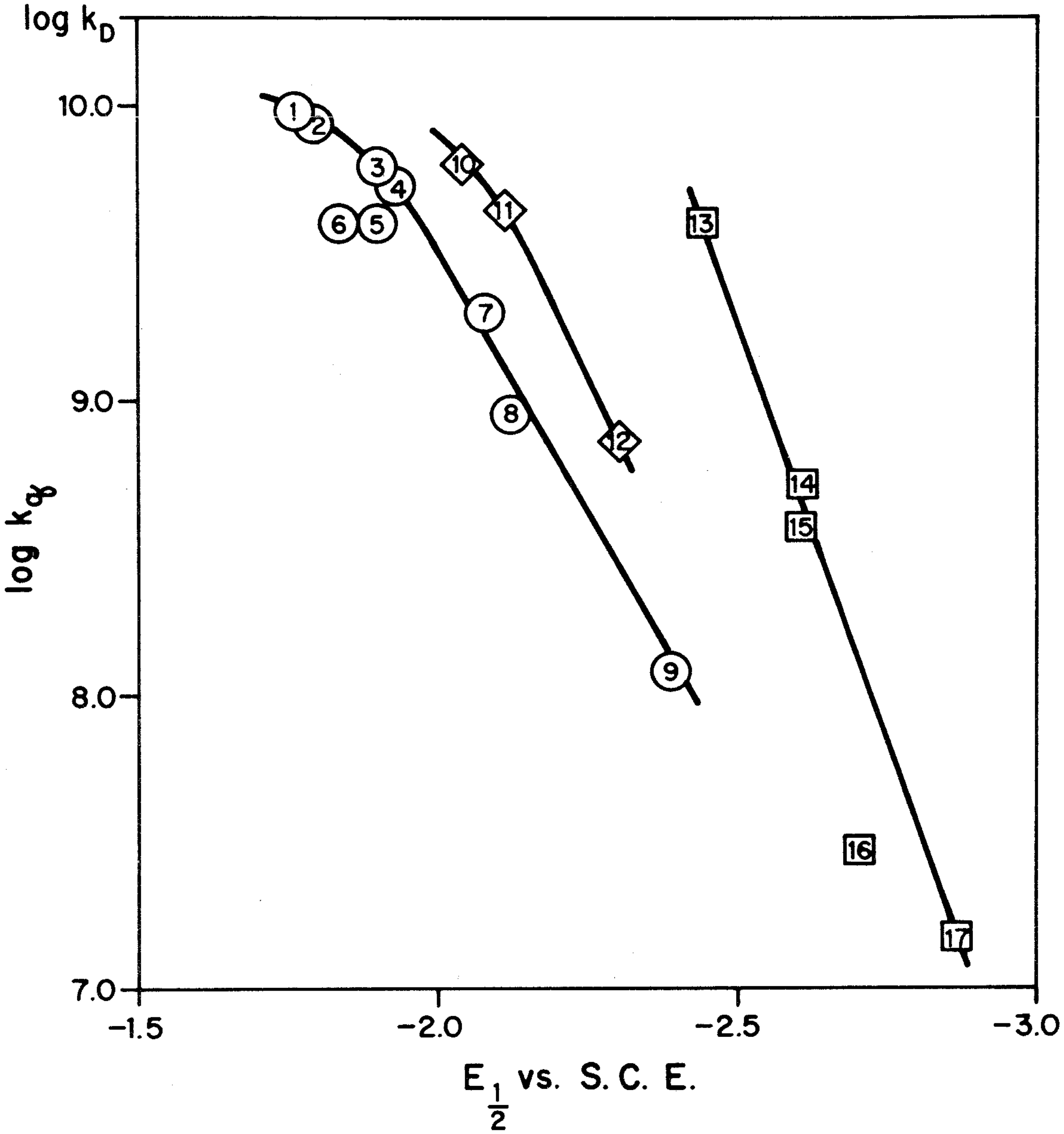
Table V lists the results for the chlorides, acetates, and mesylates studied here, and Figure 2 shows a plot of log k_q vs. quencher reduction potential. It is clear that a linear correlation for all the quenchers is not obtained. Within the various series (chlorides, acetates, or mesylates) linear correlations do appear.

TABLE V. Reduction Potentials of Quenchers

Quencher No.	Quencher	$E_{\frac{1}{2}}$ vs. S.C.E. (volts)
1	$ClCH_2CN$	-1.76 ± .03
2	p-$ClC_6H_4CH_2Cl$	-1.79 ± .03
3	p-$FC_6H_4CH_2Cl$	-1.90 ± .03
4	$C_6H_5CH_2Cl$	-1.93 ± .03
5	p-$CH_3C_6H_4CH_2Cl$	-1.90 ± .03
6	$ClCH_2COOCH_3$	-1.84 ± .03
7	$CH_2=CHCH_2Cl$	-2.08 ± .03
8	$ClCH_2CONH_2$	-2.12 ± .03
9	$ClCH_2OCH_3$	-2.39 ± .10
10	p-$ClC_6H_4CH_2OMs$	-2.03 ± .03
11	$C_6H_5CH_2OMs$	-2.11 ± .03
12	$CH_2=CHCH_2OMs$	-2.30 ± .03
13	p-$ClC_6H_4CH_2OAc$	-2.44 ± .05
14	p-$FC_6H_4CH_2OAc$	-2.61 ± .03
15	$C_6H_5CH_2OAc$	-2.60 ± .03
16	p-$CH_3C_6H_4CH_2OAc$	-2.70 ± .03
17	$CH_2=CHCH_2OAc$	-2.86 ± .05

Figure 2

Correlation of log k_q
with Quencher Reduction Potential


log k_D
log k_q
10.0
9.0
8.0
7.0
-1.5
-2.0
-2.5
-3.0
$E_{\frac{1}{2}}$ vs. S.C.E.
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

The points generally describe three straight lines. The curvature at the top of the curves may be due to a leveling effect as k_q approaches the diffusion-limited encounter rate, k_D. The results shown in Figure 2 are inconsistent with the relation of eq 26 and suggest that irreversible formation of a radical cation-radical anion pair is not involved in the quenching of DMB fluorescence by the quenchers used in this study.

The results shown in Figure 2 seem more compatible with the kinetic formulation of eqs 5 and 6. That is, fluorescence quenching is the result of enhanced radiationless decay of the excited molecule with certain vibrational modes of the quencher being involved in the dissipation of energy.

The photocyclizations of Witkop and coworkers (15) and the observation of product formation in very low quantum yield from one bimolecular quenching study of this series (16) suggest but _do not prove_ that the C-Cl, C-OMs, and C-OAc bonds are involved in the singlet quenching process. It has not been conclusively shown that photoproducts do not arise from interaction of the organic chloride function with aromatic triplets formed by intersystem crossing from unquenched aromatic singlets. Quantum yields were not determined in the photocyclizations of Witkop and in the case of bimolecular product formation the quantum yield was so low in the only case studied (16) that no clear-cut evidence for either singlet or triplet reaction could be obtained. Nevertheless, product formation implicates the vibrational modes of the C-Cl bond (for example) as a sink for the energy of electronic excitation. The suggestion is that coupling of the excited state with these modes in an exciplex provides a facile path for radiationless decay of the exciplex.

Some support for this view may be found in the work of Ogata et al. (24), who find carbon-halogen bond homolysis upon the direct irradiation of ethyl haloacetates. Furthermore, there is a possible relationship between this study and the work of Berenfel'd and Krongauz, who investigated the fluorescence of a series of substituted benzyl systems and concluded that intramolecular charge transfer plays a role in determining the probability of their radiationless decay (25). Taken together, these results suggest that C-Cl bond vibrational modes are involved in the radiationless decay processes of the chlorides used as quenchers in this study. By analogy, C-OMs and C-OAc bond vibrational modes may be important radiationless decay processes in the acetates and mesylates also. It is known that irradiation of cyclohexyl mesylate produces cyclohexene via the cyclohexyl cation and mesylate anion (26). Thus, as was the case with conjugated dienes, compounds found to be effective quenchers here have radiationless decay pathways which could be useful for the dissipation of the electronic excitation of an exciplex.

If coupling of the vibrational modes of the C-Cl, etc., bond is important in the radiationless decay mechanism, then it might be the same among a series of chlorides, acetates, or mesylates. In that case k_2 would be roughly constant within a series of chlorides, acetates, or mesylates.

While the decay rates of the exciplexes derived from DMB may be invariant for a series of chlorides, etc., used as quenchers, the equilibrium constants K need not be identical. The straight lines in Figure 2 suggest a relationship between K and the quencher reduction potential. In particular, if binding of the exciplexes is derived only from rapid, reversible, resonance charge transfer from the excited singlet to the quencher, and not to any significant degree by exciton delocalization (AQ*) or quencher-to-quenchee charge transfer (A^-Q^+), then the exciplex might be described as shown in eq 27, and K might be a function of the change in free energy of formation of the charge transfer species exactly as was predicted for k_q in eq 26.

$$(AQ)^* \equiv (A^*Q) \longleftrightarrow (A^+Q^-) \qquad (27)$$

If in the logarithmic form of eq 25, the right side of eq 26 is substituted for the log K term, eq 28 is obtained.

$$\log k_q = c_1 + c_2 E_{\frac{1}{2}} + \log k_2 \qquad (28)$$

This is the kinetic formulation for the situation in which the binding energy of the exciplex is derived from charge transfer resonance interactions, but the actual radiationless decay of the exciplex occurs with rate constant k_2 through modes which are a function only of the type of quencher and not of its reduction potential. The correlations shown in Figure 2 are entirely consistent with this formulation.

It is interesting at this point to compare the experimental values for k_q with those predicted from the more elaborate model of reversible electron transfer proposed by Rehm and Weller (14). In eq 21 the value of $\Delta E_{o,o}$ is 3.97 eV from Berlman's data (17). $E[D/D^+]$ for DMB is reported by Rehm and Weller to be 1.34 eV (14). The $e_o^2/\epsilon x$ term at $4\overset{o}{A}$ is 0.10 eV. Table VI summarizes the results. It may be seen that the comparison between k_q(calc) and k_q(exp) is not altogether bad, although most calculations fail Rehm and Weller's test of being within a factor of 2 of the experimental value.

This close correspondence between predicted and experimental k_q values does not necessarily invalidate the conclusions of the previous discussion, however. While showing a close fit to the gross value of k_q, application of eq 21 fails to predict successfully the variation of k_q from one quencher to another. In general, eq 21 predicts all the chlorides to quench with the same rate constant. This is not at all the case. As is seen in Figure 2, the k_q values of the chlorides show a systematic variation with $E_{\frac{1}{2}}$ which is successfully predicted by eq 28.

Perhaps eq 21 fails to predict the ordering of quenching rate constants because the quenching process in the present study is different from that studied by Rehm and Weller. Evidence that radical ion pair formation and exciplex charge transfer resonance

TABLE VI. Calculation of k_q from the Formulation of Rehm and Weller (14)

	Quencher	$-\Delta G_{23}$ eV(kcal/m)	$\Delta G_{23}^{\ddagger}$	Calc	Obs
1	$ClCH_2CN$	.78(18.0)	0.3145	14	9.6
2	p-$ClC_6H_4CH_2Cl$	.75(17.3)	0.3267	14	8.9
3	p-$FC_6H_4CH_2Cl$	.64(14.8)	0.3794	14	6.1
4	$C_6H_5CH_2Cl$	.61(14.1)	0.3973	13	5.5
5	p-$CH_3C_6H_4CH_2Cl$	.61(14.1)	0.3973	13	4.1
6	$ClCH_2COOCH_3$	.67(15.5)	0.3631	14	4.1
7	CH_2=$CHCH_2Cl$	.43(9.9)	0.5511	12	2.0
8	$ClCH_2CONH_2$	.39(9.0)	0.6000	12	0.89
9	$ClCH_2OCH_3$	.12(2.8)	1.378	5.6	0.12
10	p-$ClC_6H_4CH_2OMs$	.51(11.8)	0.4694	13	6.1
11	$C_6H_5CH_2OMs$	.43(9.9)	0.5511	12	4.4
12	CH_2=$CHCH_2OMs$	.24(5.5)	0.9000	9.3	0.74
13	p-$ClC_6H_4CH_2OAc$	.10(2.3)	1.511	4.7	4.1
14	p-$FC_6H_4CH_2OAc$	-.07(1.6)	3.32	0.27	0.52
15	$C_6H_5CH_2OAc$	-.06(1.4)	3.20	0.34	0.37
16	p-$CH_3C_6H_4CH_2OAc$	-.16(3.7)	4.88	0.02	0.030
17	CH_2=$CHCH_2OAc$	-.33(7.6)	8.29	0.00005	0.010

may be distinctly different interactions may be surmised by considering those points which fall off the lines in Figure 2. One such point is *p*-methylbenzyl chloride. The electrochemical reduction potentials for substituted benzyl chlorides have been reported by Streitwieser (27), who found that all substituents made the reduction potential more positive--*i.e.*, a linear Hammett correlation was not obtained. The relative values of the reduction potentials of the benzyl chlorides reported in Table 5 are in good agreement with those of Streitwieser. Streitwieser concluded that in the transition state for reduction the benzyl system had both anionic and radical character (eq 29). The polar effect, which is measured by σ, affects **2**; radical stabilization effects, which are in no way measured by σ, affect **1**.

$$\mathrm{ArCH_2Cl} \xrightarrow{e^-} \underset{\mathbf{1}}{\mathrm{ArCH_2{\cdot}Cl^-}} \longleftrightarrow \underset{\mathbf{2}}{\mathrm{ArCH_2^-Cl{\cdot}}} \qquad (29)$$

If this explanation is correct, then there is clearly a distinction between the electrochemical reduction of the compounds used as quenchers in this study and the type of charge transfer involved in the exciplexes they form. If electron transfer formed a benzyl chloride radical anion, intuition argues that the rate constants for quenching and the electrochemical reduction potentials should vary in the same systematic way upon para-substitution. That they do not suggests that there are fundamental differences between the two processes.

Although the reduction potential of p-methylbenzyl acetate was found to be more negative than that of benzyl acetate, the $E_{\frac{1}{2}}$ values do not yield a linear Hammett correlation. Effects such as those proposed by Streitwieser for the electrochemical reduction of benzyl chlorides (eq 29) may also be operating--though to a lesser degree--in the reduction of benzyl acetates.

The reason for the apparent success of eq 21 in predicting the magnitudes of k_q values may be seen in Table VII, which shows the relative influence of ΔG_{23} and $\Delta G_{23}^{\ddagger}$ on k_q. Table VII also shows the relative effect of "$\Delta G_{23}(0)^{\ddagger}$"--i.e., 2.4 kcal/mole--in determining k_q. It is interesting to note that those quenchers for which the predicted and experimental k_q's show closest correspondence, the benzyl acetates, are the only ones for which $\exp(\Delta G_{23}^{\ddagger}/RT)$ and $\exp(\Delta G_{23}/RT)$ outweigh $\exp(2.4/RT)$. The point is that the values of k_q calculated from eq 21 depend primarily on $\Delta G_{23}(0)^{\ddagger}$, which in turn depends on an empirical value chosen by Rehm and Weller to fit experimental quenching constants for the systems they studied.

It might be possible to modify eq 21 to make its predictions more closely match the experimental results, but any such change will have to make k_q more heavily dependent upon ΔG_{23} (or $E_{\frac{1}{2}}$, since that is the only variable in the present study) and will have to include a dependence on the type of quencher, whether it be chloride, acetate, or mesylate. In other words, eq 21 will have to be modified to look more like eq 28. In view of the success

TABLE VII. Comparison of Factors which Determine k_q(calc) from eq 21

Quencher	$\exp(\Delta G_{23}/RT)$	$\exp(\Delta G_{23}^{\ddagger}/RT)$	$\exp(2.4/RT)$
1	6.39×10^{-14}	1.70	57.44
2	2.08×10^{-13}	1.74	57.44
3	1.42×10^{-11}	1.90	57.44
4	4.62×10^{-11}	1.96	57.44
5	4.62×10^{-11}	1.96	57.44
6	4.35×10^{-12}	1.85	57.44
7	5.54×10^{-8}	2.53	57.44
8	2.53×10^{-7}	2.75	57.44
9	8.86×10^{-3}	11.23	57.44
10	2.24×10^{-9}	2.21	57.44
11	5.53×10^{-8}	2.53	57.44
12	9.30×10^{-5}	4.57	57.44
13	2.06×10^{-2}	12.8	57.44
14	14.89	271.4	57.44
15	10.62	221.6	57.44
16	515.4	3.77×10^{3}	57.44
17	3.72×10^{5}	1.19×10^{6}	57.44

eq 28 has in correlating rate constants, there appears to be no great utility in such a modification.

The Rehm-Weller calculations were originally applied to a large number of organic compounds which were, in general, fairly rigid aromatic compounds which (a) showed fluorescence and (b) had available π electron systems for interaction and extensive electron delocalization. For some of the quenchers studied in this investigation, _e.g._, chloromethyl methyl ether, it is difficult to imagine the existence of a radical anion as a species with a finite lifetime.

The results of this study are entirely compatible with the general kinetic formulation of eqs 5 and 6, which were originally written for quenching by conjugated dienes. The results in Figure 2 suggest an explanation for the deviation of quadricyclene and norbornadiene from the diene quenching plot of Evans (12). If the binding energies of the exciplexes formed from excited naphthalene singlets and a series of conjugated dienes or strained hydrocarbons varies only with the ionization potentials of the quenchers, then a plot of log k_q _vs_. ionization potential should be linear _only for those compounds which have the same_ k_2; _i.e._, for compounds whose structures are closely related. If the radiationless decay of such exciplexes occurs primarily through twisting about the carbon-carbon double bonds (28), then k_2 rates for a series of dienes might be roughly the same. Norbornadiene and quadricyclene, however, might have different k_2's, the relative magnitude depending on their radiationless decay efficiencies, and might not fit the diene line. These same compounds would still show correlations with quencher electron affinity for quenching a series of naphthalene compounds, exactly as was demonstrated by Solomon, Steel, and Weller (11). This explanation is strongly supported by a recent report by Taylor (29) that a series of olefins and dienes show a good correlation of log k_q with quencher ionization potential, but that a series of strained hydrocarbons (quadricyclene, norbornadiene, tricyclo [4.1.0.0^{2,7}]-heptane, and bicyclo-[2.1.0]-pentane) show a distinctly different linear correlation.

CONCLUSION

The conclusion of this study is that the experimental data do not allow exclusion of either the radical pair quenching model which results in the kinetic formulation of eq 21 or the enhanced radiationless decay model which predicts the kinetic formulation of eq 26, though they are qualitatively more consistent with the latter. It can be concluded, however, that caution should be observed in interpreting structure-reactivity relationships in fluorescence quenching. For example, if only organic chlorides had been studied here, the results would have been consistent with eq 26. Consideration of mesylates and acetates also suggests that it is necessary to consider radiationless decay processes of the exciplex in any complete description of singlet quenching interactions.

EXPERIMENTAL

Materials

Solvents. *Acetonitrile* was Matheson, Coleman, and Bell Spectroquality grade. *1,4-Dimethoxybenzene* (Aldrich) was recrystallized twice from hexane by Dr. M. T. McCall. *Ethanol* (U. S. Industrial Chemicals Co.) was absolute reagent grade.

Quenchers. *Chloroacetonitrile* (Matheson, Coleman, and Bell) was distilled twice from phosphorous pentoxide; a center cut (bp 120-121°) was taken each time. Analysis by vpc on both QF-1 and Carbowax 20M columns showed the material to be $\gg$99% pure. *Chloromethyl methyl ether* (Aldrich) had been previously distilled by Dr. M. T. McCall. It was filtered through anhydrous potassium carbonate and redistilled. A center cut (bp 57.2-58.5°) was taken. *Allyl acetate* (Eastman Organic Chemicals) was distilled and a center cut (bp 116-117°) was passed through grade I alumina (25 g) and further purified by bulb-to-bulb vacuum distillation. *Benzyl acetates* were synthesized by treating the corresponding benzyl alcohols (commercial materials) with acetic anhydride in pyridine, as illustrated by the synthesis of *p*-fluorobenzyl acetate: pyridine (5.5 g) was added to acetic anhydride (6.6 g, 0.065 mol). *p*-Fluorobenzyl alcohol (8.0 g, 0.059 mol) was added slowly with swirling, and an exotherm was noted. The solution was heated on a steam bath for 2 hrs; then it was allowed to cool. Water was added and the two phase system was extracted three times with 50 ml portions of ether. The ether extracts were washed five times with 10-15 ml portions of aqueous 10% hydrochloric acid, twice with saturated aqueous potassium carbonate, twice with saturated aqueous sodium chloride, and then dried over anhydrous magnesium sulfate. The solution was concentrated on the rotary evaporator. The products were distilled under vacuum and a center cut was taken in each case.

Ethyl trifluoroacetate (Calbiochem) was distilled and a center cut (bp 59.9-60.1°) was taken. *2-Chloroacetamide* (Matheson, Coleman, and Bell) was recrystallized twice from water by Dr. M. T. McCall. *Benzyl chloride* (Matheson, Coleman, and Bell), *p-chlorobenzyl chloride*, *p-fluorobenzyl chloride*, and *p-methylbenzyl chloride* (Aldrich) were distilled by Dr. M. T. McCall. *Methyl chloroacetate* (Matheson, Coleman, and Bell) was doubly distilled by Dr. M. T. McCall. *Allyl chloride* (Matheson, Coleman, and Bell) was distilled by Dr. M. T. McCall. *Acetic acid* (Du Pont), *acetic anhydride* (Baker), and *trifluoroacetic anhydride* (Matheson, Coleman, and Bell) were used as received.

The mesylates were prepared from the corresponding alcohols by the procedure of Hudson and Withey (30) except that sodium hydroxide was omitted from the reaction mixture. Comparable yields were obtained. *Allyl mesylate* was vacuum distilled (bp 52-53°, 1.5 Torr). *Benzyl mesylate* was purified by bulb-to-bulb vacuum distillation. *p-Chlorobenzyl mesylate*, a solid, decomposed upon attempted vacuum sublimation. The product was recrystallized repeatedly from 30 : 70 benzene : hexane and had mp 48-53°.

Instruments

Fluorescence spectra were taken on an Aminco-Bowman Spectrophotofluorometer. Absorption spectra were obtained on a Cary Model 14 Recording Spectrophotometer.

Measurements

Samples were prepared in duplicate or triplicate in 13 x 100 mm Pyrex test tubes using 3 ml of solutions of *ca.* 1.5×10^{-2} *M* DMB and varying concentrations of quencher. The tubes were degassed by the freeze-pump-thaw technique and were sealed under a pressure of $<5 \times 10^{-4}$ Torr.

Relative fluorescence intensities were determined and values of k_q were obtained from linear plots of I_f^o/I_f *vs.* quencher concentration.

Determination of Reduction Potentials

Reduction potentials were determined in the laboratory of Professor F. L. Lambert of Occidental College, Los Angeles, California. The solvent was doubly-distilled N,N-dimethylformamide (Eastman) containing 0.01 M tetraethylammonium perchlorate (G. Frederick Smith) as the supporting electrolyte. Potentials were determined in conventional fashion using a Beckman Electroscan 30 in a three electrode configuration with platinum wire as the auxiliary electrode and a saturated calomel reference electrode. The working electrode was the end of a vitreous carbon rod (3 mm in diameter) obtained from the Tokai Electrode Manufacturing Company, Tokyo, Japan, mounted *via* heat shrinkable polyolefin tubing in a glass tube with a drop of mercury making contact between the lead wire and the carbon rod. The normal resistance between working and auxiliary electrodes was 2000 ohms; all half-wave potentials were corrected for internal resistance. Prior to each run the carbon electrode was cleaned by gentle manual polishing on Linde 3A alumina wetted with DMF; it was then rinsed with DMF and mounted in the electrolytic cell. Ten ml of 0.01 M tetraethylammonium perchlorate in DMF was added, after which the calomel reference and the platinum auxiliary electrodes were put in place and the cell was flushed with nitrogen. A blank run was made to establish the absence of reducibles. About 1.5 μl of the liquid sample (or an appropriate volume of DMF solution of a solid sample) was added *via* Hamilton syringe. The solution was again flushed with nitrogen and a number of polarograms were recorded in the repetitive mode of the Electroscan 30. The half-wave potential was determined in standard fashion for the three polarograms after the initial run.

For some measurements (as indicated), acetonitrile which had been distilled from phosphorous pentoxide and redistilled from anhydrous potassium carbonate was used as solvent. Some half-wave determinations (as indicated) were made at the dropping mercury electrode. The capillary characteristics were $m = 1.20$ mg/sec and $t_{max} = 4.9$ sec (open circuit, Hg height = 66.1 cm) with the electrode immersed in 0.01 M tetraethylammonium perchlorate in DMF.

REFERENCES

1. (a) A. A. Lamola, Ph. D. Thesis, California Institute of Technology, Pasadena, California, 1965.

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

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

3. L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, J. Amer. Chem. Soc., 88, 3665.

4. L. M. Stephenson and G. S. Hammond, Pure Appl. Chem., 16, 125 (1968).

5. L. M. Stephenson, D. G. Whitten, and G. S. Hammond, "The Chemistry of Ionization and Excitation," G. R. A. Johnson and G. Scholes, eds., Taylor and Francis Ltd., London, 1967 , pp. 35-42.

6. S. Murov and G. S. Hammond, J. Phys. Chem., 72, 3797 (1968).

7. (a) R. S. Cooke, Ph. D. Thesis, California Institute of Technology, Pasadena, California, 1970.

   (b) R. S. Cooke and G. S. Hammond, J. Amer. Chem. Soc., 92, 2739 (1970).

8. D. A. Labianca, G. N. Taylor, and G. S. Hammond, J. Amer. Chem. Soc., 94, 3697 (1972) and references therein.

9. A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968).
10. S. P. Van, Ph. D. Thesis, California Institute of Technology, Pasadena, California, 1970.
11. B. S. Solomon, C. Steel, and A. Weller, *Chem. Commun.*, 927 (1969).
12. T. R. Evans, *J. Amer. Chem. Soc.*, **93**, 2081 (1971).
13. A. M. North, *Quart. Rev.*, **20**, 421 (1966).
14. D. Rehm and A. Weller, *Israel J. Chem.*, **8**, 259 (1970).
15. O. Yonemitsu, H. Nakai, Y. Kanaoka, I. L. Karle, and B. Witkop, *J. Amer. Chem. Soc.*, **91**, 4591 (1969) and references therein.
16. M. T. McCall, G. S. Hammond, O. Yonemitsu, and B. Witkop, *J. Amer. Chem. Soc.*, **92**, 6991 (1970).
17. I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," second edition, Academic Press, New York, 1971 , pp. 162-163.
18. *Ibid.*, pp. 32-38.
19. The inherent singlet lifetime may be calculated from a formula developed by Strickler and Berg (20), but the difference in the lifetimes of DMB in acetonitrile and ethanol so calculated would be well within the experimental error of the absorption spectra measurements.
20. S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, **37**, 814 (1962).

21. The fluorescence quantum yield should be corrected for solvent index of refraction change (22), but the difference due to the correction is small compared to the experimental uncertainty in the fluorescence measurement.

22. J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, New York, 1967 , p. 98.

23. M. T. McCall, unpublished results.

24. Y. Ogata, T. Itoh, and Y. Izawa, *Bull. Chem. Soc. Jap.*, **42**, 794 (1969).

25. V. M. Berenfel'd and V. A. Krongauz, *Dokl. Akad. Nauk SSSR*, **162**, 1300 (1965).

26. K. Schaffner, *Pure. Appl. Chem.*, **16**, 75 (1968).

27. A. Streitwieser and C. Perrin, *J. Amer. Chem. Soc.*, **86**, 4938 (1964).

28. G. N. Taylor and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 3687 (1972).

29. G. N. Taylor, *Chem. Phys. Lett.*, **10**, 355 (1971).

30. R. F. Hudson and R. J. Withey, *J. Chem. Soc.*, **B**, 237 (1966).

PART III

A New Method for the Determination of Intersystem Crossing Quantum Yields

INTRODUCTION

Understanding photochemical processes requires detailed knowledge of the fate of the energy of electronic excitation. A molecule excited by light to its first excited singlet state may undergo a number of processes, including fluorescence, chemical reaction, radiationless decay to the ground electronic state, energy transfer, or intersystem crossing to an excited triplet state (1). The excited triplet state may exhibit chemical reaction, phosphorescence, radiationless decay to the ground electronic state, energy transfer, and other processes. Quantum yields of fluorescence may be measured without great difficulty (2,3). Quantum yields of photochemical reaction induced by direct excitation may also be determined. Although it is not always certain whether chemical change occurs from the excited singlet or triplet state (4), the multiplicity of the reactive state may often be assigned on the basis of sensitization with triplet sensitizers. Determining the fraction of singlets which undergo radiationless decay from the first excited singlet is much more difficult since no emission or photochemical product appearance which can be conveniently measured is directly associated with this pathway.

It should be possible to determine the fraction of excited singlets which undergo radiationless decay by subtracting the sum of the quantum yields of fluorescence (Φ_f), intersystem crossing (Φ_{isc}), and singlet state photochemical reaction from unity. Unfortunately, quantum yields of intersystem crossing are often not known with certainty; this is especially true in the case of benzene derivatives.

A number of procedures have been devised for the measurement of intersystem crossing quantum yields. Lamola and Hammond (5) used the sensitized isomerization of dienes to determine Φ_{isc} for polycyclic aromatics, aromatic amines, and aromatic carbonyl compounds. The method involved measuring the amount of cis-trans isomerization sensitized by an organic compound relative to that caused by benzophenone ($\Phi_{isc} \equiv 1.0$) under identical conditions. The values measured by this technique must be corrected for aromatic singlets quenched by the diene, however (6).

Cundall has used the sensitized isomerization of olefins to measure values of Φ_{isc} for benzene in the gas phase (7) and for benzene, toluene, and o-xylene in solution (8, 9). This procedure will be discussed in more detail below.

Gouterman and coworkers have applied the method of flash calorimetry to the determination of Φ_{isc} for anthracene. The intersystem crossing yield is calculated from the ratio of slow to total (10^{-5} cal) heating following flash excitation of the sample (10). Because of the specialized instrumentation required, the method has not found general use.

Eisinger et al. (11) used the method of esr absorption intensity, relative to that of triphenylene as standard, to determine a value of 0.44 for the intersystem crossing yield of naphthalene. This is about half the presently accepted value (12). Furthermore, the method is only applicable for aromatics with triplet lifetimes $> 10^{-2}$ sec.

Triplet-triplet absorption in flash spectroscopy was used by Porter (13) to determine Φ_{isc} for anthracene and other polycyclic aromatics, but the method requires that triplet state extinction coefficients be known accurately.

Parker and Joyce (14) measured delayed fluorescence from a triplet energy acceptor, such as perylene, to determine intersystem crossing quantum yields for several sensitizers, but the method is complicated by competitive absorption and the resultant direct production of triplets by the triplet acceptor.

Sandros (15) measured the intensity and lifetime of sensitized biacetyl phosphorescence at varying biacetyl concentrations and calculated values for sensitizer Φ_{isc} assuming that the biacetyl phosphorescence quantum yield is unity. The method is complicated by photodecomposition of biacetyl. In addition, for compounds whose triplet lifetimes are not much longer than their singlet lifetimes, biacetyl fluorescence must also be measured to correct for singlet energy transfer.

Another method, reported by Kellogg and Bennett (16) and by Ermolaev and Sveshnikova (17), involved measuring long range triplet-singlet energy transfer from aromatic hydrocarbons to fluorescent dyes in plastic films. One requirement for this procedure is that the hydrocarbon phosphorescence must show spectral overlap with the dye absorption spectrum.

Wilkinson and coworkers have developed an elegant method for the determination of intersystem crossing yields (12). The method requires the measurement of relative fluorescence intensities of flash spectrscopic triplet-triplet absorption in solutions containing constant concentrations of the aromatic hydrocarbon and varying concentrations of a heavy atom additive, such as xenon, which quenches fluorescence by inducing intersystem crossing. When F and F^o are the fluorescence intensities with and without the heavy atom additive and D_T and $D_T{}^o$ are the corresponding triplet-triplet absorption intensities, it can be shown that $F^o/F = \Phi_{isc}(F^oD_T/FD_T{}^o - 1) + 1$. Using this relationship, Wilkinson has measured Φ_{isc} for a number of polycyclic aromatic hydrocarbons.

Although these methods for determining intersystem crossing yields have been developed, values of Φ_{isc} for benzene derivatives remain largely unknown (18). Most of the methods described above are only marginally applicable in these cases. The singlet-triplet energy transfer method of Kellogg and Bennett (16) has not been extended to such compounds, probably because of the poor spectral overlap of triplet phosphorescence with suitable acceptors. The sensitized delayed fluorescence technique fails because the triplet energy acceptor absorbs at longer wavelengths than do the benzenes. The method of absolute flash spectroscopic triplet-triplet absorption intensities of Porter (13) and the heavy atom perturbation technique of Wilkinson (12) fail because benzene derivatives typically do not show triplet-triplet absorption in flash spectroscopy (19).

Morrison (20) has used the method of Lamola and Hammond (5) to measure Φ_{isc} for toluene in solution. However, since the sensitizer must be irradiated at wavelengths at which the diene also absorbs, the results are complicated by the necessity of correcting for light absorbed by the diene and the resulting diene isomerization (21), as well as for toluene singlets quenched at nearly the rate of diffusion by the diene. Recent preliminary evidence suggests that singlet-sensitized isomerization may be an important complication also (22).

Cundall's use of sensitized isomerization of simple olefins in solution is based on the assumption that $\Phi_{c\rightarrow t} + \Phi_{t\rightarrow c} = \Phi_{isc}$. Actually, the sum of $\Phi_{c\rightarrow t}$ and $\Phi_{t\rightarrow c}$ is the product of the intersystem crossing yield of the sensitizer and the efficiency of triplet energy transfer to the isomeric olefins. Cundall's assumption that the efficiency of energy transfer is 100% may be true for benzene, but it is clearly not the case for toluene. Morrison (23) has shown that the efficiency of triplet energy transfer from toluene to cis-2-heptene is 50% greater than that for transfer to the trans isomer. Furthermore, the decay ratio--the relative yield of trans to cis isomers from olefin triplets--which is 1.0 for benzene sensitization, is 1.15 when toluene is used. Since there is no obvious reason for expecting a "pure" olefin triplet to remember what molecule sensitized it, the intermediate responsible for the olefin isomerization may not be precisely the same when benzene and toluene are used as sensitizers. The results are reminiscent of the differing decay ratios of 2-pentene triplets reported for acetone and acetophenone sensitization, which Saltiel et al. presented as evidence for the involvement of chemically bonded intermediates in the isomerization (Schenck mechanism) (24).

The different results for benzene and toluene sensitization may be a result of the different triplet energies of the two compounds, 84 kcal/mole and 83 kcal/mole, respectively (25). The triplet energies of olefins are not known with certainty. That of ethylene is thought to be about 82 kcal/mole (26), and the triplet energies of substituted olefins are presumed to be somewhat lower (27). An alternative explanation is that substitution of the phenyl chromophore introduces steric hindrance which decreases the efficiency of energy transfer from the aromatic triplet to one or both olefin isomers. Since substitution will in general both lower the triplet energy and increase steric hindrance in the benzene derivative, the origin of the decrease in efficiency cannot be resolved on the basis of available data.

However, it would appear to be a reasonable conclusion that substituted benzenes which have lower triplet energies and greater steric hindrance than toluene might be even less efficient sensitizers. In the absence of convincing evidence to the contrary, values of Φ_{isc} measured in solution for such compounds, e.g., o-xylene (9), by Cundall's method should be interpreted with caution.

The one method discussed above which may be applied with any confidence to benzene derivatives is that reported by Sandros, who measured Φ_{isc} for benzene, toluene, p-xylene, and fluorobenzene. For these compounds, however, the singlet lifetimes are greater than the triplet lifetimes (15), and the analysis is thus complicated.

Most of the methods described above suffer from the requirement of specialized instrumentation and experimentally tedious procedures. In order that the decay of electronically excited singlets be better understood there is a need for a general procedure for the determination of intersystem crossing yields, especially for benzene derivatives, which is both convenient and accurate. The next section describes such a method and presents the results for some substituted benzenes.

THE METHOD AND RESULTS

The Method in Principle

The method presented here combines features from the procedures of Lamola and Hammond (5) and Horrocks and Wilkinson (12). The aromatic compound (**A**) which is to be studied is irradiated in solutions containing a "triplet counter" (**C**). In principle, **C** may be any molecule which exhibits a reaction, such as cis-trans isomerization, dimerization, or reaction with another species, which may be sensitized by $\mathbf{A}^{*(3)}$. It will be shown that the present method, unlike those of Lamola and Hammond or Cundall, does not require knowledge of either the efficiency of energy transfer from $\mathbf{A}^{*(3)}$ to **C** or the efficiency of $\mathbf{C}^{*(3)}$ in producing sensitized product (**T**). One restriction on **C** is that it should not absorb at wavelengths at which **A** is irradiated. In principle, corrections for such absorption and singlet photochemical reaction, if any, could be made (*cf.*, ref. 20), but with the great variety of triplet counters available it should be possible to choose a system in which these complications are avoided. To solutions of **A** and **C** are added varying concentrations of a heavy atom fluorescence quencher (**H**) which quenches fluorescence by inducing intersystem crossing. Determining the relative decrease in fluorescence intensities and the relative increase in quantum yields for the appearance of **T** allows determination of the intersystem crossing yield of **A**.

The kinetic formulation below lists the processes considered in the derivation of the relevant equations:

$\mathbf{A} \xrightarrow{h\nu} \mathbf{A}^{*(1)}$	excitation	(1)
$\mathbf{A}^{*(1)} \xrightarrow{k_2} \mathbf{A} + h\nu'$	fluorescence	(2)
$\mathbf{A}^{*(1)} \xrightarrow{k_3} \mathbf{A}$	singlet radiationless decay	(3)
$\mathbf{C} + \mathbf{A}^{*(1)} \xrightarrow{k_4} \mathbf{A} + \mathbf{C}$	singlet quenching by **C**	(4)
$\mathbf{A}^{*(1)} \xrightarrow{k_5} \mathbf{A}^{*(3)}$	intersystem crossing	(5)
$\mathbf{H} + \mathbf{A}^{*(1)} \xrightarrow{k_6} \mathbf{A}^{*(3)} + \mathbf{H}$	enhanced intersystem crossing	(6)
$\mathbf{A}^{*(3)} \xrightarrow{k_7} \mathbf{A}$	triplet radiationless decay	(7)
$\mathbf{C} + \mathbf{A}^{*(3)} \xrightarrow{k_8} \mathbf{A} + \mathbf{C}^{*(3)}$	triplet energy transfer	(8)
$\mathbf{C}^{*(3)} \xrightarrow{k_9} \mathbf{C}$	decay of $\mathbf{C}^{*(3)}$ without chemical change	(9)
$\mathbf{C}^{*(3)} \xrightarrow{k_{10}} \mathbf{T}$	decay of $\mathbf{C}^{*(3)}$ with chemical change	(10)

In the notation used here, asterisks represent excited states and superscript numbers in parentheses indicate multiplicities of electronically excited states. Some steps which are written as unimolecular processes, *e.g.*, eqs 3, 5, and 7, may be more complex, but at constant concentrations of A they will be pseudo first order.

The effect of fluorescence quenching by C in the absence of H (eq 4) is given by eq 11:

$$F^{o}/F' = \tau_f^{o}/\tau_f' = 1 + k_4\tau_f^{o}[C] \tag{11}$$

F^{o} and F' represent fluorescence intensities in the absence and in the presence of C, respectively. The corresponding singlet lifetimes are τ_f^{o} and τ_f'. Singlet quenching will be discussed in more detail below.

Equation 12 describes the relative fluorescence intensities of solutions containing constant concentrations of A and C, but varying concentrations of H.

$$F'/F = \tau_f'/\tau_f = 1 + k_6\tau_f'[H] \tag{12}$$

F and τ_f are the fluorescence intensities and fluorescence lifetimes, respectively, of A at constant concentrations of A and C, but with varying concentrations of H.

In this kinetic formulation the quantum yield for appearance of T (Φ_T') in the absence of H is given by eq 13:

$$\Phi_T' = \left[k_5\tau_f'\right]\left[\frac{k_8[C]}{k_7 + k_8[C]}\right]\left[\frac{k_{10}}{k_9 + k_{10}}\right] \tag{13}$$

The first term in parentheses is the intersystem crossing quantum yield attenuated by singlet quenching. The second term represents the efficiency of energy transfer from $\mathbf{A}^{*(3)}$ to **C**. The last term is the fraction of $\mathbf{C}^{*(3)}$ states which lead to the formation of **T**. The quantum yield for the appearance of **T** in the presence of **H** (Φ_T) is given by eq 14:

$$\Phi_T = \left[k_5\tau_f + k_6\tau_f[\mathbf{H}]\right]\left[\frac{k_8[\mathbf{C}]}{k_7 + k_8[\mathbf{C}]}\right]\left[\frac{k_{10}}{k_9 + k_{10}}\right] \tag{14}$$

The first term in parentheses is the quantum yield for the production of triplets in the presence of **H**, and the other terms have the same meaning as in eq 13.

Dividing eq 13 by eq 14 gives the ratio of quantum yields for the appearance of **T** with and without added fluorescence quencher (eq 15).

$$Y_T/Y_T' = \Phi_T/\Phi_T' = \frac{k_5\tau_f + k_6\tau_f[\mathbf{H}]}{k_5\tau_f'} \tag{15}$$

If all samples receive the same light dose, the ratio of quantum yields (Φ_T/Φ_T') will be equal to the ratio of chemical yields (Y_T/Y_T') for the appearance of **T**. Combining eqs 11, 12, and 15 gives eq 16, which predicts that a plot of $(F^o/F')(F'/F - 1)$ *vs.* $(Y_T/Y_T')(F'/F) - 1$ should be linear with slope Φ_{isc}.

$$\frac{F^o}{F'}\left(\frac{F'}{F} - 1\right) = \Phi_{isc}\left[\frac{Y_T}{Y_T'} \cdot \frac{F'}{F} - 1\right] \tag{16}$$

The method requires measurement of relative fluorescence intensities of $\underset{\frown}{A}$ and relative yields for isomerization of $\underset{\frown}{C}$ in solutions with constant concentrations of $\underset{\frown}{A}$ and $\underset{\frown}{C}$, but with varying concentration of $\underset{\frown}{H}$. The ratio F^{o}/F' is determined from the relative fluorescence intensities of solutions with the identical concentrations of $\underset{\frown}{A}$ but without $\underset{\frown}{C}$. Since only relative measurements with the same sensitizer are involved, neither the efficiency of energy transfer nor the triplet counter decay ratio need be known. This feature is a major advantage over other methods employing sensitized cis-trans isomerization (5,8).

Assumptions in the Present Method

Before discussing the experimental test of eq 16, it is necessary to consider some assumptions which were implicit in its derivation. Specifically, processes represented by eqs 17-20 were not considered above.

$\underset{\frown}{H} + \underset{\frown}{A}^{*(1)} \xrightarrow{k_{17}} \underset{\frown}{A} + \underset{\frown}{H}$ quenching without enhancement of intersystem crossing (17)

$\underset{\frown}{H} + \underset{\frown}{A}^{*(3)} \xrightarrow{k_{18}} \underset{\frown}{A} + \underset{\frown}{H}$ quenching of $\underset{\frown}{A}^{*(3)}$ (18)

$\underset{\frown}{H} + \underset{\frown}{C}^{*(3)} \xrightarrow{k_{19}} \underset{\frown}{C} + \underset{\frown}{H}$ quenching of $\underset{\frown}{C}^{*(3)}$ (decreased yield of $\underset{\frown}{T}$) (19)

$$\underset{\frown}{H} + \underset{\frown}{C}^{*(3)} \xrightarrow{k_{20}} \underset{\frown}{T} + \underset{\frown}{H} \qquad \text{quenching of } \underset{\frown}{C}^{*(3)} \qquad (20)$$

(increased yield of $\underset{\frown}{T}$)

Intuition suggests that the last two processes will probably not be significant. The lifetimes of olefin triplets are not known with certainty, but in fluid solution they must be very short. If either of the two processes should be important, curvature should appear in plots based on eq 16; the curvature would be upward if the process represented by eq 19 is the more important, downward if that suggested in eq 20 predominates (*vide infra*).

Equation 18 represents the quenching of $\underset{\frown}{A}^{*(3)}$ by $\underset{\frown}{H}$. This process seems unlikely for several reasons. Even if energy transfer does not occur on every collision, sensitization of "triplet counters" (eq 8) must provide a fast trapping process for aromatic triplets; in the presence of a reasonably high concentration of $\underset{\frown}{C}$, the lifetime of $\underset{\frown}{A}^{*(3)}$ is likely to be short enough that quenching by $\underset{\frown}{H}$ is not significant. Furthermore, McGlynn and coworkers (28) found that the rate constant for radiationless decay of naphthalene triplets was essentially the same in ethyl bromide solvent as in ethyl alcohol. This result provides more evidence that heavy atom enhancement of $T_1 \rightarrow S_0$ intersystem crossing is not important in the present case. If such quenching should occur, however, upward curvature in plots based on eq 16 would be predicted (*vide infra*). This discussion assumes that $\underset{\frown}{H}$ is not a species which will react chemically with aromatic triplets.

The interaction represented by eq 17 seems intuitively the least likely, but it is the most difficult to rule out experimentally. If such a process is important, it may be shown that eq 16 becomes eq 21; i.e., the values of Φ_{isc} determined from linear plots of eq 16 will be too large by the factor $(k_6 + k_{17})/k_6$.

$$(F^o/F')(F'/F - 1) = \Phi_{isc}([k_6 + k_{17}]/k_6)(Y_T F'/Y_T' F - 1) \tag{21}$$

Since the energy difference between S_1 and S_o is even larger than that between S_o and T_1 and since the heavy atom fluorescence quencher functions through spin-orbit coupling (29), which shows its greatest effect on spin-forbidden transitions, it does not seem likely that this process can be much more important than that in eq 18. Medinger and Wilkinson (30) considered this process in their study of the intersystem crossing yields of anthracene derivatives, as determined by flash spectroscopic triplet-triplet absorptions with enhancement of triplet production by bromobenzene. They found that for many compounds

$$\Phi_f + \Phi_T(1 + k_{17}/k_6) = 1 \tag{22}$$

within experimental error. Since it followed that

$$\Phi_f + \Phi_T(1 + k_3/k_5) = 1 \tag{23}$$

for these compounds, the authors concluded that either $k_{17} \ll k_6$ or $k_{17}/k_6 = k_3/k_5$ for all the compounds studied. Since the latter condition seemed unlikely for a series of anthracene derivatives with triplet yields ranging from 0.75 to 0.12, they concluded that singlet quenching by the heavy atom fluorescence quencher as represented by eq 17 was probably not an important process. The assumptions that the processes in eqs 17-20 may be neglected will be considered further in the discussion section.

Fluorescence Quenching by Olefins

A quenching process which can have a significant effect on values of Φ_{isc} measured by the procedure described here is that of singlet quenching by olefinic triplet counters (eq 4). The rates at which simple olefins quench the fluorescence of benzene and its simple derivatives is the subject of some controversy in the literature. Cundall has reported that "pure olefins, free from dienes and oxidation products" quench the fluorescence of benzene and toluene at about 2×10^5 $\underline{M}^{-1}$ sec^{-1} (8), while Morrison has reported that trans-2-heptene quenches toluene fluorescence at 1.5×10^7 $\underline{M}^{-1}$ sec^{-1} (23). In order to evaluate the importance of singlet quenching by olefins which could be used as triplet counters in the present investigation, singlet quenching was investigated using cis- and trans-2-pentene freshly distilled from lithium aluminum hydride. Analysis of the olefins by glpc indicated that 1,3-pentadienes were present in less than 0.01% in each isomer. The results are summarized in Table I. While the value observed

TABLE I. Fluorescence Quenching by *cis*- and *trans*-2-Pentene[a]

Compound	*cis*-2-Pentene $k_4(\underline{M}^{-1}sec^{-1}) \times 10^{-7}$	*trans*-2-Pentene $k_4(\underline{M}^{-1}sec^{-1}) \times 10^{-7}$
Anisole	10	3.4
Toluene	3	0.65
Benzene	4	—

[a] These values were determined with the assistance of Dr. L. Lorenc.

for quenching toluene by the trans olefin is somewhat less than that reported by Morrison, all the quenching rate constants are considerably larger than the value of 2×10^5 $\underline{M}^{-1}\text{sec}^{-1}$ reported by Cundall. It is concluded that singlet quenching may be an important process when the 2-pentenes are used as triplet counters. (Actually, it is of little consequence whether singlet quenching occurs through the process indicated in eq 4 or whether impurities are involved. As long as the decreased number of $\underset{\frown}{A}^{*(1)}$ states which results from the addition of $\underset{\frown}{C}$ are taken into consideration, the result is the same.)

Assuming for the moment that the values indicated in Table I do represent singlet quenching by $\underset{\frown}{C}$, the ordering of the rate constants there does not provide much insight into the nature of the quenching interaction. The larger rate constant for quenching anisole fluorescence than for quenching that of toluene seems inconsistent with structure-reactivity relationships observed in the quenching of substituted naphthalenes by conjugated dienes. In those cases some authors have suggested quencher to quenchee charge transfer as an important factor (31). The slightly greater rate constant for quenching benzene than toluene fluorescence by the cis isomer is consistent with those views, but greater steric hindrance in toluene may mask more fundamental variations affecting k_4 values (32).

The Experimental Method

The heavy atom fluorescence quencher used in this study was xenon, which has been shown to quench singlets by inducing intersystem crossing (17). *cis*-2-Pentene was used as the "triplet counter," and the appearance of *trans*-2-pentene (**T**) was monitored by glpc. Concentrations of the aromatic compound in isooctane solution were chosen so as to give an optical density of 2.2 or greater at 254 nm, the wavelength which was used both for fluorescence measurements and for irradiation for sensitized olefin isomerization. Solutions of identical concentrations of **A**, one containing 0.05 - 0.10 *M* *cis*-2-pentene were prepared. The samples were degassed by four freeze-pump-thaw cycles at $< 10^{-4}$ Torr in round quartz tubes (13 mm o.d.). After the fourth pumping, a varying amount of xenon was bulb-to-bulb distilled into selected tubes, one at a time. The maximum concentration of xenon achieved must have been < 0.1 *M*, the solubility limit of xenon in isooctane (33). The tubes were sealed and were allowed to warm to room temperature over several hours before fluorescence spectra were recorded. The tubes were then irradiated simultaneously at 254 nm in a merry-go-round apparatus (34) to < 4% conversion. Appearance of *trans*-2-pentene, relative to *n*-pentane as an internal standard, was determined by glpc.

Results

In order to evaluate the method described above as a procedure for the determination of intersystem crossing yields in solution, anisole, mesitylene, and toluene were chosen for study. Anisole was of interest because of its relation to another investigation (35). Its low triplet energy, 80.7 kcal/mole (18), is probably less than that of cis-2-pentene, so it could not be studied by the Cundall technique. Toluene had been studied by a number of investigators (8, 15, 20) so the experimental results could be compared with the values in the literature. Mesitylene was selected because it has both lower triplet energy, 80.1 kcal/mole (18), and greater steric hindrance than toluene. It was argued above that either or both of these factors would make the Cundall method even more unreliable than it is in the determination of Φ_{isc} for toluene.

Table II summarizes the results in isooctane solution at room temperature for the three compounds studied, and plots of $(F^o/F')(F'/F - 1)$ vs. $(F'/F)(Y_T/Y_T') - 1$ are shown in Figure 1. Straight lines with linear correlation coefficients $\geq .995$ are observed in each case. Values of Φ_{isc} obtained from the slopes are shown in Table III.

The estimated error limits in Table III are primarily the result of uncertainties in the relative fluorescence intensities. Fluorescence from solutions in round quartz tubes was observed at 90^o to the exciting light. Slight variations in tube diameter can

TABLE II. Effect of Xenon on Fluorescence and Sensitized Cis-Trans Isomerization

Compound	[C]	F^o/F'	F'/F	Y_T/Y_T'
Anisole	0.10 M	1.16	1.00	1.00
			1.21	1.10
			1.41	1.18
			1.60	1.26
			2.00	1.27
Mesitylene	0.05 M	1.02	1.00	1.00
			1.14	1.06
			1.19	1.10
			1.27	1.14
			1.39	1.19
Toluene	0.05 M	1.05	1.00	1.00
			1.24	1.16
			1.33	1.30
			1.74	1.45
			1.86	1.47

Figure 1

Determination of Intersystem Crossing Quantum Yields of Anisole (o), Mesitylene (△), and Toluene (□) in Isooctane Solution

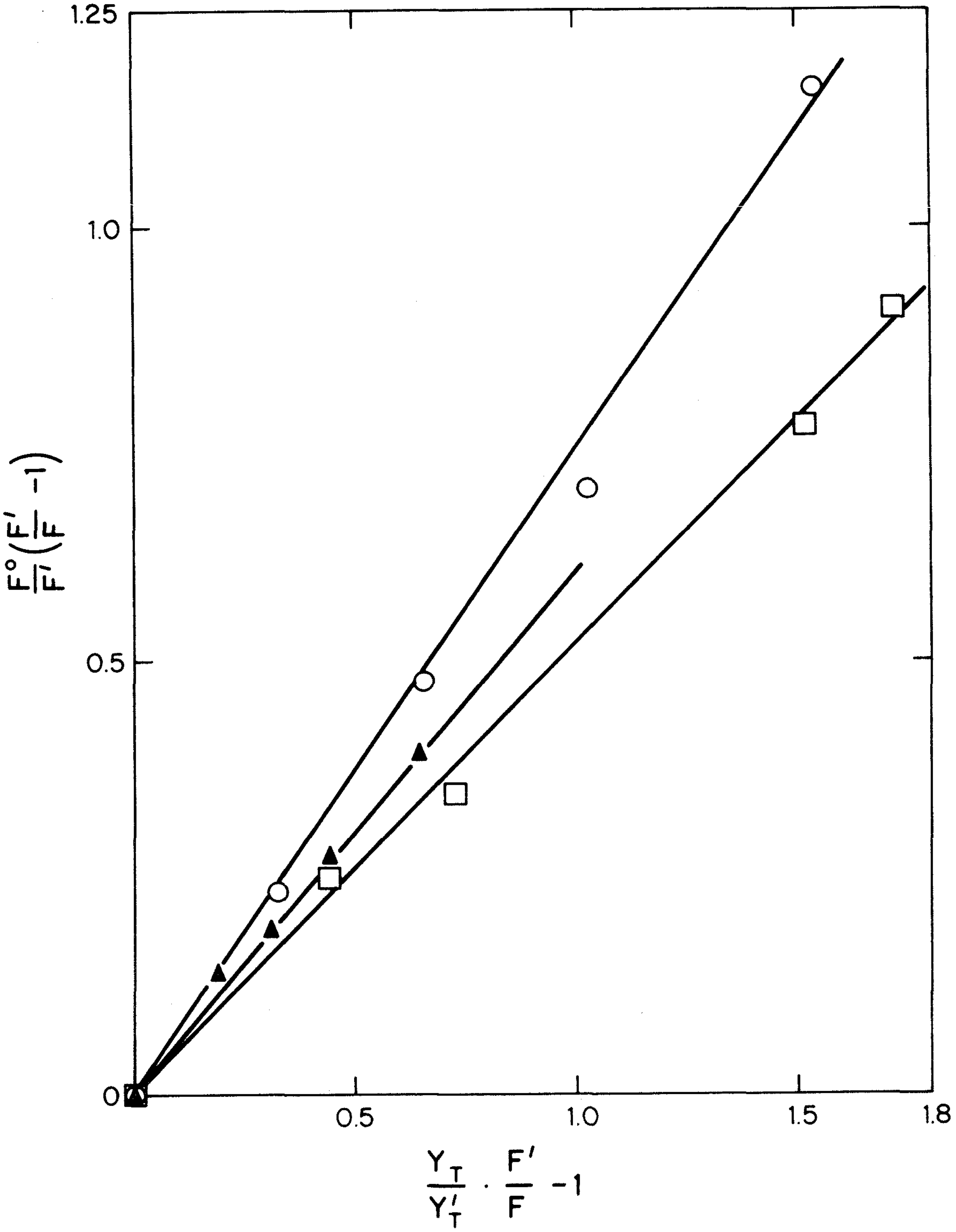

1.25
1.0
0.5
0
0.5
1.0
1.5
1.8
$\frac{F^\circ}{F'}\left(\frac{F'}{F}-1\right)$
$\frac{Y_T}{Y'_T}\cdot\frac{F'}{F}-1$

TABLE III. Intersystem Crossing and Fluorescence Quantum Yields in Isooctane Solution

Compound	Φ_{isc}	Φ_f[36]	$\Phi_{isc} + \Phi_f$	Φ_{isc}(literature)
Anisole	0.74 ± .04	0.24 ± .01	0.98 ± .05	
Mesitylene	0.60 ± .03	0.13 ± .01	0.73 ± .04	
Toluene	0.52 ± .03	0.14 ± .01	0.66 ± .04	0.53 (15) 0.46 (8) 0.34 (20)

have significant effects on the fluorescence ratios observed since the optical densities of the solutions were greater than 2 at the exciting wavelength.

Table III also shows fluorescence quantum yields for these compounds in isooctane solution; they were determined by comparing the respective fluorescence intensities to those of cyclohexane solutions of equal optical density and were corrected for solvent index of refraction (36). Values of Φ_f are essentially the same in both solvents.

The only one of the compounds studied here for which Φ_{isc} had been reported is toluene, and literature values are also shown in Table III. The present determination, 0.52, agrees well with that of Sandros (0.53) but is larger than the other two values. Cundall's value of 0.46 (8) is probably low because of the inefficiency of energy transfer to the trans isomer. Cundall measured only $\Phi_{c\to t}$; $\Phi_{t\to c}$ was calculated assuming the ratio of $\Phi_{t\to c}/\Phi_{c\to t}$ is the same for toluene as was observed for benzene (0.95). In view of Morrison's report (23) that the ratio is really 1.15 ± .15, Cundall's value may be corrected to give $\Phi_{isc} = 0.49 \pm .04$. Another complicating factor may be that Cundall's value was measured in neat toluene. Recent evidence indicates that singlet excimers may increase benzene intersystem crossing yields (37); however, Morrison reports no concentration dependence of Φ_{isc} for toluene in the range 0.02 - 5 M.

There are no obvious reasons why the value of Φ_{isc} reported by Morrison should be in error. The value of 0.34 was measured with piperylene isomerization and may not be adequately corrected for singlet quenching and other complicating factors. (The "uncorrected" value was 0.076) Another reason may be that Morrison's degassing procedure involves purging solvents with argon, which may not remove all oxygen from the solutions. Although it is possible that Morrison's value of 0.34 is an accurate measurement, it seems inconsistent with the values measured in this study and two others by three quite different methods.

It may be seen from Table III that the sum of $\Phi_{isc} + \Phi_f$ is unity, within experimental uncertainty, for anisole, but that the sum is considerably less for mesitylene and toluene. A significant fraction of the excited singlets of these two compounds must decay without fluorescence or intersystem crossing. This result is in contrast to that obtained for polycyclic aromatics, for which the sum of $\Phi_{isc} + \Phi_f$ generally is near unity (17).

Table IV shows the fluorescence, radiationless decay, and intersystem crossing rate constants for the compounds studied here (calculated from the relationship $k_n = \tau_f^o/\phi_n$, where τ_f^o has the meaning indicated on page 121). It is interesting to note that values for k_3 show only a slight variation among the three compounds, and that the variation in k_5 is not much greater. It would be premature to speculate on the origins of these differences. Further study with a number of benzene derivatives may provide a more secure basis

TABLE IV. Rate Constants for Processes which Depopulate $\underset{\frown}{A}^{*(1)}$

Compound	$\tau_f^{o\,a}$ (sec) x 10^9	k_2 (sec^{-1}) x 10^{-7}	k_3 (sec^{-1}) x 10^{-7}	k_5 (sec^{-1}) x 10^{-7}
Anisole	8.3	2.9	0.24	8.9
Mesitylene	26.5	0.36	0.74	1.6
Toluene	34	0.41	1.0	1.5

[a] τ_f^o has the meaning given on page 121. Lifetimes are published values for cyclohexane solution (3). They are identical, within experimental error, in isooctane solution (36).

for the discussion of singlet radiationless decay processes.

Accuracy of the Method

The lack of curvature in the lines in Figure 1 suggests that quenching processes described in eqs 18-20 are not significant sources of error. The good agreement of the value of Φ_{isc} measured for toluene with two of the three previously reported values does not entirely confirm the accuracy of the method, but it is a satisfying indication that intuitive concepts about the type of quenching in eq 17 are probably correct. It may be concluded that the method presented here is a reliable, convenient procedure for determining intersystem crossing quantum yields.

DISCUSSION

Extension of the Method to the General Case

In principle the present method may be extended in a variety of ways. For example, the determination of relative fluorescence intensities might be replaced by determination of relative yields of singlet photoproduct. Any process which is characteristic of the singlet state may be used as the "singlet counter," and any process which is characteristic of the triplet state may serve as the "triplet counter." By using lower energy triplet counters, such as dienes, intersystem crossing yields for compounds with triplet energies much lower than those of simple olefins may be determined. Other heavy atom additives, such as bromobenzene, may serve as **H** in these cases if they do not absorb light at the wavelength at which **A** is excited. Quina (36) has determined Φ_{isc} for naphthalene using *cis*-1,3-pentadiene as the triplet counter and ethyl bromide as **H**. His value, 0.79, is in good agreement with that reported by Horrocks and Wilkinson, 0.82 (12).

Other Applications of the Method

After the work described here was completed, it was learned that somewhat related studies have been described. Cundall (38) has reported that the fluorescence of *o*-xylene and its photorearrangement to m-xylene are quenched with the same rate constant by xenon and has concluded that the rearrangement occurs from the singlet state. Bensasson et al. (39) used added xenon to increase the intensity of a transient absorption in the pulsed laser photolysis of benzene. Using a kinetic formulation which was essentially that of Horrocks and Wilkinson, these workers presented evidence that the transient absorption was due to a benzene triplet excimer.

Further possibilities include application of intersystem crossing enhancement to elucidate the mechanisms of photochemical reactions in bichromophoric systems (40-42) and other systems in which the multiplicity of the reacting states is not clearly defined. In addition, it should also be possible to apply the principles discussed here to the study of photochemical and photophysical processes in the gas phase.

Concluding Remarks

The results of this study indicate that the method presented here can be a convenient, useful technique for the determination of intersystem crossing yields of aromatic compounds and should thus be helpful in understanding the decay processes of electronically excited states, especially for benzene derivatives. In addition, the use of the enhancement of intersystem crossing as a photochemical tool to identify the multiplicities of excited states which lead to photochemical products is a particularly attractive potential application of the present method.

EXPERIMENTAL

Instruments

A Hewlett-Packard Model 700 gas chromatograph with flame ionization detectors was used for gas-liquid phase chromatography (glpc). Integrals were recorded on a Hewlett-Packard Model 3307B electronic integrator. Fluorescence spectra were recorded on Aminco-Bowman or Perkin-Elmer Model MPF-3 spectrophotometers.

Materials

Xenon was Airco analyzed research grade; the analysis supplied with the sample indicated 10.4 ppm krypton as the only impurity detectable by mass spectrometry. Benzene (Matheson, Coleman, and Bell, Spectroquality) and toluene (Harleco, Fluorometric grade) were used as received. Mesitylene (Aldrich, Gold Label, 99+%) was distilled from sodium (bp 162.9-163.0^{o}). Anisole had been purified for another study (35). Pentane had been purified by the method of Murray and Keller (43) and distilled from lithium aluminum hydride. Isooctane (Eastman Organic Chemicals, Spectro grade) was used as received.

cis-2-Pentene (Chemical Samples Co., 99%) and trans-2-pentene (Chemical Samples Co., 99.9%) were distilled from lithium aluminum hydride and stored at $< 0^{o}$ until used. The cis isomer used in isomerization measurements was from a lot which, fortuitously, was > 99.8% pure. Both isomers were seen by glpc to contain levels of diene impurity too low to measure (< 0.01%).

Determination of Singlet Quenching by Olefins

Isooctane solutions containing equal concentrations of the aromatic compound (O D ca. 0.2 at λ_{max}) and varying concentrations of olefin were added to 13 mm round quartz tubes equipped with grease seals and ground glass joints. The solutions were degassed by the freeze-pump-thaw process, and the tubes were sealed under a pressure of $\leq 5 \times 10^{-4}$ Torr.

Determination of Intersystem Crossing Quantum Yields

Two isooctane solutions with the same concentration of the aromatic compound were prepared; one of these also contained 0.05 or 0.10 M cis-2-pentene as the triplet counter and ca. 2×10^{-3} M n-pentane as internal standard. Aliquots (4.0 ml) of the solutions were transferred to quartz tubes (described above). The solutions were degassed by four cycles of the freeze-pump-thaw process at pressures of $2 - 5 \times 10^{-4}$ Torr. After the fourth pumping, xenon was admitted to some of the tubes, one at a time, in the following manner: a glass tube with known volume (2.5 ml) between two stopcocks was used to connect the xenon bulb to the vacuum line. By alternately opening and closing its stopcocks, any number of aliquots of the same volume of xenon gas could be bulb-to-bulb distilled into a selected tube. (The pressure inside the xenon flask, originally 754 Torr, decreased slightly with each addition, so the number of moles of xenon added decreased slightly during the course of the experiments described here. This simply required adding more aliquots of xenon in the later experiments than in the earlier experiments.) All tubes were then sealed without being reopened to the vacuum line.

After they had warmed to room temperature over several hours in the dark, the relative fluorescence spectra (excitation wavelength 254 nm) were taken with the Perkin-Elmer spectrophotometer. The solutions were then irradiated at 254 nm for 14 - 18 hrs in a merry-go-round apparatus (34). Solutions were analyzed at least twice by glpc using a 22 ft x $\frac{1}{8}$ in column of 25% β,β'-oxydipropionitrile coupled with 15 ft x $\frac{1}{8}$ in of 5% silver nitrate in β,β'-oxydipropionitrile, both on 60/80 mesh Chromosorb W, operated at room temperature.

REFERENCES

1. The terms used in this part have their usual meanings; cf., J. N. Pitts, F. Wilkinson, and G. S. Hammond, Adv. Photochem., **1**, 1 (1963), or N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, 1967 .
2. For a more complete discussion, see J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, London, (1970).
3. I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, 1971 .
4. The cis-trans isomerization of stilbene provides an interesting example; cf., S. Sharafy and K. A. Muszkat, J. Amer. Chem. Soc., **93**, 4119 (1971) and references therein.
5. A. A. Lamola and G. S. Hammond, J. Chem. Phys., **43**, 2129 (1965).
6. L. M. Stephenson, Ph. D. Thesis, California Institute of Technology, Pasadena, California, 1968 .
7. R. B. Cundall and P. A. Griffiths, Disc. Faraday Soc., **36**, 111 (1963) and references therein.
8. R. B. Cundall and W. Tippett, Trans. Faraday Soc., **66**, 350 (1970).
9. R. B. Cundall and A. J. R. Voss, Chem. Commun., 116 (1969).

10. J. B. Callis, M. Gouterman, and J. D. S. Danielson, *Rev. Sci. Inst.*, **40**, 1599 (1969).

11. M. Guéron, J. Eisinger, and R. G. Schulman, *Mol. Phys.*, **14**, 111 (1968).

12. A. R. Horrocks and F. Wilkinson, *Proc. Roy. Soc., Ser. A*, **306**, 257 (1968) and previous papers.

13. P. G. Bowers and G. Porter, *Proc. Roy. Soc., Ser. A.*, **299**, 348 (1967).

14. C. A. Parker and T. A. Joyce, *Chem. Commun.*, 234 (1966).

15. K. Sandros, *Acta Chem. Scand.*, **23**, 2815 (1969).

16. R. E. Kellogg and R. G. Bennett, *J. Chem. Phys.*, **41**, 3042

17. V. L. Ermolaev and E. B. Sveshnikova, *Opt. Spectry.* (English Translation), **14**, 320 (1964).

18. For a summary of reported data, see P. S. Engel and B. M. Monroe, *Adv. Photochem.*, **8**, 245 (1971).

19. G. Porter and M. W. Windsor, *Proc. Roy. Soc., Ser. A.*, **245**, 238 (1958).

20. W. Ferree, Jr., J. B. Grutzner, and H. Morrison, *J. Amer. Chem. Soc.*, **93**, 5502 (1971).

21. J. Saltiel, L. Metts, and M. Wrighton, *J. Amer. Chem. Soc.*, **92**, 3227 (1970).

22. J. S. Winterle and G. S. Hammond, unpublished results.

23. H. Morrison, J. Pajak, and R. Peiffer, *J. Amer. Chem. Soc.*, **93**, 3978 (1971).

24. J. Saltiel, K. R. Neuberger, Mark Wrighton, *J. Amer. Chem. Soc.*, **91**, 3658 (1969).

25. D. F. Evans, *J. Chem. Soc.*, 2753 (1969); Y. Kanda and R. Shimada, *Spectrochim. Acta*, **17**, 279 (1961). A value of 82.3 kcal/mole has also been reported for the toluene triplet (18).

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

27. M. Itoh and R. S. Mullikan, *J. Phys. Chem.*, **73**, 4332 (1969).

28. S. P. McGlynn, M. J. Reynolds, G. W. Daigre, and N. D. Christodoyleas, *J. Phys. Chem.*, **66**, 2499 (1962).

29. (a) D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).
    (b) M. Kasha, *J. Chem. Phys.*, **20**, 71 (1952).

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

31. T. R. Evans, *J. Amer. Chem. Soc.*, **93**, 2081 (1971).

32. D. A. Labianca, G. N. Taylor, and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 3679 (1972).

33. H. L. Clever, *J. Phys. Chem.*, **62**, 375 (1958).

34. F. G. Moses, R. S. H. Liv, and B. M. Monroe, *Mol. Photochem.*, **1**, 245 (1969).

35. F. A. Carroll, this dissertation, p. 1.

36. F. H. Quina, personal communication.

37. R. B. Cundall, L. C. Pereira, and D. A. Robinson, *Chem. Phys. Lett.*, **13**, 253 (1972).

38. R. B. Cundall and A. J. R. Voss, *Chem. Commun.*, 902 (1968).

39. R. V. Bensasson, J. T. Richards, and J. K. Thomas, *Chem. Phys. Lett.*, **9**, 13 (1971).

40. H. Kristinsson and G. S. Hammond, *J. Amer. Chem. Soc.*, **89**, 5968 (1967).

41. E. C. Sanford and G. S. Hammond, *J. Amer. Chem. Soc.*, **92**, 3497 (1970).

42. D. DeKeukeleire and G. S. Hammond, unpublished results.

43. E. C. Murray and R. N. Keller, *J. Org. Chem.*, **34**, 2234 (1969).