INFORMATION TO USERS

This dissertation was produced from a microfilm copy of the original document. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the original submitted.

The following explanation of techniques is provided to help you understand markings or patterns which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting thru an image and duplicating adjacent pages to insure you complete continuity.

2. When an image on the film is obliterated with a large round black mark, it is an indication that the photographer suspected that the copy may have moved during exposure and thus cause a blurred image. You will find a good image of the page in the adjacent frame.

3. When a map, drawing or chart, etc., was part of the material being photographed the photographer followed a definite method in "sectioning" the material. It is customary to begin photoing at the upper left hand corner of a large sheet and to continue photoing from left to right in equal sections with a small overlap. If necessary, sectioning is continued again — beginning below the first row and continuing on until complete.

4. The majority of users indicate that the textual content is of greatest value, however, a somewhat higher quality reproduction could be made from "photographs" if essential to the understanding of the dissertation. Silver prints of "photographs" may be ordered at additional charge by writing the Order Department, giving the catalog number, title, author and specific pages you wish reproduced.

72-22,579

NARANG, Rajinder Singh, 1943-
  INDUCED PHOTOLYSIS OF ALKYL HALIDES.

  Colorado State Univeristy, Ph.D., 1972
  Chemistry, general

University Microfilms, A XEROX Company , Ann Arbor, Michigan

THESIS

INDUCED PHOTOLYSIS OF ALKYL HALIDES

Submitted by

Rajinder S. Narang

In partial fulfillment of the requirements

for the Degree of Doctor of Philosophy

Colorado State University

Fort Collins, Colorado

March, 1972

COLORADO STATE UNIVERSITY

March, 1972

WE HEREBY RECOMMEND THAT THE THESIS PREPARED

UNDER OUR SUPERVISION BY RAJINDER S. NARANG ENTITLED

INDUCED PHOTOLYSIS OF ALKYL HALIDES BE ACCEPTED AS

FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY.

Committee on Graduate Work

Adviser

Head of Department

ii

PLEASE NOTE:

Some pages may have

indistinct print.

Filmed as received.

University Microfilms, A Xerox Education Company

ABSTRACT OF THESIS

INDUCED PHOTOLYSIS OF ALKYL HALIDES

1, 1, 1-trichloro-2, 2-bis(p-chlorophenyl)ethane (DDT) was photolyzed in the presence of various inducers like amines, ketones, sulphides, etc., with light of wavelength 3100 $\overset{\circ}{A}$. DDT was decomposed to varying degree by different inducers. Compounds which are easily oxidized are better inducers for the decomposition of DDT. Photoreaction of DDT and N, N-diethylaniline in methanol in air yielded 1, 1-dichloro-2, 2-bis(p-chlorophenyl)ethane (11%), 1, 1-dichloro-2, 2-bis(p-chlorophenyl)ethylene (12%), 4, 4'-dichloro benzophenone (10.8%), methyl 1, 1-bis(p-chlorophenyl)acetate (31%), α, α-bis(p-chlorophenyl)-p-diethylamino acetophenone, and diethylaniline hydrochloride as major products. Cis and trans isomers of 1, 1, 4, 4-tetrakis(p-chlorophenyl)-2-butene, 1, 1-bis(p-chlorophenyl)-2-(p-diethylaminophenyl)-2-methoxy ethylene, 1, 1-bis(p-chlorophenyl)-2, 2-bis (p-diethylaminophenyl) ethylene are the minor products. The photoreaction of DDT with diethylaniline or triphenylamine is not quenched by piperylene or naphthalene. The reaction of DDT with diethylaniline has a quantum yield of 0.57 calculated for the disappearance of DDT.

The photoreaction of decyl bromide and N, N-diethylaniline with 3100 $\overset{\circ}{A}$ light yielded N-ethylaniline (2.7%), decane (13.5), o-decyl-N, N-diethylaniline (56.8%), p-decyl-N, N-diethylaniline (30.6%) and diethylaniline hydrobromide (69%) as the major products. The reaction is rather insensitive to solvent effects and is not quenched by piperylene. When the reaction is carried out in the presence of n-butylmercaptan the yield of n-decane is increased, indicating the formation of decyl radicals in the intermediate stage. It has a quantum yield of 0.377 calculated for the disappearance of decyl bromide.

Both of the above reactions seem to involve an electron transfer from the amine to the halide. It can take place from ground state or excited state charge transfer complex of amine-alkyl halide or from the singlet of the amine to the alkyl halide.

Rajinder S. Narang
Department of Chemistry
Colorado State University
Fort Collins, Colorado 80521
March, 1972

iv

Dedicated to my parents

Dr. and Mrs. K. S. Narang

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation and gratitude to his adviser, Dr. Larry L. Miller, for his constant guidance, original ideas and great patience throughout this work. Sincere thanks are expressed to Dr. F. R. Stermitz, Dr. K. Watkins and Dr. R. E. Johnsen for their help in preparing the dissertation. Thanks are also due to Dr. K. Debruin for helpful discussions.

Acknowledgement is made of the financial support from Colorado Agricultural Experimental Station.

The help from a number of past and present graduate students of the chemistry department in formulating new ideas has been appreciated by the author. He also expresses his thanks to all the people who helped in drafting and typing the dissertation.

Finally, appreciation and thanks go to my wife, Neelam, for her constant cares and encouragement, not to mention her patience, during the entire period of research.

TABLE OF CONTENTS

LIST OF TABLES

viii

LIST OF FIGURES

CHAPTER I

INTRODUCTION

1, 1, 1-trichloro-2, 2-bis(p-chlorophenyl)ethane, more commonly known as DDT has been used as a very effective insecticide for over thirty years. In recent years people have become aware of its long persistence in the environment and its adverse ecological effects. This has drawn the attention of a number of workers in a variety of scientific fields to eliminate DDT and other chlorinated pesticides from the environment. In our work we have attempted to degrade DDT photochemically by using it in conjunction with other chemical compounds. These compounds can absorb sunlight and transfer energy to DDT which could induce its degradation.

The main objectives of the present research are (1) to determine which class of compounds are most effective for dechlorination of alkyl halides; (2) to determine the photoproducts; and (3) to propose possible pathways in which they can arise.

CHAPTER II

LITERATURE REVIEW

Photochemistry of DDT

The first indication that DDT was sensitive to light was found
by Linquist and co-workers (1). They observed that DDT lost insec-
ticidal activity when exposed as a thin layer on plywood boards or
glass petri dishes to a G.E. 30 watt tube for 72 hours. Turell (2)
and others (3) found the same to be true in agricultural fields. This
led Gunther (3) to propose that light may have some catalytic effect
on dehydrohalogenation of DDT.

Wichmann and co-workers (4) reported that ultraviolet light had
no effect on pure solid DDT, 1, 1-dichloro-2,2-bis(p-chlorophenyl)
ethylene (DDE) and 4,4'-dichlorobenzophenone (DDCO), while in
solution some of the DDT had decomposed by the time solvent had
evaporated. They also observed DDE in solution decomposed faster
than DDT while DDCO was unaffected.

Fleck (5, 6) was the first one to attempt to isolate the photo-
products of DDT. He irradiated DDT in ethanol with a 360 watt
mercury lamp for 16 hours in quartz tubes. He showed that one mole
of hydrogen chloride was evolved per mole of DDT reacted and
was able to isolate a product by fractional crystallization in about

10% yield. He identified this by chemical means to be 2, 3-dichloro-1, 1, 4. 4-tetrakis (p-chlorophenyl)-2-butene. A γ-valerolactone solution of DDT on irradiation in an open petri dish yielded DDCO. To explain this he proposed DDE is first formed by elimination of HCl from DDT and the double bond so formed is further oxidized.

Mitchell (7) spotted various pesticides including DDT on paper, irradiated those with 2537 Å light and observed the decomposition of DDT. He did not try to isolate the products. Roburn (8) photolyzed DDT as a thin film with a germicidal lamp which had main output at 2537 A for 2-3 hours. Glc analysis of the reaction mixture showed the presence of three volatile products. He identified one product as DDE, the second had retention times very similar to DDCO, but was unable to identify the third product. He suggested DDCO is formed by the ozonolysis of DDE as some ozone is always present under the uv lamp.

Miller et al. (9) studied the photodecomposition of solid and degassed cyclohexane solutions of DDT with 2537 Å light in some detail. From glc and tlc analyses they identified 1, 1-dichloro 2, 2-bis (p-chlorophenyl) ethane (DDD), DDE, DDCO, p-chlorobenzoic acid and 1, 1-bis (p-chlorophenyl)acetic acid as the major products. DDE and DDD are the primary photoproducts which degrade to a further extent. In the presence of a radical scavenger, such as n-butyl mercaptan, the yield of DDD increased. It decreased when iodine

was used for the same purpose. This suggested the formation of an

intermediate radical which in turn leads to the formation of primary

photoproducts. These observations along with low quantum yields

for the reaction led them to propose a short chain mechanism.

$$Ar = -C_6H_4-Cl$$

$$DDT \longrightarrow I + \cdot Cl$$

$$I + DDT \longrightarrow DDD + II$$

$$I + Cl\cdot \longrightarrow DDE + HCl$$

$$DDT + Cl\cdot \longrightarrow II + HCl$$

$$Cl\cdot + C_6H_{14} \longrightarrow HCl + \cdot C_6H_{13}$$

$$I + II \longrightarrow DDT + DDE$$

Plimmer et al. (10) studied the photooxidation of methanol solutions

of DDT and DDE in considerable detail. They identified about 40

products by connecting a gas chromatograph with a mass

spectrometer and picking off the volatile components. Most of the photoproducts from DDE were the same as from DDT, but in addition these contained some products with a fluorene structure. These were proposed to arise by the photocyclization of DDE. It was also observed that the nature of the photoproducts was dependent on the wavelength of the light used. For example, with light of wavelength shorter than 2600 $\overset{o}{A}$ ring chlorines were displaced; whereas these were not affected when light of wavelength greater than 2600 $\overset{o}{A}$ was used. A mechanism similar to the one porposed by Miller et al. (9) was proposed to explain the formation of various products.

Sherman and co-workers (11) recently studied the γ-radiation induced dechlorination of DDT in 2-propanol. They found DDD, HCl and acetone as the major products. A radical chain mechanism was proposed with chains of the order of twelve or more. They also claimed this to be true in the case of photochemical reaction of DDT, which is in conflict with the short chain mechanism proposed by Miller et al. (9).

In recent years reports (12, 13, 14) have been published on the sensitized photo-isomerizations of various diene pesticides such as aldrin, dieldrin, etc.

Dieldrin   Photodieldrin

Ivie and Casida (15) have also screened quite a few pesticide-sensitizer combinations by spotting the pesticide and the sensitizer on a tlc plate, irradiating with sunlight and then developing the plate to see how many photoproducts are formed. They did not try to isolate the products but observed that different sensitizers do not have the same activity for all the pesticides.

Photochemistry of Amines in the Presence of Halides

Lewis and Lipkin (16, 17) were the first to observe the photo-oxidations of tertiary amines in solid glasses, with a cation radical of the amine being the only product.

This process was studied by a number of other workers (18, 19). Albrecht and Cadogan (20) found that photoionisation of N, N, N',N'-tetramethyl-p-phenylenediamine was a two photon process.

Collins (21) was the first to observe that carbon tetrachloride solutions of amines (triethylamine, benzylamine, etc.) turned opaque when exposed to sunlight for 24-72 hours. Amine hydrochloride could be isolated from the reaction mixture. Wheeler (22) and others (23, 24a and b, 25, 26) had observed that metals (Cu, Fe), metal salts and oxygen can have a great effect on the rapidity and course of reaction. Asscher (24a and b) proposed a free radical mechanism for reactions of this type.

Stevenson and Coppinger (27) studied the photoreaction of carbon tetrachloride with alkyl amines (triethylamine). They isolated amine hydrochloride and chloroform as the two photoproducts. They also measured the uv spectra of triethylamine with added chloroform, fluorotrichloromethane, carbon tetrachloride and bromotrichloromethane. It was observed that either a 1:1 charge transfer complex is formed or an interaction occurs in 1:1 pairs to give rise to contact charge transfer spectra. In either case, the use of carbon tetrachloride results in absorptivity above 300 nm and consequently accounts for the photosensitivity of amine solutions. Davis and Farmer (28) have reported the formation of weak charge transfer complexes between aromatic amines (N, N-dimethylamine, N, N, N', N'-tetramethyl-p-phenylenediamine) and polyhaloalkanes (carbon tetrachloride, chloroform). They suggested that amine-CCl_4

reactions go through the formation of a complex in which the donor is in an excited state.

Kurz and co-workers (29) studied the dark and photochemical reactions of bromotrichloromethane with the derivatives of 1,4-dihydropyridine in methanol.

The quantum yield of the reaction varied from 7 to 80 depending on the conditions. The quantum yield drops to about 1 in the presence of dihydroanthracene which acts as a scavenger for trichloromethyl radicals. Reaction is initiated photochemically but continues by a nonphotochemical chain process.

The reaction schemes shown:

MeO_2C ... CO_2Me pyridine ring with N-R, $+ \cdot CCl_3 \longrightarrow$ H_3CO_2C ... H$\cdot$ ... CO_2CH_3 pyridine ring N-R $+ CHCl_3$

H_3CO_2C ... H$\cdot$ ... CO_2CH_3 pyridine ring N-R $+ BrCCl_3 \longrightarrow$ H_3CO_2C ... CO_2CH_3 pyridine ring N-R $+ Br^- + \cdot CCl_3$

Miller and co-workers (30) carried out a thorough study of the reaction of carbon tetrachloride with n-butylamine in the presence of uv light, metals or metal salts. This study was conducted with or without oxygen being present.

$$CCl_4 + nBuNH_2 \xrightarrow{\;2537\, \overset{o}{A}\;} Bu\overset{+}{N}H_3\overset{-}{Cl} + C_2Cl_6 + CHCl_3 + NH_3$$
$$+ \; CH_3CH_2CH_2CH = NCH_2CH_2CH_2CH_3$$

The above reaction can also be initiated by visible light when the concentration of amine exceeded 0.4M. It continues by a nonphoto-chemical process. The quantum yields varied from 1-100 which can be explained by the formation of a radical chain. The latter is initiated by the absorption of light on the part of the charge transfer complex formed between carbon tetrachloride and n-butyl amine. The chain is propagated by trichloromethyl radicals. Reaction is inhibited by dihydroanthracene. In the presence of oxygen, the yields

of chloroform and hexachloroethane decreased sharply, whereas

N, N'-dibutyl urea was formed in considerable amount. Furthermore,

oxygen did not change the rate of primary reaction. The following

mechanism which is very similar to that suggested by others (27, 29)

was proposed

$$RNH_2 \cdot CCl_4 \longrightarrow \overset{+}{R}NH_2 \overset{-}{C}l + \cdot CCl_3$$

$$\overset{+}{R}NH_2 \overset{-}{C}l + RNH_2 \longrightarrow RNH_3 Cl + R\overset{\cdot}{N}H$$

$$\cdot CCl_3 + RNH_2 \longrightarrow HCCl_3 + R\overset{\cdot}{N}H \text{ or } R'\overset{\cdot}{C}HNH_2$$

$$R\overset{\cdot}{N}H \text{ (or } R'\overset{\cdot}{C}HNH_2) + CCl_4 \longrightarrow RNClH \text{ (or } R'CHClNH_2) + \cdot CCl_3$$

$$RNClH \text{ (or } R'CHClNH_2) + RNH_2 \longrightarrow R'CH = NH + RNH_3 \overset{-}{C}l$$

$$R'CH = NH + RNH_2 \longrightarrow R'CH = NR + NH_3$$

$$2 \cdot CCl_3 \longrightarrow C_2 Cl_6$$

Pac and Sakurai (31) investigated the photoreactions of de-

gassed solutions of dimethylaniline in the presence of acids. When

the reaction was carried out with increasing concentrations of hydro-

chloric acid in Pyrex tubes (to cut down the absorption below 2900 Å)

the yields of benzene increased, indicating that benzene was derived

from the protonated dimethylaniline while free N, N-dimethylaniline

acts as a sensitizer. They proposed a mechanism involving the

formation of an excimer, in which N, N-dimethylaniline was in its

lowest singlet state and the protonated N, N-dimethylaniline was in the

ground state.

Primary process

$$DMA + h\nu \longrightarrow DMA^{*s}$$

$$DMA^{*s} + AN \longrightarrow [DMA^{*s}\text{----}AN]$$

$$[DMA^{*s}\text{----}AN] \longrightarrow DMA^+ + AN^-$$

$$AN^- \longrightarrow Ph + RN(CH_3)_2$$

Secondary process

$$DMA + CH_2O \longrightarrow Me_2N-\left[\bigcirc\right]_{/2} CH_2$$

IV

$$IV + DMA \longrightarrow Crystal\ Violet$$

Walsh and Long (32) had reported the photodecomposition of arylmethyl ammonium salts in oxygen free 1% methanolic solutions with 2537 Å light.

$$Y = Cl,\ Br,\ I,\ PhCO_2,\ BF_4,\ etc.$$

$$R = H,\ OCH_3,\ CH_3,\ F,\ etc.$$

Reaction in the case of Y = I proceeds smoothly while in the case of Y = BF_4 or Cl no reaction takes place. They observed there was a lot of association in solution of the compounds where Y = I which is missing when Y = Cl, BF_4. They claimed that the reaction goes through a direct charge transfer excitation of the associated ions, e.g.,

$$ArX^+Y^- \xrightarrow{h\nu} [ArX, Y]^* \longrightarrow A_r \cdot + X \cdot + Y \cdot$$

Latowski (33) in his study of the photolysis reaction between N, N-dimethylaniline and various monohalobenzenes proposed the formation of exciplex in the intermediate state. Recently, Sakurai et al. (34) had studied the same reaction. They observed an emission band at 372 nm with complete quenching of fluorescence in nonpolar solvents. This emission could not be observed in polar solvents. Using this, along with the kinetic data, they could establish the formation of an exciplex as an intermediate and proposed the following general mechanism to explain photochemistry:

$$D \xrightarrow{h\nu} D^s$$
$$D^s \xrightarrow{k_1} D$$
$$D^s + I \longrightarrow (D^+ \text{----} \bar{I})$$
$$(D^+ \text{----} I) \longrightarrow D + I$$
$$\phantom{(D^+ \text{----} I)} \longrightarrow D^+ + I^-$$
$$I^- \longrightarrow Ph \cdot + X \cdot$$

D = DMA,   I = halobenzene

Hammond and co-workers (35) observed that methyl chloro-
acetate and chloroacetamide quench the fluorescence of aromatic
compounds such as N, N-dimethylaniline, indole, anisole, etc. They
also noted that the fluorescence from N-chloroacetyl-3, 4-dimethoxy-
phenethylamine is significantly less than that from N-acetyl-3, 4-
dimethoxyphenethylamine. This can only be explained on the basis of
intramolecular singlet quenching by the chloro substituted amide.

The photochemistry which is observed from these types of
compounds (36, 37, 38)

and from the reaction of 1, 4 dimethoxybenzene and methylchloro-
acetate can be explained by supposing that the C-Cl bond of the

major product

quencher was involved in the internal conversion process in which

the electronic excitation of the complex formed is converted to

vibrational energy. This could lead to the rupture of carbon-halogen

bond and thus the observed photoreactions. They proposed a general

mechanism to account for the photoproducts which in essence was the

same as proposed by Sakurai et al. (34).

Recently Fitzgerald and co-workers (53) had studied the photo-

oxidation of N, N'-diphenyl-p-phenylenediamine (DPPD), N, N'-

dimethyl-N, N'-diphenyl-p-phenylenediamine (DMDPPD), N, N, N', N'-

tetraphenyl-p-phenylenediamine (TPPD) and p-hydroxy-diphenylamine

(HDPA) in chloroform. Hydrogen ion and phosgene were found along

with several other photoproducts. Also, the quantum yields in the

case of TPPD and HDPA were doubled when the reaction was carried

out in the presence of oxygen. The following mechanism is proposed

to account for the above observations:

$$A \longrightarrow {}^1A^*$$

$${}^1A^* \longrightarrow A + h\nu_f$$

$${}^1A^* \longrightarrow {}^3A^* \longrightarrow A$$

$${}^1A^* + CHCl_3 \longrightarrow A^{+\cdot} + Cl^- + \dot{C}HCl_2$$

$$\dot{C}HCl_2 + O_2 \longrightarrow CHCl_2O_2\cdot$$

$$CHCl_2O_2\cdot \longrightarrow CHClO + ClO\cdot$$

$$CHClO \longrightarrow HCl + CO$$

$$ClO\cdot + CHCl_3 \longrightarrow COCl_2 + HCl + Cl\cdot$$

$$Cl\cdot + A \longrightarrow A^{+\cdot} + \bar{C}l$$

CHAPTER III

EXPERIMENTAL

Instrumentation

Gas chromatography--A F & M Hewlett-Packard model 5750 gas chromatograph equipped with a flame ionization detector was used. The following columns were used.

Column 1. Teflon-lined aluminum tubing, 6 ft x 1/4 in, packed with 10% DC-200 on Chromosorb Q (60/80 mesh)

Column 2. A 6 ft x 1/4 in glass column packed with 5% SE 30 on Chromosorb W (100 mesh)

Column 3. A 6 ft x 1/8 in stainless steel column packed with 5% SE-30 on Chromosorb W (100 mesh)

Column 4. A 6 ft x 1/4 in glass column packed with 10% DC-200 and 15% QF-1 on Chromosorb W (60/80 mesh)

Column 5. A 6 ft x 1/4 in Teflon-lined aluminum column packed with 10% DC-200 and 15% QF-1 on Chromosorb W (60/80 mesh)

General operating conditions for the DDT experiments were columns 220-240°C, injection port 235°C, detector 350-370° and carrier gas flow of 50 ml/min. For the decyl bromide reaction

mixtures, the column temperature employed was 160°. Any other

conditions used are described along with the specific experiments.

Infrared spectroscopy -- All spectra were obtained on a Perkin

Elmer model 457 Grating Infrared Spectrometer. Samples were

examined either embedded in micro KBr pellets or contained in

micro cells in the form of solutions.

Nuclear Magnetic Resonance spectroscopy -- All spectra were

obtained on a Varian A-60 A spectrometer. Carbon tetrachloride

with 2% TMS or deuterochloroform with 1% TMS used as a solvent.

Ultraviolet-visible spectroscopy -- Spectra were either taken on

Perkin Elmer model 402 or a Bausch and Lomb model 505 equipped

with one cm quartz cells.

Mass spectrometer -- Mass spectra were obtained on an Associated

Electronic Industries model MS-12 using a direct probe.

Column chromatography -- Baker silica gel (80 mesh) or acid-

washed alumina pH 4.1 was used. All the solvents used for elution

were reagent grade and were distilled once before use. Columns

used were 36" x $1\frac{1}{2}$" and were packed with 45-60 g of the packing

used. In most cases 50-70 ml fractions were collected every 15

minutes using an automatic fraction collector. The columns were

always run nonstop. Depending upon the conditions 2-5 fractions

were combined, concentrated and examined using either glc or nmr

methods. In general, the nmr method was employed as most of the components do not elute from glc columns.

Thin layer chromatography -- Silica gel plates, 5 x 10 cm, were used to check the purity of compounds obtained from column chromatography. Plates were developed with hexane: ether mixtures in varying ratios (1:1, 2:1, 1.5:1), or with chloroform, benzene or methanol.

Melting points --- These were measured with a Fisher-Johns apparatus and are uncorrected.

Irradiation --- A Rayonet reactor fitted with 16, 21-watt lamps with major output at 3130 Å was used for irradiation. The reactor also was equipped with a merry-go-round operating at a speed of 5 rpm. The latter had space for eight test tubes (20-30 ml). Containers used for irradiation of solutions were either Pyrex Erlenmeyer flasks or Pyrex test tubes closed with rubber septums.

In most cases yields were determined by glc. Standard solutions (0.1 molar) were prepared in carbon tetrachloride. Injections using the same volume of standard solutions and reaction mixtures were made. Analyses of any reaction mixture were performed in a single run. A standard solution was injected before and after the reaction mixtures were tested. This was done to detect any variation in peak areas which might occur during the analysis. Peak areas were determined using the formula:

$$\text{area} = \text{peak height} \times \text{width at half height}$$

Gas chromatographic-mass spectroscopic analysis utilized a Perkin Elmer model 881 gas chromatograph equipped with flame ionization detector. The latter was connected to an AE1 MS-12 mass spectrometer through a Biemann splitter. Operating conditions for the gas chromatograph were, detector 270°, column $130\text{-}230^{\circ}$ with a 10 minute hold at the lower temperature followed by a 10°/min temperature programming. Carrier gas flow was 50 ml/min. A concentrated irradiated solution of decyl bromide and DEA after washing with dilute hydrochloric acid was injected and the desired peaks as these eluted from the column were picked up on the mass spectrometer.

Quantum yield determination.

(A) The method.

The method developed by Moore and Ketchum (39) for a benzophenone-benzhydrol actinometer was used. According to Moore and Ketchum, the quantum yield for a benzene solution which is 0.1 M in benzophenone and 0.1 M in benzhydrol is 0.69. The actinometer solutions were degassed by three freeze and thaw cycles to 0.005 mm of mercury and sealed under vacuum. All samples were run in parallel with the actinometer for the same length of time and the same volumes were used for both. Also the same kind of

tubes were used for both. The amount of benzophenone reacted was calculated after each photolysis by comparison of the uv spectra at 350 nm.

(B) The Calculations (40)

The quantum yields were calculated by using the following equations

$$\text{molecules reacted} = (6.023 \times 10^{23} \text{ molecules/mole})(V_s)(C_s)(\%S)$$

where
V_s = volume of irradiated sample in liters.

C_s = concentration of irradiated sample in moles/liter.

$\%S$ = percent completion of sample reaction.

$$\text{photons absorbed} = \frac{\text{molecules of actinometer which have reacted}}{\text{molecules of actinometer which have reacted/photon absorbed}}$$

$$\text{molecules of actinometer which have reacted/photon absorbed} = \phi_A$$

where ϕ_A = quantum yield of actinometer

$$\text{molecules of actinometer which have reacted} = 6.023 \times 10^{23} \text{ molecules per mole}(V_A)(C_A)(\%A)$$

where
V_A = volume of actinometer in liters

C_A = concentration of actinometer in moles/liter

$\%A$ = percent completion of actinometer reaction

$$\text{thus photons absorbed} = \frac{(6.023 \times 10^{23} \text{ molecules/mole})(V_A)(C_A)(\%A)}{\phi_A}$$

$$\phi = \frac{(6.023 \times 10^{23})(V_s)(C_s)(\%S)}{(6.023 \times 10^{23})(V_A)(C_A)(\%A)}$$

$$V_A = V_s = 7 \text{ or } 5 \text{ ml.}$$

$$= \frac{(C_s)(\%S)(\phi_A)}{(C_A)(\%A)}$$

The amount of reaction of S was determined by peak areas in glc while the amount of A was determined from the absorbancies in uv at 350 nm before and after the reaction.

Photolysis of tritolylamine and carbon tetrachloride

Tritolylamine (386 mg, 1.435 mmol) and carbon tetrachloride (1.07 mmol) were irradiated in spectral grade acetonitrile (50 ml). Three ml aliquots were taken after every 5 min and diluted to 10 ml with acetonitrile and the visible spectrum was taken. The reaction mixture turns green and an absorption band starts appearing at 675 nm which absorbs maximally after 45 min and disappears after 1 hr and 15 min. This was identified as the tritolylaminium ion by comparison with the uv spectrum of tritolylaminium ion prepared by the oxidation of tritolylamine with iodine (41).

Irradiation of DDT with various inducers and determination of HCl

(A) DDT (100 mg, 0.2821 mmol) was dissolved, with equivalent amounts of the inducers listed in Table I, in spectral grade cyclohexane (50 ml) in Erlenmeyer flasks fitted with rubber septums. These flasks were placed in the Rayonet reactor and photolyzed for 5 hrs. After irradiation 5 ml of distilled water was added to the reaction mixture, the mixture shaken for a couple of minutes and titrated against standard sodium hydroxide using phenolphthalein as indicator. This determined the amount of HCl produced.

(B) The above experiment was repeated with inducers listed in Table II. A 1:1 mixture of cyclohexane and isopropyl ether (50 ml) was used as a solvent.

Photolysis of DDT with increasing concentration of DEA

DDT (700 mg, 1.9747 mmol) was dissolved in cyclohexane (350 ml). Seven 50 ml aliquots of this solution were taken in Erlenmeyer flasks fitted with rubber septums, and to these varying amounts of DEA were added (Table III). Irradiation of these for 5 hrs. and determination of the amount of hydrochloric acid, as written above, gave the result in Table III.

Photolysis of degassed solutions of DDT and DEA

A solution of DDT (0.2821 mmol) and DEA (1.675 mmol) in a Pyrex tube with a long stem was degassed by three freeze-thaw

cycles, sealed in vacuum and irradiated for 12 hr. The seal was broken and 5 ml of distilled water added. The solution obtained was titrated against 0.0433 N sodium hydroxide. A total of 11.6 ml of the base were consumed.

Quenching Studies

(A) A solution of DDT (400 mg, 1.1284 mmol) and DEA (0.4 g 2.68 mmol) was prepared in cyclohexane (200 ml). Three 50 ml aliquots of this solution were taken in three Erlenmeyer flasks. Piperylene (1 ml, 10 mmol) was added to one flask, naphthalene (304 mg, 2 mmol) to a second and a third was used as a blank. These solutions were irradiated for 5 hr. and glc analysis, using column 4, showed that in every case 50% of the DDT had reacted.

(B) DDT (100 mg, 0.2821 mmol), triphenylamine (80 mg, 0.327 mmol) and naphthalene (2 mmol) was dissolved in cyclohexane (50 ml) and irradiated for 5 hr. in an Erlenmeyer flask. Glc analysis on column 4 showed that about 30% of the DDT had reacted.

Identification of photoproducts of DDT and DEA reaction

DDT (12 g, 33.9 mmol) and DEA (12 g, 80.5 mmol) in methanol (500 ml) were irradiated in Pyrex tubes using a merry-go-round for 8 hr. Concentration of the reaction mixture and chromatography on a silica gel column (400 g) was performed. 1 liter to 1500 ml fractions were collected with the following solvents, fraction A and B

with Skeely Solve H (SSH), C with CCl_4:SSH (1:1), D with CCl_4, E with CCl_4:benzene (1:1), F with benzene, G with $CHCl_3$ and H with $CHCl_3$ and methanol (9:1). These fractions were concentrated on a rotary evaporator at 40-70° and transferred to 10 ml vials with acetone and kept at 5° until further analysis.

Fraction A --- Glc analysis on column 4 at temperature 228° showed three major peaks with retention times 18 min 24 sec; 25 min; 30 min respectively. These were identical with the retention times for authentic samples of DDE, DDD and DDT. The retention times of the components of fraction A and authentic DDE, DDD and DDT did not vary from each other on decreasing the column temperature to 200° or increasing to 240°. Also they were identical on column 2.

Fraction B --- A white solid separated when acetone was added to the concentrate of fraction B. The white solid was filtered. Glc analysis of the filtrate showed the presence of DDT, DDD and DDE, while the white solid would not elute from column 4. It was recrystallized from benzene and dried. Its nmr spectrum (Fig. 1) showed a singlet at $\delta 6$ (1H) and aa'bb' multiplet at 7.25 (8 H). The mass spectrum showed a molecular ion of 564 with M, M+2, M+4, M+6, and M+8 peaks in the ratio 0.7:1.31:1.2:0.58:0.2 indicating the presence of six chlorine atoms (42). Other major peaks were 494, 492, 496, 459, 457, 420, 418, 416, 385, 383, 381, 347, 245, 294, 292, 260, 258, 236, 234, 200, 198, 165, and 138. It melted at 235° (lit 232°) (6).

The nmr spectrum was identical with an authentic sample of cis

1, 1, 4, 4-tetrakis(p-chlorophenyl)-2-butene.

Fraction C --- Glc analysis of this fraction showed the presence of

very minor amounts of DDT, DDD and DDE.

Fraction D --- It was rechromatographed on a silica gel column

(60 g). Fifty ml fractions were collected up to fraction 90 and after

that 300 ml fractions. The fractions 1-10 were eluted with SSH,

11-41 with SSH:CCl_4 (9:1), 42-90 with SSH:CCl_4 (8:2), 91 with CCl_4,

92, 93 with benzene and 94 with $CHCl_3$.

The fractions 36-50 were combined after analysis by nmr. A

white solid which is insoluble in acetone is obtained. It was crystal-

lized from benzene and it melted at 278°. Its nmr spectrum (Fig. 2)

showed a broad singlet at δ 5.5 (1H) and a aa'bb' quartet (8H) with

$δ_a$ = 7.2 $δ_b$ =7.6 and J_{ab} = 10 Hz. Its mass spectrum gave a parent

ion of m/e 564 with M, M+2, M+4, and M+6 ions in the ratio 1:1.94:

1.49:0.7. The other prominent ions were 499, 497, 462, 460, 458,

427, 425, 423, 388, 386, 238, 236, 202, 200, 165 and 117. It is

identified as trans-1, 1, 4, 4-tetrakis(p-chlorophenyl)-2-butene.

Analysis of fraction 91 --- Analytical tlc runs on this fraction showed

the presence of at least two components. The fraction was concen-

trated and spotted on two preparative silica gel tlc plates (20 x 20 x

0.2 cm). These plates were first developed with a mixture of

chloroform and hexane (2.5:1) and again with a 1:1 chloroform-hexane

mixture. A total of five bands were formed on each plate. These bands were cut out individually and stirred with ether (80 ml for each band) for half an hour. The silica gel was filtered off, solutions were concentrated and nmr spectra were taken. The third band in both plates had identical spectra and at least two components, while the other bands were too dilute for further work up.

The third band from both plates was combined and chromatographed on an acid alumina column (45 g). All fractions collected were 50 ml. The fractions 1-42 were eluted with SSH, 43-55 with CCl_4 and 56-65 with benzene.

The fraction 43 after removing the solvent gave an nmr spectrum (Fig. 3) with three singlets at 3.8 (3H), 4.9 (1H) and 7.3 (8H). Its mass spectrum showed a molecular ion with m/e equal to 294 with M, and M+2 ions in the ratio 1.5:1. The prominent mass spectral peaks are 296 (13%), 294 (20%), 237 (66.5%), 235 (100%), 200 (4.1%), 198 (8.7%), 166 (3%), 165 (28%), 141 (3%), 139 (10%) and 111 (3.5%). The infra-red spectrum (Fig. 10) showed a strong peak at 1735 cm^{-1}. This compound is identified as methyl-1, 1-bis(p-chlorophenyl)acetate by matching its spectra with the ones in literature (51).

The fraction 46 was concentrated and crystallized from ethanol. A yellow solid is obtained. Its nmr spectrum (Fig. 4) has a triplet at δ1.1 (6H), a singlet imposed on a quartet at 3.3 (7H) and a

multiplet at 6.8 (12H). Mass spectrometry gave a molecular ion of 425 with M, M+2 and M+4 peaks in the ratio 1.2:0.9:0.11, indicating the presence of two chlorine atoms. Other prominent peaks are 412, 410, 384, 382, 340, 338, 275, 274, 272, 240, 239, 199, 170, 164, 163, 162, 133, 105, 104, 91, 77 and 49. This compound was identified as 1,1-bis(p-chlorophenyl)-2-(diethylaminophenyl)-2-methoxy ethylene.

Analysis of fractions 92 and 93 --- These were rechromatographed on an acid alumna column (45 g). All fractions collected were 50 ml. Nothing eluted with SSH. A yellow band moved down with a CCl_4:SSH mixture (1:1). This band was collected in fractions 2, 3 and 4. Another yellow band was eluted with CCl_4 and collected in fractions 10-13. Two more yellow bands were eluted with benzene and chloroform but these did not give any identifiable nmr spectra.

The third fraction was concentrated and crystallized from ethanol. A dirty white solid crystallized out, which melted at 142°. It gave an nmr spectrum (Fig. 5) which had only an aa'bb' quartet centered at δ7.6. Its mass spectrum gave a molecular ion of 250 with M and M+2 in the ratio 1.5:1 indicating the presence of two chlorine atoms. The major mass spectral peaks are 252 (28.6%), 250 (43.6%), 217 (2.7%), 215 (7.3%), 141 (36.4%), 139 (100%) 113 (6%) and 111 (31.8%). Its infra-red and nmr spectra and mp matched with an authentic sample of 4,4'-dichlorobenzophenone (DDCO).

The filtrate of fraction three was combined with fraction 4 and chromatographed on a silica gel column (10 g). All fractions collected were 20 ml. The fractions 1-5 were eluted with SSH, 6-13 with carbon tetrachloride and 14 with benzene. Nmr spectrum of fraction 8 showed three singlets at $\delta 3.8$ (3H), 4.9 (1H) and 7.3 (8H) which are identical with the spectrum obtained for methyl-1, 1-bis (p-chlorophenyl)acetate.

Fraction E --- It was rechromatographed on a silica gel column (60 g). The following fractions 1-10 were eluted with SSH, 11-20 with $SSH:CCl_4$ (3:1), 21-53 with CCl_4 54-61 with CCl_4:benzene (3:1), 62-147 with CCl_4:benzene (1:1), 148-176 with benzene, 171-231 with benzene:$CHCl_3$ (1:1), 232-246 with $CHCl_3$ and 247-260 with $CHCl_3$ and methanol mixture (9:1).

The fractions 1-10 gave a white solid on concentration which was insoluble in acetone and melted at 278°. It was identical with the material from the fractions 36-50 of fraction D.

The fractions 30-140 contained one major component. These were concentrated and crystallized from benzene. White crystals (mp 114°) were obtained and these gave nmr spectra (Fig. 6) with a triplet at $\delta 1.3$(6H), quartet 3.16 (4H), aa'bb' quartet, δ_a=6.4 (2H), δ_b =7.7 (2H) and a singlet at 7.3 (8H). Its mass spectrum gave a molecular ion of 411 with M and M+2 in the ratio 1.4:0.9. The infra-red spectrum (Fig. 11) shows a strong band at 1665 cm^{-1}. This compound is identified as α,α-bis(p-chlorophenyl)-p-diethylaminoacetophenone.

Elemental analysis: Calculated for $C_{24}H_{23}Cl_2NO$

C=69.95; H=5.58; Cl=16.99; found C=69.71; H=5.75; Cl=16.99.

Rechromatography of fractions 162-260 did not give any isolatable components.

Fraction F --- A yellow solid had separated on standing and was filtered off. The filtrate was chromatographed on a silica gel column (60 g). The following fractions (50-70 ml) were collected; 1-17 were eluted with CCl_4, 18-43 with CCl_4:benzene mixture (9:1), 44-49 with CCl_4:benzene (4:1), 50-68 with CCl_4:benzene (3:2), 69-85 with CCl_4: benzene (1:1), 86-126 with benzene, 127-182 with benzene:$CHCl_3$ (1:1) and 183-190 with $CHCl_3$ containing 2% methanol.

The fractions 65-86 contained only the DDCO. From the rest of the fractions nothing could be isolated.

The yellow solid obtained above was crystallized from a 1:1 mixture of benzene and methanol. Yellow crystals were obtained (mp 253°) which gave a nmr spectrum (Fig. 7) with a triplet at δ1.2 (12H), quartet 3.3 (8H), and a multiplet centered at 6.8 (16H). Its mass spectrum showed a molecular ion of 542 with M and M+2 peaks in the ratio 1.4:0.9, required for two chlorine atoms. It is identified as 1,1-bis(p-chloro phenyl)-2,2-bis(p-diethylaminophenyl)ethylene. Elemental analysis Calculated for $C_{34}H_{36}Cl_2N_2$

C=75.4; H=6.62; found C=74.31; H=6.69

Fraction G --- The solution was evaporated to dryness. Ether was added to the dark brown mass and a brown solid separated out. After filtering and recrystallizing it from carbon tetrachloride it was identified as diethylaniline hydrochloride by matching its nmr and ir spectrum and mp with an authentic sample.

Fraction I --- It was mostly diethylaniline and an uncharacterisable brown solid.

Effect of irradiation time on the reaction of DDT and DEA and product distribution

DDT (1.416 g, 3.99 mmol) and DEA (1.2 g, 8.05 mmol) were dissolved in methanol (total volume 50 ml). Seven 4 ml aliquots of this solution were placed in Pyrex tubes and irradiated these for different lengths of time (Table IV). The disappearance of DDT was followed by glc on column 4 at 228°. It was observed that it was not possible to separate DDE and methyl-1, 1-bis(p-chlorophenyl) acetate. The following procedure was adopted to calculate the amounts of DDE and the ester.

Chromatographic runs were recorded for all the reaction mixtures and the peak areas were recorded. The methanol was then completely removed using a rotary evaporator at 80°. The concentrated solutions were diluted to 1 ml with deuterochloroform and 10 μl of toluene was added to every solution as an internal standard. Nmr spectra were taken and the amount of methyl-1, 1-bis

(p-chlorophenyl)acetate was calculated. Glc peak areas correspond-ing to this amount of methyl-1, 1-bis(p-chlorophenyl)acetate were calculated. These areas were subtracted from the peak area obtained for the peak with r.t. 18 min 24 sec so that the true area due to DDE and the mmols of DDE formed could be estimated. Glc runs were also made on the dueterochloroform solutions and the amount of DDCO formed was calculated. The peak areas of the two unknowns were also determined from these chromatographic runs.

Photolysis of DDD and DDE with DEA

DDD (1.272 g, 4 mmol) and DEA (1.2 g, 8.05 mmol) were dissolved in methanol (net volume 50 ml). Also a solution of DDE (1.234 g, 4 mmol) and DEA (8.05 mmol) was prepared in methanol (total volume 50 ml). Eight 4 ml aliquots of these solutions were placed in Pyrex tubes and irradiated for different lengths of time (Tables V, VI). The consumption of DDD and DDE was determined by glc on column 4. Areas of the unknowns were also recorded. DDD photolysis gave one product with retention time same as DDCO, while DDE gave a product with retention time 16 min and 24 sec and no DDCO.

Photoreaction of decyl bromide and DEA

Decyl bromide (11.5 g) and dodecanol (10 g) were dissolved in dimethylformamide (DMF) so that the net volume was 100 ml.

Seven 10 ml aliquots of this solution were placed in Pyrex tubes.
Different amounts of DEA (Table VII) were added and the solutions
photolyzed for 36 hrs. The consumption of decyl bromide was deter-
mined by glc on column 1 at 160°.

Identification of photoproducts of decyl bromide and DEA reaction

Decyl bromide (5.75 g, 27.2 mmol) and DEA (10 g, 67 mmol)
in DMF (160 ml) was irradiated in Pyrex tubes for 44 hr. Water was
added to the reaction mixture, and then it was extracted with ether.
The water soluble portion was kept. The ether extract was washed
with dilute hydrochloric acid and again with water. It was dried over
magnesium sulphate and marked as AW. The acid extract was
neutralized with dilute sodium hydroxide and extracted with ether.
After washing with water it was dried over magnesium sulphate and
marked as AE.

After evaporation to dryness the water solution obtained above
produced a brown solid, which after crystallization from carbon
tetrachloride gave nmr, ir and mp identical with an authentic sample
of diethylaniline hydrobromide.

Analysis of AE on glc using column 1 showed a peak with a
retention time of 3 min at column temperature of 140°. This was
identical with the retention time of N-ethylaniline and it remained so
at varying column temperatures and on different columns.

Glc of solution AW using temperature programming from 130° 230° with a hold at 130° for 10 minutes and raised at the rate of $10^{\circ}/$ min showed five major peaks with retention times in minutes of 3.6, 15.6, 21.8, 28 and 33.2. The peak with retention time 15.6 minutes was due to decyl bromide.

Peaks with retention times 3.6, 28 and 33.2 minutes were analyzed by mass spectrometry and gave spectra with molecular ions 142, 289 and 289 respectively. The peaks were collected using a 9:1 splitter. The attempt to collect the material with retention time 21.8 min failed.

The peak with retention time 3.6 min and molecular ion 142 is due to n-decane as shown by comparison of its nmr spectrum and glc retention time with an authentic sample of n-decane. The compound with retention time 33.2 min had a mass spectrum with molecular ion of 289 and major peaks of 289 (22), 274 (100), 134 (40), 105 (10) and 91 (14). The nmr spectrum (Fig. 8 showed a multiplet $\delta 7.0$-6.2 (4H) quadruplet 3.2 (4H), 2.3 (2H) and 1.4-.08 (25H). This was identified as p-decyl- N, N-diethylaniline. The compound with retention time 28.0 min had a mass spectrum with major peaks at m/e (relative intensity): 289 (1), 274 (2), 218 (50), 134 (17) 105 (22), 92 (95) and 91 (100), gave nmr spectrum (Fig. 9) broad singlet 9.70 (4H), quadruplet 2.87 (4H), 2.6 (2H) and 1.4-0.8 (25H). This was identified as o-decyl-N, N-diethylaniline.

Solvent effect and relative yields

Decyl bromide (7 g, 34.5 mmol), diethylaniline (10 g, 72.5 mmol) and dodecanol (6 ml) were mixed. Four 5 ml aliquots of this solution were taken in Pyrex tubes, and to each of these were added 15 ml of one of the following solvents DMF, methanol, benzene and cyclohexane. These were irradiated for 36 hrs, followed by glc analysis using column 2. The following conditions were used, column 170° with a carrier gas flow of 45 ml/min for determining the loss of decyl bromide and the yields of o- and p-decyl anilines. A column temperature of 70° and a flow 30 ml/min was used for determining the yields of n-decane and N-ethylaniline. After glc analysis solutions were concentrated and extracted with dry ether. The solid left after ether extraction was diethylaniline hydrobromide, which was weighed to determine the amount of hydrogen bromide evolved (Table VIII).

Photolysis of decyl bromide and DEA with added n-butyl mercaptan, piperylene and triethylamine

A solution of decyl bromide (45.2 mmol), DEA (100 mmol) and dodecanol (5 g) in methanol (80 ml) was prepared. Four 15 ml aliquots of the above solution were taken in Pyrex tubes. n-BuSH (2 ml) was added to one, triethylamine (2 ml) to a second, piperylene (2 ml) to a third, and the fourth one was run as a blank. Photolysis for 36 hr followed by glc analysis showed that n-decane was present

in 10% excess in the n-BuSH solution as compared to the blank. The decyl bromide consumption in all four cases was 20-23.5%. An irradiated solution containing triethylamine yielded a solid on concentration which was identified as triethylamine hydrobromide.

Photolysis of decyl bromide and DEA in benzene in the presence of piperylene

A solution of decyl bromide (2 g), DEA (3 g) dodecanol (1 g), piperylene (2 g) in benzene (17 ml) was irradiated for 36 hours. Glc analysis showed 20% of the decyl bromide had reacted.

Photolysis of decyl bromide and triethylamine

A solution of decyl bromide (1 g), triethylamine (2 ml), dodecanol (1 g) in methanol (17 ml) was photolyzed. Glc analysis showed no loss of decyl bromide.

Kinetic studies of photoreaction of decyl bromide and DEA

A solution of decyl bromide (11.05 g), DEA (14.9 g) and dodecanol (10 g) in DMF was prepared so that the total volume of solution was 250 ml. Aliquots (15 ml) of this solution were taken and irradiated for different lengths of time. The loss of DEA and decyl bromide was followed by glc on column 1 using attenuation settings of 128 for DEA and 64 for decyl bromide (Table IX). Graphs with the values of Table IX for zero, first and second order did not give straight lines.

UV studies

A solution of DEA (5 μl) in EtOH was prepared. Five 25 ml aliquots of this solution were taken and added successively were 1.1, 2, 3.1, 4.1 and 5 μl of decyl bromide to these and their uv spectra recorded. Spectra with added decyl bromide did not show any change in the absorbancy of the band between 290 nm and 320 nm obtained in a solution containing only DEA.

Photolysis of benzyl sulphide and DEA

A solution of benzyl sulfide (1 g) and DEA (2 g) in methanol (17 ml) was irradiated for 44 hr. Glc analysis did not show any loss of benzyl sulfide.

Photolysis of n-BuI, n-BuBr and n-BuCl with Dimethylaniline

Prepared solutions of n-BuI, n-BuBr and n-BuCl in benzene such that these contained 0.01 M of halides, 0.03 M of DMA and 1.5 ml of toluene and the total volume was 10 ml. These solutions were irradiated for 96 hours. The reaction was followed by nmr, by integrating the areas for methylene protons next to halogen and of methyl protons of toluene at start and at the end. It showed 27% of n-BuBr, 12% n-BuCl and 10% of n-BuI had reacted.

Quantum yields

The following solutions of benzophenone (0.91 g) and benzhydrol (0.92 g) in benzene (50 ml), DDT (1.41 g) and DEA (1.2 g) in methanol

(net vol. 100 ml) and decyl bromide (1.105 g), DEA (1.49 g) and

dodecanol (1 ml) in methanol such that total volume was 25 ml were

prepared. The uv spectrum of the benzophenone and benzhydrol

solution was recorded by diluting 0.5 ml of this solution to 10 ml with

benzene. Two 5 ml aliquots and two 7 ml aliquots of this solution

were taken in identical Pyrex tubes with long stems. These tubes

were degassed by three freeze thaw cycles to 0.005 mm of Hg and

sealed in vacuo.

Quantum yield of DDT and DEA reaction

Three 5 ml aliquots of the DDT solution were taken in Pyrex

tubes which were similar to the actinometer tubes. These were

photolyzed with two actinometer tubes containing 5 ml of solution for

5 min. The amount of DDT reacted was determined by glc on column

4 at 240° using triphenyl methane as an internal standard which was

added after irradiation. The percent of DDT lost in three tubes was

12.24, 12.2 and 12.4. The percent benzophenone reacted was deter-

mined by recording the uv spectrum of the irradiated solution after

diluting 0.5 ml of this solution to 10 ml; the percentage lost were 5.9

and 5.9. The quantum yields were calculated for disappearance of

DDT using the equation derived earlier, which for three runs were

0.57, 0.57 and 0.58.

Quantum yield of decyl bromide and DEA reaction

Two 7 ml aliquots of decyl bromide solution prepared above were placed in Pyrex tubes. These were irradiated along with two actinometer tubes (containing 7 ml of solution) for 30 minutes and the loss of benzophenone was determined as done above, which was 23.5% in both and of decyl bromide by glc, which was 6.3% and 6.5%. Quantum yields for the reaction were 0.37 and 0.38.

CHAPTER IV

RESULTS

Tritolylamine when photolyzed in the presence of carbon tetrachloride in acetonitrile with 3100 $\overset{o}{A}$ light gave a colored product. This product had a band in the visible region with a maximum absorption at 675 nm identifying it as the cation radical of tritolylamine.

DDT was decomposed by photolysis in the presence of inducers (Table I, II) in Pyrex Erlenmeyer flasks closed with rubber septums with 3100 $\overset{o}{A}$ light in a Rayonet reactor. The extent of decomposition was crudely estimated by extracting the product mixture with water and titrating the acid in the aqueous phase (Table I, II). DDT decomposition depended upon the nature of the inducer; compounds with low ionization potentials like aromatic amines were efficient inducers while benzophenone and p-nitrotoluene, which are not easily photooxidized, did not induce the decomposition of DDT.

Photoreaction of DDT and diethylaniline (DEA) was studied in detail. A constant amount of DDT (100 mg) was photolyzed with varying amounts of DEA (Table III) for 5 hrs. The amount of DDT decomposition increased until the molar ratio of DDT:DEA was 1:2 and was relatively unaffected with greater amounts of DEA. The photoreaction of DDT (100 mg, 0.2821 mmol) and DEA (100 mg,

0.672 mmol) was not quenched either by piperylene (1.376 g, 20 mmol) or by napthalene (304 mg, 2 mmol) and had a quantum yield of 0.57 calculated for the amount of DDT reacted.

The following decomposition products from 8-hour irradiation of DDT (12 g) and DEA (12 g) in methanol (500 ml) were identified either on the basis of their glc retention times or isolation by column chromatography and characterization by physical techniques (for details see experimental). The structures of the products are:

I   DDD

II   DDE

III   DDCO

IV

methyl-1, 1-bis-(p-chlorophenyl)acetate

X

N,N-Diethylaniline hydrochloride

V

1, 1-bis(p-chlorophenyl)-2-

(p-diethylaminophenyl)-2-methoxyethylene

VI

1, 1-bis(p-chlorophenyl)-2, 2-

bis(p-diethylaminophenyl)ethylene

VIII

cis 1, 1, 4, 4-tetrakis(p-chlorophenyl)-2-butene

trans 1, 1, 4, 4-tetrakis(p-chlorophenyl)-2-butene

VII

α, α-bis(p-chlorophenyl)-p-diethylaminoacetophenone

In addition to these there were two more volatile, unidentified products present with glc retention times of 10 min and 16 min and 24 sec (Table IV). Elemental analysis was performed for compounds VI and VII; it could not be carried out for V and IX because of lack of pure compounds.

Photolysis of DDT (0.32 mmol) and DEA (0.7 mmol) in methanol (4 ml) was carried out in rubber septum closed Pyrex tubes using a merry-go-round for different lengths of time (Table V). Glc analysis of the reaction mixtures showed that the amount of DDD and DDE reached a maximum value and then either stayed the same or decreased. The concentration of methyl-1, 1-bis (p-chlorophenyl) acetate as shown by nmr analysis increased with the length of irradiation (Table V).

DDD (0.32 mmol) with DEA (0.7 mmol) and DDE (0.32 mmol) with DEA (0.7 mmol) in methanol (4 ml) were irradiated for different lengths of time (Table VI, VII). Glc analysis of the reaction mixtures showed DDE gave a product with retention time 16 min and 24 sec, while DDD showed a peak with the retention time the same as that of DDCO. Nmr analysis on both reaction mixtures did not show the presence of methyl-1, 1-bis-(p-chlorophenyl)acetate.

Photoreaction of n-decyl bromide and DEA with 3100 $\overset{o}{A}$ light

It was observed that photoreduction of decyl bromide increased with increasing concentration of DEA until the molar ratio of decyl bromide to DEA was 1:2 (Table VII). The reaction was not quenched by piperylene and its rate was insensitive to the solvent polarity. In cyclohexane, benzene, methanol and dimethyl formamide (DMF) the relative rates are 1, 1.5, 1.5 and 1.8, respectively (Table VIII). Also, the ultraviolet spectrum of diethylaniline was not affected when

increasing amounts of decyl bromide were added. This suggests that a ground state complex may not be playing any role in the photo-reaction.

The reaction products were identified either by glc retention times or by collecting them from the glc (see experimental) and characterizing them by physical techniques. They are: n-decane, monoethylaniline, o- and p-decyl-N, N-diethylaniline, and diethyl-aniline hydrobromide. Their relative yields are listed in Table VIII.

O- and p-isomers were identified on the basis of their differences in nmr spectra. In the o-isomer the diethylamine group is twisted out of the plane of the ring causing the aromatic protons to collapse to a singlet (43) and quartet due to methylene protons to be deshielded (44).

It was also observed that the photoreaction was not affected by air or added triethylamine. In the presence of n-butyl mercaptan the yield of n-decane increased by 10% indicating the formation of decyl radicals.

TABLE I

Photoreaction of DDT with Various Inducers

Inducer $M \times 10^{-3}$	HCl formed Moles $\times 10^5$	DDT Consumed[1] Moles $\times 10^5$
Triphenylamine (7)	1.35	6.5
N N diethylamiline (13)	16	8.7
Benzophenone (6)	0	0
Quinoline (7)	0	0
Diphenyl sulphide (6)	1.5	2
p-Nitrotoluene	0	0
1, 4 Dimethylaniline (8.3)	9.11	
Pyridine (6)	00	
Quinoxoline (6)	00	
Triphenylphosphine (4)	1.53	
2, 2'Bipyridine (6)	00	
O-Aminophenol (3)	7.35	
Anisdine (6)	6.64	
Diphenylamine (3)		

[1] determined by glc

TABLE II

Photoreaction of DDT with Various Inducers

Inducer $M \times 10^3$	HCl formed moles $\times 10^5$	DDT consumed[1] moles $\times 10^5$
Benzidine (6)	6.6	5.6
p-Phenylenediamine (7)	20	6.5
0-Aminobiphenyl (3)	0.6	
2-Aminopyridine (3)	1.47	
1-Aminoanthraquinone (7)	0	0
Phenothiazine (3)	1.2	

[1]determined by glc

TABLE III

Photoreaction of DDT with Varying Amounts of DEA

Amount of DDT used	Ml of DEA used	HCl formed moles $\times 10^4$
100 mg	0.01	5.48
"	0.02	9.9
"	0.03	13.4
"	0.05	19.5
"	0.1	24.96
"	0.15	25.6
"	0.25	26.62

TABLE IV

Irradiation Time Effect and Product Distribution of DDT and DEA Reaction

	Area of Unknowns in cm.		DDE Formed m.moles $\times 10^2$	DDD Formed m.moles $\times 10^2$	$DDCO_2CH_3$[1] Formed m.moles $\times 10^2$	DDCO Formed m.moles $\times 10^2$	DDT Consumed 10^2
Hour	r.t. = 10 min	r.t. = 16 min 24 sec					
1/2	+	0.99	0.53	1.7	1.02		7.17
1	+	2.75	1.66	2.19	2.1	+	11.8
2	1.0	4.4	3.09	2.26	3.07	+	14.3
4	1.6	4.5	4.35	2.09	4.85	+	19.5
6	1.84	4.8	3.6	2.34	6.15	2.0	22.8
7	2.6	5.06	2.84	2.19	7.2	2.5	23.1

[1]Methyl-1, 1-bis(p-chlorophenyl)acetate

+ indicates it was detected

48

TABLE V

Photoreaction of DDE with DEA

Time in Hrs.	Percent DDE Consumed	Area of Unknown Rt = 16 min 24 sec
1/2	13.5	0.38
1	21.5	0.6
2	27	1.17
4	41.2	1.49
5	48.8	1.6
6	50.8	1.8

TABLE VI

Photoreaction of DDD and DEA

Time in Hrs.	DDD Consumed m moles x 10^2	DDCO Formed m moles x 10^2
1/2	1.0	
1	5.4	1.84
2	8.24	1.7
4	14.20	4.5
5	16.08	5.0
6	19.6	7.4
7	21.6	7.5

TABLE VII

Photoreaction of Decyl Bromide with DEA

Tube	Amount of DEA Added in Grams	Percent DEA Consumed	Percent DBr[1] Consumed
1	0.149	46.9	9
2	0.298	55.3	17.5
3	0.447	34.75	32.4
4	0.745	31.5	43.2
5	1.49	21.2	51.4
6	2.98		55.2
7	7.45		56.1

[1]Decyl bromide

TABLE VIII

Solvent Effect and Yields of Decyl Bromide and DEA Photoreaction

Solvent	Percent Decyl Br Consumed	Product Yields				
		Decane	Monoethyl Aniline	o-decyl DEA	p-decyl DEA	DEA HBr
Methanol	30	8.7	1.8	51	33.4	63
DMF	37	13.5	2.7	56.8	28.1	69
Benzene	30	15.0	2.5	49.2	30.6	83
Cyclohexane	20	21.7	3.6	48.5	30.8	88

51

TABLE IX

Kinetic Studies of Photoreaction of Decyl Bromide and DEA

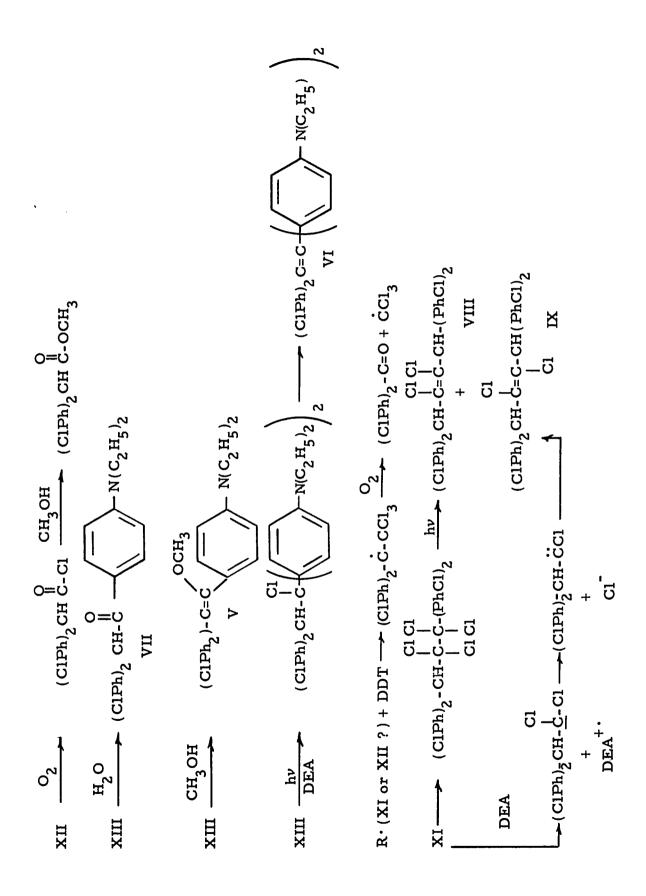| Time in Hours	Percent DEA Reacted	Percent Decyl Bromide Reacted
1		9.4
2	12.6	15.8
4	14.7	24.2
6	21.2	27.1
10	30.6	40.4
13	37.75	48.4
22	39.0	53.6
32	46.2	60.2
42	48.5	65.7
54	49.75	68.8
78	53.00	77.1
116	54.8	81.6

CHAPTER V

DISCUSSION

It is clear from the results that compounds which are easily oxidized and which also form relatively stable cation radicals are effective inducers for the decomposition of DDT. Aromatic amines are compounds of choice while compounds like benzophenone, p-nitrotoluene, etc., are not effective and are difficultly ionized.

These results point to an electron transfer process and seem to rule out an inducing mechanism involving energy transfer from triplet state of sensitizer to the organic halide (45). Energy transfer is not functionality dependent but depends on the triplet energy E_T of the sensitizer. In this case benzophenone (E_T = 69 K.cal.) is completely ineffective as a sensitizer and triphenylamine (E_T = 70 K. cal.) is effective. Quenching experiments further rule out a triplet-state energy-transfer mechanism. We will, therefore, speak of inducers rather than sensitizers to differentiate between processes involving chemical reaction and those involving energy transfer.

The decomposition of DDT induced by DEA produced DDD (11%) DDE (12%), DDCO (10.8%) methyl-1, 1-bis(p-chlorophenyl)acetate (31%), α,α-bis(p-chlorophenyl)-p-diethylaminophenylacetophenone

and diethylaniline hydrochloride as the major products. Cis and

trans isomers of 1, 1, 4, 4-tetrakis(p-chlorophenyl)-2-butene, 1, 1-bis

(p-chlorophenyl)-2, 2-bis (p-diethylaminophenyl) ethylene and 1, 1-bis

(p-chlorophenyl)-2-(p-diethylaminophenyl)-2-methoxy-ethylene were

the minor products. There are two more unidentifiable products.

One of these products, which has the retention time of 16 min 24 sec

is also obtained in the photolysis of DDE and DEA. Crude analysis

of this reaction indicates that no DDCO is formed but DDCO is

obtained from the photoreaction of DDD and DEA. The following

mechanism which involves the initial formation of radical (XI) and

then may proceed by either radical or ionic pathways is proposed:

Primary Process

$$DEA \xrightarrow{\ h\nu\ } DEA^{*}$$

$$DEA^{*} + DDT \longrightarrow DEA^{+\cdot} + Cl^{-} + (ClPh)_{2}\text{-}CH\text{-}\dot{C}Cl_{2}$$

$$XI$$

Secondary Process

$$(ClPh)_{2}\ CH\text{-}\dot{C}Cl_{2}$$
$$XI$$

→ DDD + DDE (Disproportionation)

$$O_{2} \longrightarrow (ClPh)_{2}\ CH\text{-}CCl_{2} \overset{O\text{-}O\cdot}{|}$$
$$XII$$

$$DEA \longrightarrow (ClPh)_{2}\ CH\text{-}\overset{Cl}{\underset{Cl}{|\ |}}C\text{-}\underset{}{\bigcirc}\text{-}N(C_{2}H_{5})_{2}$$
$$XIII$$

$$\text{XII} \xrightarrow{\text{O}_2} (ClPh)_2 CH \overset{O}{\overset{\|}{C}} - Cl \xrightarrow{\text{CH}_3\text{OH}} (ClPh)_2 CH \overset{O}{\overset{\|}{C}} - OCH_3$$

$$\text{XIII} \xrightarrow{\text{H}_2\text{O}} (ClPh)_2 CH-C \overset{O}{\overset{\|}{}} \quad N(C_2H_5)_2 \qquad \text{VII}$$

$$\text{XIII} \xrightarrow{\text{CH}_3\text{OH}} (ClPh_2)-C=C \overset{OCH_3}{} \quad N(C_2H_5)_2 \qquad \text{V}$$

$$\text{XIII} \xrightarrow[\text{DEA}]{h\nu} \left((ClPh)_2 CH-C \overset{Cl}{} \quad N(C_2H_5)_2 \right)_2 \longrightarrow (ClPh)_2 C=C \quad N(C_2H_5) \Big)_2 \qquad \text{VI}$$

$$R\cdot (\text{XI or XII} ?) + \text{DDT} \longrightarrow (ClPh)_2 - \overset{\cdot}{C} - CCl_3 \xrightarrow{\text{O}_2} (ClPh)_2 - C=O + \overset{\cdot}{C}Cl_3$$

$$\text{XI} \longrightarrow (ClPh)_2 - CH - \overset{Cl\ Cl}{\underset{Cl\ Cl}{\overset{|\ \ |}{C - C}}} - (PhCl)_2 \xrightarrow{h\nu} (ClPh)_2 CH - \overset{Cl\ Cl}{\underset{}{\overset{|\ \ |}{C = C}}} - CH - (PhCl)_2 \quad \text{VIII} \quad + \quad (ClPh)_2 CH - \overset{Cl}{\underset{Cl}{\overset{|}{C}}} = C - CH(PhCl)_2 \quad \text{IX}$$

$$(ClPh)_2 CH - \overset{Cl}{\overset{|}{\underline{C}}} - Cl \xrightarrow{\text{DEA}} (ClPh)_2 CH \cdot \overset{..}{C} Cl + DEA^{+\cdot} + (ClPh)_2 CH \cdot \overset{..}{C} H \cdot \overset{..}{C} Cl + Cl^-$$

The proposed mechanism is very speculative. It seems useful, however, to put forward the most reasonable hypothesis that can be formulated. Alternative mechanisms have been envisaged, but have not been included. The formation of DDD and DDE are easily rationalized in terms of intermediate radical XI (9, 10). Indeed, we suspect that this radical can eventually lead to all the diverse DDT photoproducts. We have found no evidence for loss of halogen from the rings in these induced photolyses.

The formation of DDCO has been previously suggested (9, 10) to involve the above sequence and indeed we find that oxygen is necessary for DDCO formation and that DDE does not produce DDCO. This obviates the mechanism of Fleck at least under our conditions. It is suspected that the 1, 1-bis(p-chlorophenyl)-2-(diethylamino-phenyl)-2-methoxy ethylene (V) and a, a'-bis (p-chlorophenyl) diethylamino acetophenone (VII) are formed from XII. The studies of decyl bromide-DEA photolysis indicated that coupling of these compounds with concomitant hydrogen chloride formation should be important in DDT photochemistry. This dihalide will, however, be quite reactive. Photochemically it could lead to substitution of a second diethylaniline moiety, thus compound VI. The diethylaniline function in XIV also activates the halides toward chemical reaction. Gem dihalides having an a-aryl group can be readily hydrolyzed to ketones in the presence of acid or base (49). In an acidic medium

the rate limiting step is the ionization of the gem-dihalide to form a carbonium ion. The rate of this reaction is increased almost 100 fold if an electron donating group like methoxy is present in the para position of the phenyl ring (50). In the present case the ionization of XIII is made possible by the acidity of the medium (pH = 4.2) and the presence of a diethylamino group in the para position of the phenyl ring. An intermediate carbonium ion formed can be either trapped by methanol or water and eventually form V and VII.

Mechanisms proposed for the formation of cis and trans 1,1,4,4-tetrakis(p-chlorophenyl)-2-butene do not have any strong precedent. The processes however suggested above are simply the only pathways that seem feasible.

The decomposition of DDT proceeds at approximately the same rate in a closed flask in an oxygenated solution or in solution degassed by a nitrogen stream or by freeze thawing. It should be noted, however that the reaction in the absence of oxygen is completely different. Only DDD is produced and triplet energy transfer is indicated as the sensitization mechanism (52). The reactions of the cation radical derived from the inducer depend on its structure. A dark brown polymer is, for example, formed from diethylaniline.

The nature of DEA* and Ph_3N* has been investigated by the addition of compounds that quench the triplet state. Photolysis induced by diethylaniline was not quenched by piperylene or naphthalene,

and triphenylamine induction was not quenched by naphthalene. In each case, formation of a triplet excited state is feasible, but, since electron transfer from the triplet state of an amine would be an intermolecular process and cannot be quenched, this process is ruled out. It seems that electron transfer from the singlet of the inducer or charge transfer complex or a radical chain process remain mechanistically viable explanations for the observed photochemical reaction.

Photoreaction of decyl bromide and DEA

Decane seems diagnostic for intermediate decyl radicals. This is confirmed by the effect of added n-butyl mercaptan which does not change the rate of decyl bromide disappearance, but does improve the yield of decane. N-Ethylaniline is considered indicative of an intermediate diethylaniline cation radical which loses a methylene hydrogen (46, 47). Indeed, combination of geminatly formed decyl radicals and diethylaniline cation radicals can account for the major products, 5 and 6, and rationalize the exceptionally high yield of the ortho isomer, 5.

The following scheme then explains the products and is also consistent with all available mechanistic information:

DEA (S_0) ⟶ DEA (S_1) ⟶ $[1 - - - - 2]^*$

1

where 2 = Decyl Bromide

$[1 - - - - 2]^*$ ⟶ [structure: benzene ring with $\overset{+\cdot}{NEt_2}$] + $\dot{C}_{10}H_{21}$ + Br^-

$C_{10}H_{21}$ + [structure: benzene ring with $\overset{+\cdot}{NEt_2}$] ⟶ $C_{10}H_{22}$ + [structure: benzene ring with Et-N=$CHCH_3$] $\xrightarrow{H_2O}$ [structure: benzene ring with $HNEt$]

3

4

[structure: benzene ring with NET_2 and $C_{10}H_{21}$ ortho] + [structure: benzene ring with NEt_2 and $C_{10}H_{21}$ para] + H^+

5

6

$C_{10}H_{21} \xrightarrow{XH} C_{10}H_{22}$

$\dot{C}_{10}H_{21}$ + ⟶ 5 + 6
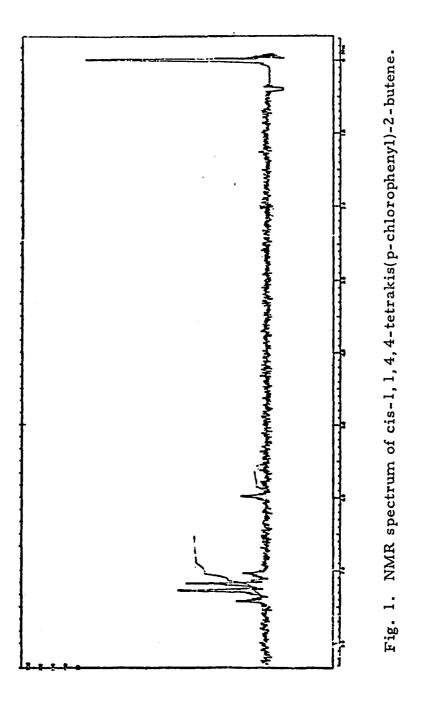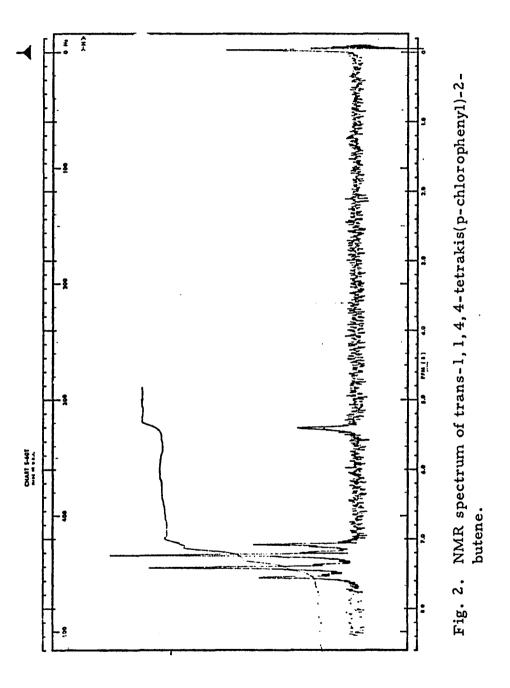
Since no change in the uv spectrum could be detected when decyl

bromide was added to a diethylaniline solution, it is suspected that

photolysis of a ground state complex between 1 and 2 is not occurring.

Instead, the light is absorbed by 1 producing an excited singlet which

reacts with (48). The obvious alternative pathway via the triplet of 1

is eliminated because the reaction in benzene is not quenched by

piperylene or oxygen. We therefore have indirect evidence for all of

the species in the scheme except the exciplex. It is included because

Tosa, Pac and Sakurai found evidence for an excited complex in a

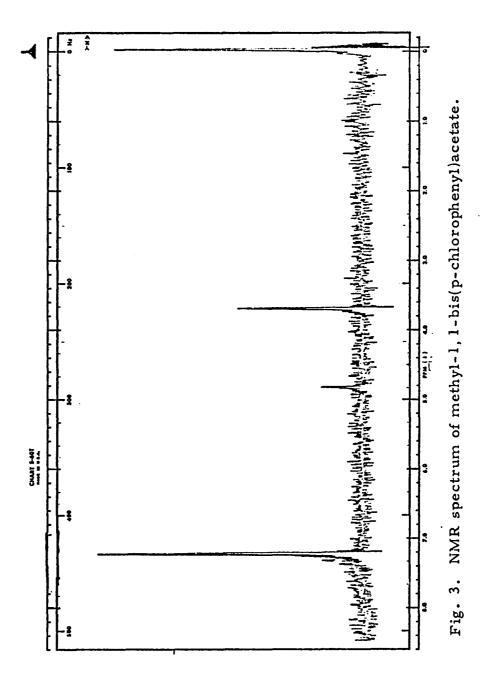very similar reaction (34). They studied the photolysis of

dimethylaniline in the presence of chlorobenzene and found emission

from a species containing both reactants. Furthermore, photopro-

ducts suggestive of charge transfer were isolated. Even more

recently Hammond, McCall, Yonemitsu and Witkop (35) have made a

similar proposal to explain the fluorescence quenching of electron-
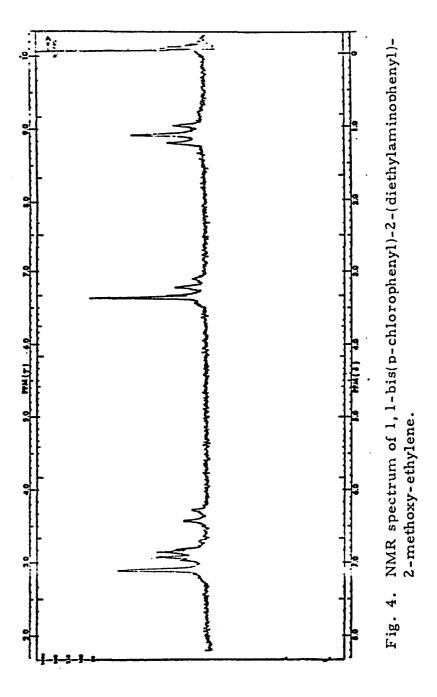
rich aromatics by ethyl chloroacetate.

Solvent effects on photoreactions involving electron transfer are

of considerable current interest (47, 48). In the present case

the quantum yield for decyl bromide disappearance is rather insensi-

tive to solvent polarity. The relative rates are cyclohexane (1.0),

benzene (1.5), methanol (1.5), dimethylformamide (1.8). This is

similar to the very small fluorescence quenching rate constant varia-

tions which have been found in other systems involving charge trans-

fer. A related point of potential interest is the relationship between

ionization potential of the donor, electron affinity of the acceptor and

the feasibility of electron transfer. Although it is clear that a good

donor and acceptor are necessary for this sort of reaction, (35, 48)

more subtle or quantitative relationships between the efficiency of

reaction and these energetic parameters have not been thoroughly

explored. Qualitative experiments and the literature suggest that a

wide variety of organic halides will be relatively efficient acceptors.

Intriguing contradistinctive cases are presented by sulfides and

disulfides. These compounds are very easy to reduce and yet it is

found that neither diethylaniline nor triphenylamine will induce the

reductive decomposition of dibenzyl sulfide, dibenzyl disulfide or
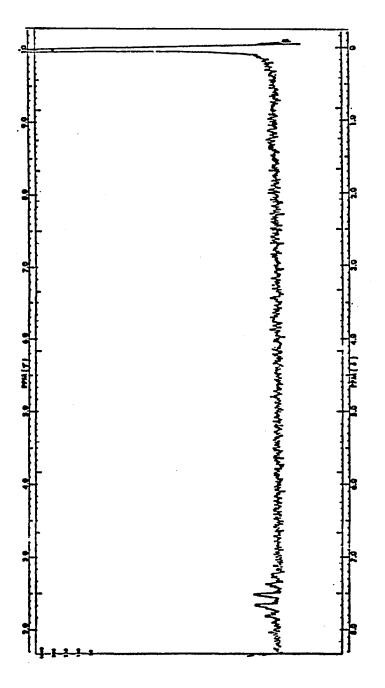
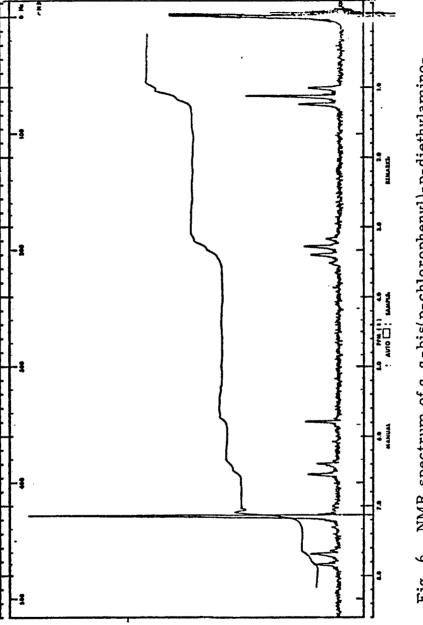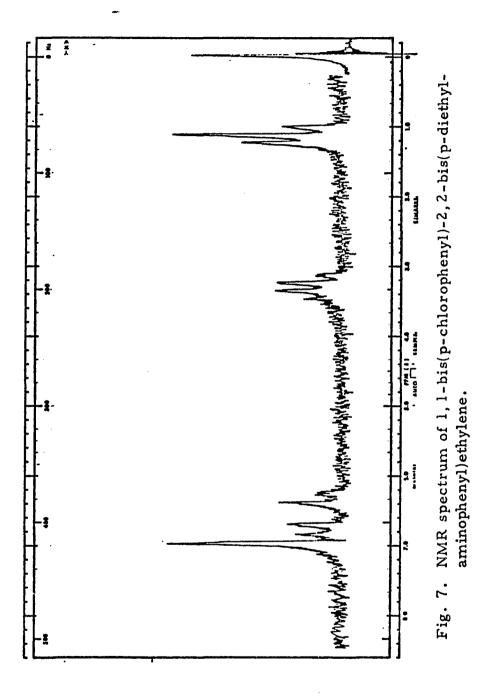tertbutyl disulfide when irradiated in ethanol.

Fig. 1. NMR spectrum of cis-1,1,4,4-tetrakis(p-chlorophenyl)-2-butene.

Fig. 2. NMR spectrum of trans-1,1,4,4-tetrakis(p-chlorophenyl)-2-butene.

Fig. 3. NMR spectrum of methyl-1,1-bis(p-chlorophenyl)acetate.

Fig. 4. NMR spectrum of 1,1-bis(p-chlorophenyl)-2-(diethylaminophenyl)-2-methoxy-ethylene.

Fig. 5. NMR spectrum of 4,4'-dichlorobenzophenone.

Fig. 6. NMR spectrum of α,α-bis(p-chlorophenyl)-p-diethylamino-acetophenone.
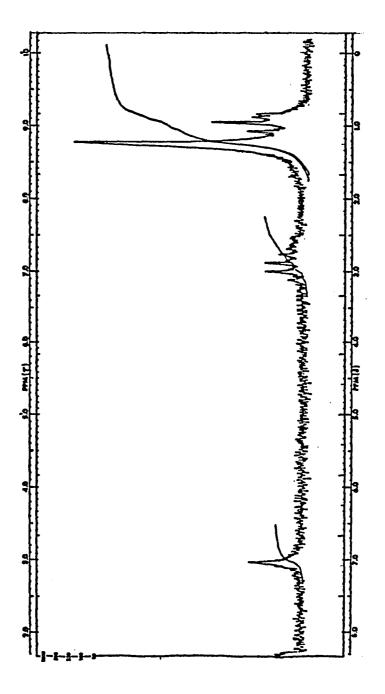
Fig. 7. NMR spectrum of 1,1-bis(p-chlorophenyl)-2,2-bis(p-diethyl-aminophenyl)ethylene.
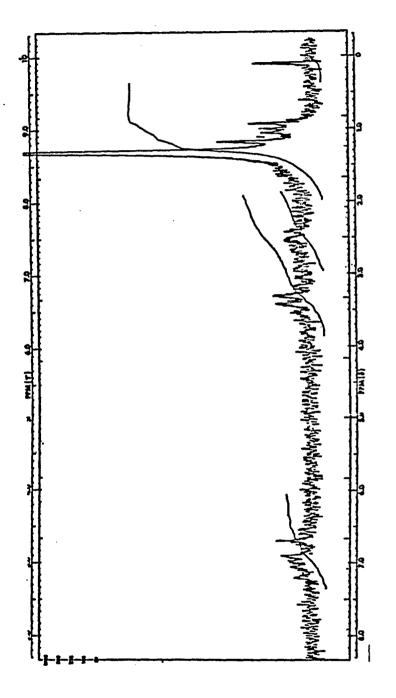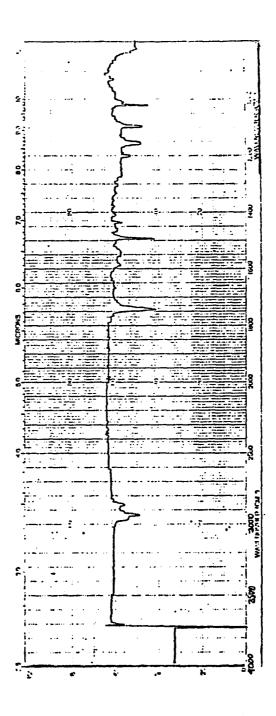
Fig. 8. NMR spectrum of p-decyl-N, N-diethylaniline.

Fig. 9. NMR spectrum of o-decyl-N, N-diethylaniline.

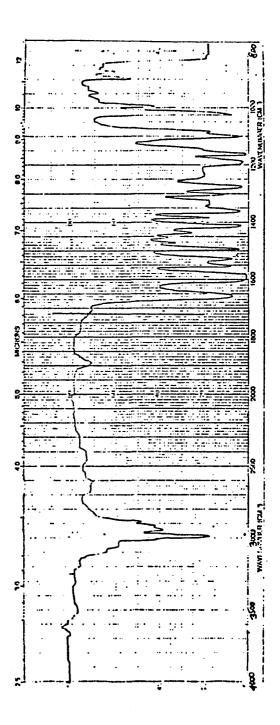Fig. 10. IR spectrum of methyl-1,1-bis(p-chlorophenyl)acetate.

Fig. 11. IR spectrum of α,α-bis(p-chlorophenyl)-p-diethylaminoacetophenone.

REFERENCES

1. A. W. Linquist, A. J. Howard and A. H. Madden; J. Econ. Entomol., <u>39</u>, 55 (1943)

2. F. M. Turrel; Calif. Citrograph, <u>28</u>, 287 (1943)

3. F. A. Gunther; J. Chem. Ed., <u>22</u>, 238 (1945)

4. H. J. Wichmann, W. I. Patterson, P. A. Clifford, A. K. Klein and H. V. Clayborn; J. Assoc. Office Ag. Chem., <u>29</u>, 218 (1946)

5. E. E. Fleck; Ind. Eng. Chem., <u>40</u>, 706 (1948)

6. E. E. Fleck; J. Amer. Chem. Soc., <u>71</u>, 1034 (1949)

7. L. C. Mitchell; J. Ass. Offic. Agric. Chem., <u>44</u>, 645 (1961)

8. J. Roburn; Chem. Ind., (London), <u>38</u>, 1555 (1963)

9. A. R. Mosier, W. D. Guenzi and L. L. Miller; Science, <u>164</u>, 1083 (1969)

10. J. Plimmer, B. E. Hummer and U. I. Klingebiel; Science, <u>167</u>, 67 (1970)

11. R. Evans, N. Edwin, C. Ralowski and W. V. Sherman; J. Phys. Chem., <u>75</u>, 2762 (1971)

12. D. G. Crosby, G. L. Henderson; J. Agric. Food Chem., <u>15</u>, 888 (1967)

13. G. W. Ivie and J. E. Casida; ibid, <u>19</u>, 410 (1971) and ref. cited therein

14. W. R. Benson, P. Lombardo, I. J. Egry, R. D. Ross, Jr.; ibid, <u>19</u>, 857 (1971)

15. G. W. Ivie and J. E. Casida; ibid, <u>19</u>, 405 (1971)

16. G. N. Lewis and D. Lipkin; J. Amer. Chem. Soc., <u>64</u>, 2801 (1942)

17. G. N. Lewis and J. Bigeleisevy; ibid, <u>65</u>, 2424 (1943)

18. H. Linschitz, J. Rennat and T. M. Korn; ibid, <u>76</u>, 5839 (1954)

19. W. E. Mayer and A. C. Albrecht; J. Phys. Chem.; <u>66</u>, 1168 (1962)

20. K. D. Cadogan and A. C. Albrecht; ibid, <u>72</u>, 424 (1969)

21. R. F. Collins; Chem. Ind. (London), 704 (1957)

22. N. H. Cromwell, P. W. Foster and M. M. Wheeler; ibid, 228 (1954)

23. G. J. Beichl, J. E. Colwell and J. G. Miller; ibid, 203 (1960)

24a. M. Asscher and D. Vofsi; J. Chem. Soc., 2261 (1961)

24b. M. Asscher; Chem. Ind. (London), 1430 (1965)

25. M. Pasez and J. Bartor; Bull. Soc. Chem. France, 1172, (1963)

26. G. Drefahland, G. Heublein; J. Prakt. Chem., <u>20</u>, 323, (1963)

27. D. P. Stevenson and G. M. Coppinger; J. Amer. Chem. Soc., <u>84</u>, 149 (1962)

28. K. M. C. Davis and M. F. Farmer; J. Chem. Soc. B 28 (1967)

29. J. L. Kurz, R. Hutton and F. H. Westheimer; J. Amer. Chem. Soc., <u>83</u>, 584 (1961)

30. W. J. Lautenberger, E. N. Jones and J. G. Miller; ibid, <u>90</u>, 1110 (1968)

31. C. Pac and H. Sakurai; Tet. Lett. 1865 (1968)

32. T. D. Walsh and R. C. Long; J. Amer. Chem. Soc., <u>89</u>, 3943 (1967)

33. T. Latowski; Z. Naturforsch, <u>23a</u>, 1127 (1968)

34. T. Tosa, C. Pac and A. Sakurai; Tet. Lett., 3635 (1969)

35. G. S. Hammond, M. T. MacCall, O. Yonemitsu and B. Witkop; J. Amer. Chem. Soc., <u>92</u>, 699 (1970)

36. O. Yonemitsu, H. Nakai, Y. Kanaoka, I. Karle and B. Witkop; ibid, 91, 459 (1969)

37. O. Yonemitsu, T. Tokuyamma, M. Chaykousky and B. Witkop; ibid, 90, 776 (1968)

38. O. Yonemitsu, Y. Okuno, Y. Kanaoka, I. Karle and B. Witkop; ibid, 90, 6522 (1968)

39. W. M. Moore and M. Ketchum; ibid, 84, 1368 (1962)

40. A. E. Hoeft; M.S. Thesis, Colorado State University (1971)

41. R. I. Walter; J. Amer. Chem. Soc., 77, 5999 (1955)

42. R. M. Silverstein and G. C. Bassler; "Spectrometric Identification of Organic Compounds, " John Wiley, New York, N.Y., p. 29

43. W. F. Reynolds and T. Schafer, Can. J. Chem., 41, 2339 (1963)

44. I. Yamaguchi and S. Brownstein; J. Phys. Chem., 67, 525 (1963)

45. J. G. Calvert and J. N. Pitts, "Photochemistry, " John Wiley, New York, N.Y., 2nd Ed. (1967), p. 601

46. N. L. Weinberg and H. R. Weinberg; Chem. Rev., 68, 449 (1968)

47. L. A. Hall, G. T. Davis, D. H. Rosenblatt, H. K. R. Williams, J. Amer. Chem. Soc., 89, 1163 (1967)

48. Other electron transfers via singlets have been demonstrated. See for example: W. Ware and H. P. Richter; J. Chem. Phys., 48, 1595 (1968); H. G. R. Seely, J. Phys. Chem., 69, 1779 (1965)

49. "The Chemistry of the Carbonyl Group, " Saul Patai, Editor. John Wiley Interscience Publishers, N.Y., New York (1966), p. 182

50. L. J. Andrews and W. W. Kaeding, J. Amer. Chem. Soc., 1007, (1951)

51. L. H. Keith, A. L. Alford and A. W. Garrison, J. Ass. Offic. Anal. Chem., 52, 1074-92 (1969)

52. Unpublished work of G. Nordblom

53. E. A. Fitzgerald Jr., P. Wuelfing Jr., and H. H. Richlot, J. Phys. Chem., 74, 2118 (1970)