MECHANISTIC STUDIES ON THE SENSITIZED PHOTOCHEMISTRY OF BIS(2,4-PENTANEDIONATO)COPPER(II)

by

Gonzalo E. Buono-Core
B.Sc., Catholic University (Chile), 1975

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
in the Department
of
Chemistry

SIMON FRASER UNIVERSITY
July 1981

APPROVAL

Name: Gonzalo E. Buono-Core

Degree: Doctor of Philosophy

Title of Thesis: Mechanistic Studies on the Sensitized Photochemistry of Bis(2,4-Pentanedionato)-Copper(II)

Examining Committee:

Chairperson: Dr. T.N. Bell

Dr. Y.L. Chow
Senior Supervisor

Dr. R.K. Pomeroy
Supervisory Committee

Dr. A.C. Oehlschlager
Supervisory Committee

Dr. A.G. Sherwood
Internal Examiner

Dr. J.C. Scaiano
Division of Chemistry
National Research Council

Date Approved: August 12, 1981

PARTIAL COPYRIGHT LICENSE

I hereby grant to Simon Fraser University the right to lend my thesis, project or extended essay (the title of which is shown below) to users of the Simon Fraser University Library, and to make partial or single copies only for such users or in response to a request from the library of any other university, or other educational institution, on its own behalf or for one of its users. I further agree that permission for multiple copying of this work for scholarly purposes may be granted by me or the Dean of Graduate Studies. It is understood that copying or publication of this work for financial gain shall not be allowed without my written permission.

Title of Thesis/Project/Extended Essay

"Mechanistic Studies on the Sensitized Photochemistry of

Bis(2,4-Pentanedionato)Copper(II)"

Author: ______________________
(signature)

Gonzalo E. BUONO-CORE
(name)

16/12/81
(date)

ABSTRACT

Bis(2,4-pentanedionato)copper(II), Cu(acac)$_2$, quenched the triplet states of ketones and polynuclear aromatic hydrocarbons efficiently, but only certain ketones successfully sensitized the photoreduction of Cu(acac)$_2$ under nitrogen in alcohols or tetrahydrofuran to give black precipitates. These were tentatively identified as polymeric (2,4-pentanedionato)-copper(I) complex.

The bimolecular rate constants of quenching of several sensitizers by Cu(acac)$_2$ in methanol were determined by flash photolysis experiments. The lack of correlation with the triplet state energies of the sensitizers suggest that a classical energy transfer process for quenching is unlikely. A sensitization mechanism via an electron transfer within an excited complex is proposed to explain the decomposition of Cu(acac)$_2$. A good agreement with Weller's equation for electron transfer quenching supports the proposed mechanism.

The benzophenone sensitized photoreduction of Cu(acac)$_2$ was more efficient in solvents with better hydrogen donating power, indicating that hydrogen abstraction is a critical step in the reaction. The kinetic analysis indicated that the efficiency of the photoreduction is determined by the partition of the excited complex between a successful reaction, involving hydrogen abstraction from the solvent, and an unsuccessful one, involving reverse electron transfer to give the starting materials.

In the presence of various ligands, L, the sensitized photolysis gave copper(I) complexes, Cu(acac)L_x, that were readily oxidized by air or photolyzed to form metallic copper with the exception of Cu(acac)$(PPh_3)_2$ which was stable to both reactions. In the presence of dienes, the photoreaction of $Cu(acac)_2$ yielded rearranged olefins probably via an unstable olefin complex of copper(I). For example, 1,5-cyclooctadiene gave good yields of the 1,3-isomer, whereas cis-trans isomerization was observed for trienes in the presence of hydrogen. The transient Cu(acac) could also be intercepted by terminal acetylenes to give stable copper(I) acetylide σ-type complexes, or by disubstituted acetylenes to give π-acetylene complexes.

The acetylacetonyl radical generated during the reaction could be trapped (in poor hydrogen donor solvents) with reactive olefins such as norbornene, 1-hexene or neo-hexene. The isolation and characterization of the addition products showed that the radical reacts exclusively as a carbon radical.

To F.I.A.

To Jaime.

To my parents.

ACKNOWLEDGEMENTS

The author wishes to express his gratitude to the following persons:

To Dr. Y.L. Chow for his guidance and genuine interest throughout this work.

To Dr. R.K. Pomeroy for his supervision during six months of this research and numerous helpful discussions.

To fellow members from Dr. Chow's group for their collaboration and friendship. Special thanks to Dr. K. Iwai and Dr. B. Marciniak for helping to solve many problems related to this research.

To Dr. Harold Pierce, Falko Tilgner and all the technical staff for their valuable assistance.

To Leslie Vincent for having to put up with my handwriting and doing an excellent job in typing this thesis.

To Carol Beddard at NRC, Ottawa, for doing the flash photolysis experiments and Peter Hoang for doing the cyclic voltammetry measurements.

Financial assistance from the Department of Chemistry, Simon Fraser University and Catholic University (Chile) is also gratefully acknowledged.

TABLE OF CONTENTS

LIST OF ABBREVIATIONS

acacH (or AA)	acetylacetone (2,4-pentanedione)
tfaH	1,1,1-trifluoroacetylacetone
hfaH	1,1,1,5,5,5-hexafluoroacetylacetone
bpy	α,α'-bipyridyl
o-phen	1,10-phenanthroline
DTH	2,5-dithiahexane
DPM	dipivaloylmethanato
1,5-COD	cis,cis-1,5-cyclooctadiene
1,3-COD	1,3-cyclooctadiene
t,t,t-CDT	trans,trans,trans-1,5,9-cyclododecatriene
c,t,t-CDT	cis,trans,trans-1,5,9-cyclododecatriene
c,c,t-CDT	cis,cis,trans-1,5,9-cyclododecatriene
NBD	norbornadiene
QC	quadricyclene
BP	benzophenone

LIST OF TABLES

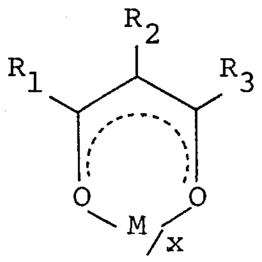
LIST OF FIGURES

CHAPTER 1

Introduction

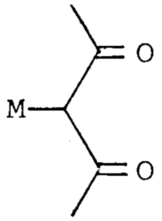
1-1 1,3-Diketonate Chelates

The physical and chemical properties of the metal β-diketonate complexes have been extensively investigated (1,2). The most common structure, studies have shown, (3) has a generalized formula shown below.

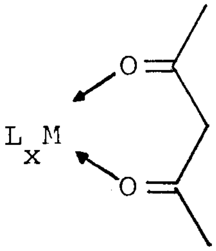


From structural, spectral and chemical evidence (3,5) the delocalized and essentially planar nature of the six-membered ring has been inferred. The number of chelated ligands may vary from one to four depending on the oxidation state of the metal. The substituent groups R_1, R_2 and R_3 may be practically any organic group. The most common ligand though is the anion of 2,4-pentanedione ($R_1 = R_3 = CH_3$, $R_2 = H$) or acetylacetonate (= acac) which has been coordinated to almost every metal and metalloid (2).

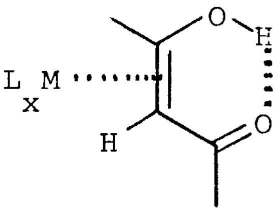
Far less numerous than oxygen-chelated acetylacetonate derivatives are those in which the metal atom is bonded directly to the C_3 atom rather than to the enolate oxygens (6,7). Among these, complexes with rhodium, iridium, palladium and platinum are well known (7). 1,3-Diketones can also in certain cases act as neutral ligands being bound either through oxygen as 1-2 or forming olefin complexes as shown in 1-3.



1-1



1-2



1-3

1-2 Spectral Properties

Three types of electronic transitions are normally observed in metal β-diketonate complexes (8).

a) Intraligand transition: this is thought to be a $\pi \rightarrow \pi^*$ transition which is characteristic of the acetylacetonate ion and normally lies in the 250-300 nm region.

b) Charge transfer transitions (or electron transfer transitions): these result from the transfer of one electron from an orbital primarily centered on the ligand to one centered on the metal (L→M), or from an orbital primarily centered on the metal to one centered on the ligand (M→L). These are usually observed in the 300-350 nm region. However, Jorgensen (9) has suggested that charge transfer transitions observed at energies higher than ligand field transitions may occur at energies higher or lower than the ligand $\pi \rightarrow \pi^*$. This is the case of $Cu(acac)_2$ in which the $\pi \rightarrow \pi^*$ transition is observed at ~293 nm while the charge transfer band is observed at ~250 nm.

c) Also observed within the chelates, particularly in the first-row transition series, are electronic transitions in the visible region, due to d-d transitions. However, since the photochemistry observed in the compounds is almost exclusively redox (8), these transitions are of less interest, although they can be of great utility in quantitative photochemical studies.

1-3 Photochemistry of 1,3-Diketonate Chelates

The excited states of the 1,3-diketonate chelates result from the absorption of a photon by a particular chromophore of the molecule. In the chelates of the first transition series, with the exception of the Cr(III) chelates (10), neither energy transfer nor luminescence has been observed. Thus, radiative processes do not seem to be important in the dissipation of electronic energy for these molecules. However, electronic energy can be dissipated via a photochemical reaction.

In the last twenty years a number of papers involving the photochemistry of coordination compounds, especially in aqueous solutions have been published (11-13), but only a few studies on β-diketonate chelates can be found (14). Nevertheless, these studies have established the general photoreactivity pattern of the first-row transition metal β-diketonates. Thus, ultraviolet irradiation of β-diketonates induces either stereochemical rearrangement (Cr) (15-18), one-electron reduction of the metal center (Mn (19), Fe (20), Co (21), Ni (22), Cu (23)) or both (Cr (15) and Rh (24-25)). A summary of these studies is shown in Table 1-1.

Lintvedt (8) has suggested that for the photoreduction reactions in alcoholic solvents, the similarity of products, the reaction kinetics and the effect of solvent seem to

Table 1-1 Photochemical Reactions of β-Diketonate Complexes

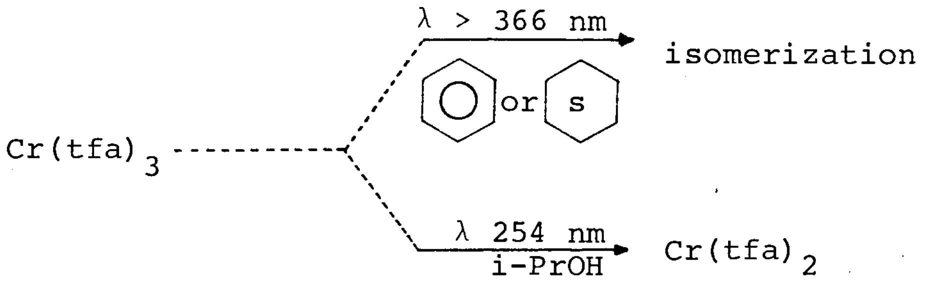
$$\mathrm{Mn(tfac)_3} \xrightarrow[\mathrm{EtOH}]{\lambda\ 254\ \mathrm{nm}} \mathrm{Mn(tfac)_2(EtOH)_2} + \mathrm{tfacH}$$

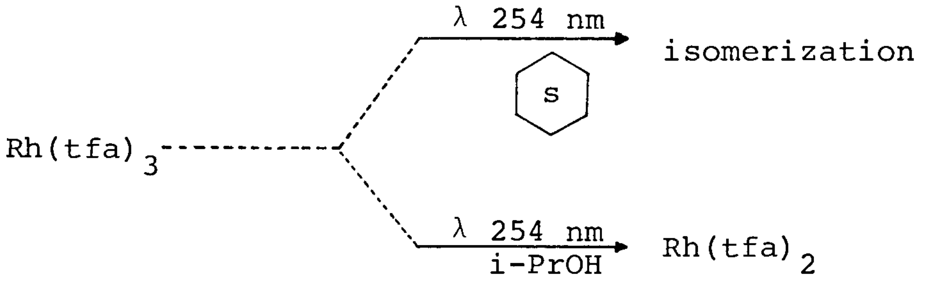
$$\mathrm{Fe(hfac)_3} \xrightarrow[\mathrm{EtOH}]{\lambda\ <350\ \mathrm{nm}} \mathrm{Fe(hfac)_2(EtOH)_2} + \mathrm{hfacH}$$

$$\mathrm{Co(tfac)_3} \xrightarrow[\mathrm{EtOH}]{\lambda\ <366\ \mathrm{nm}} \mathrm{Co(tfac)_2(EtOH)_2} + \mathrm{tfacH}$$

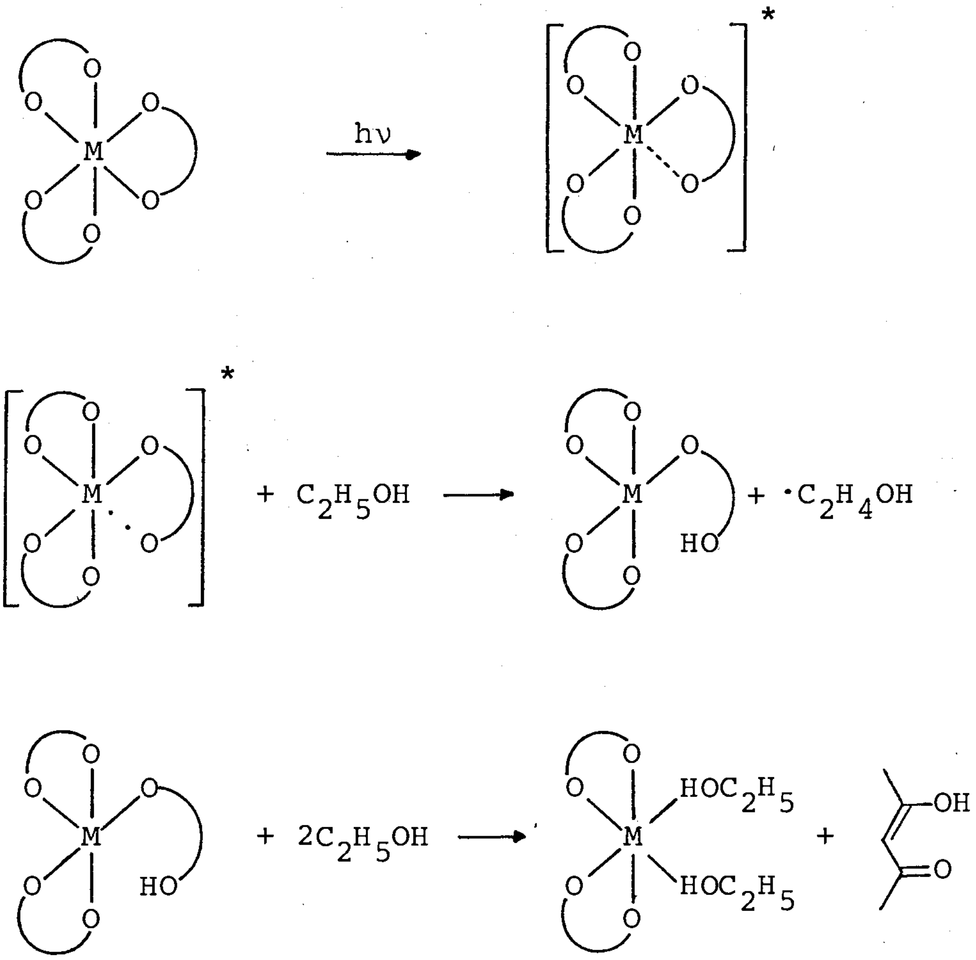
$$\mathrm{Ni(acac)_2} \xrightarrow[\mathrm{ROH}]{\lambda\ 254\ \mathrm{nm}} \mathrm{Ni^0} + 2\mathrm{acacH}$$

$$\mathrm{Cu(acac)_2} \xrightarrow[\mathrm{ROH}]{\lambda\ 254\ \mathrm{nm}} \mathrm{Cu^0} + 2\mathrm{acacH}$$





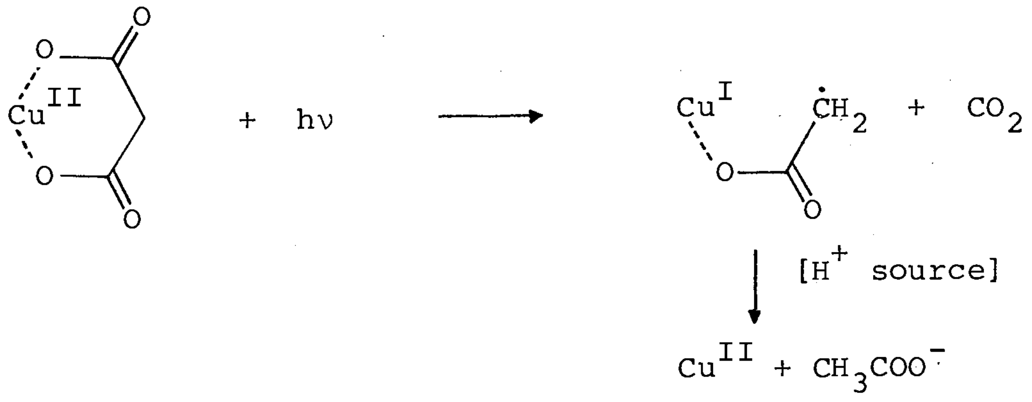
indicate a common mechanism (Scheme 1-1).



Scheme 1-1

1-4 Photochemistry of Copper Complexes

Although the photochemistry of copper(II) complexes has not yet been studied in detail, the photochemical behavior of a few Cu(II) complexes of carboxylic acids and amino acids has been reported (26). Product analysis of the photochemical reactions indicated the evolution of carbon dioxide which suggested a redox-type primary photochemical reaction. However, in the final solution only Cu(II) was found and no Cu(I) was present. Also, attempts to detect Cu(I) by flash photolysis were unsuccessful (27). It was explained that since the Cu(I) produced in the primary step is reactive, it reduces the primary ligand radicals to regenerate Cu(II). The mechanism proposed for Cu(II) malonate is shown below. It was also observed



that primary radicals produced on irradiation of Cu(II) amino acids chelates in aqueous solution using near ultraviolet light initiate vinyl polymerization (28).

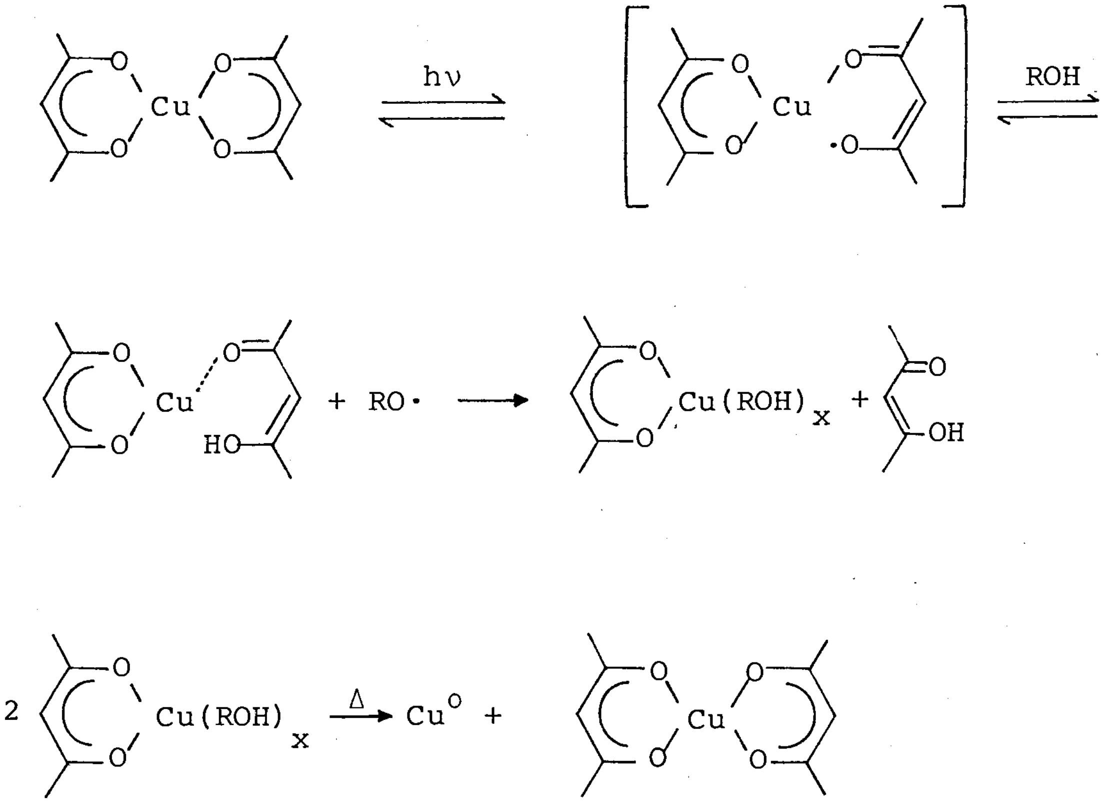
Besides the present investigation only one extensive study on the photodecomposition of Cu(II)-β-diketonate complexes can be found in the literature (19,23). This and other studies of copper compounds use direct irradiation.

When $Cu(acac)_2$ was irradiated at 254 nm in alcoholic solvents, the products were Cu^0 and acetylacetone with a low quantum yield of < 0.04 (23).

$$Cu(acac)_2 \xrightarrow[ROH]{h\nu\ (254\ nm)} Cu^0 + 2acacH$$

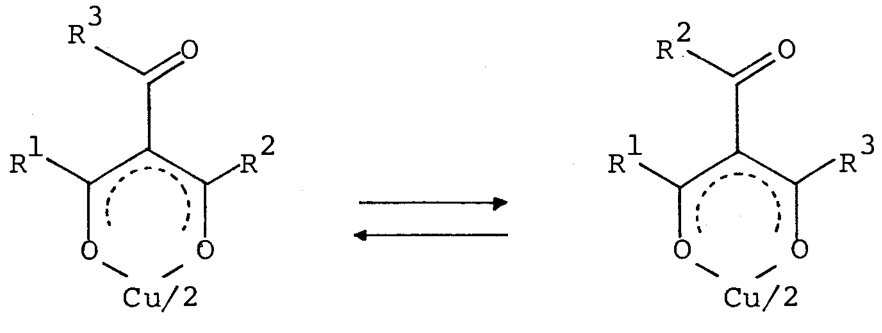
The ultraviolet spectrum of $Cu(acac)_2$ (Fig. 2-1) in ethanol consists of two bands: one at 294 nm (ε 23500) assigned by Cotton (29) to a $\pi \rightarrow \pi^*$ intraligand transition, and a second band at ~243 nm (ε 14800) assigned to a charge-transfer transition of the ligand-to-metal type (CTLM) involving the promotion of a σ-bonding or an oxygen-n-electron to a metal orbital. Since no reaction is observed upon irradiation at wavelength > 280 nm, it was assumed that the reduction is caused by migration of an electron from the ligand to the metal.

The effect of the solvent on the quantum yields, as well as the temperature dependence of the overall reduction plus the observation of a reactive intermediate species containing copper, has led Lintvedt to propose the following mechanism (23) which involves an initial photochemical reduction to a Cu(I) species followed by thermal disproportionation to Cu^{0}. Note that alkoxy radical is proposed to be formed by hydrogen atom transfer.



Scheme 1-2

A recent paper reported the photoisomerization of Cu(II) chelates of β,β'-diketoesters and of triacylmethanes in solvents photochemically inert (30). These chelates have been shown to exist as two equilibrium configurations in solution (<u>1-1</u> and <u>1-2</u>) (31). Photochemical excitation of the π-π* transition band of



<u>1-1</u> <u>1-2</u>

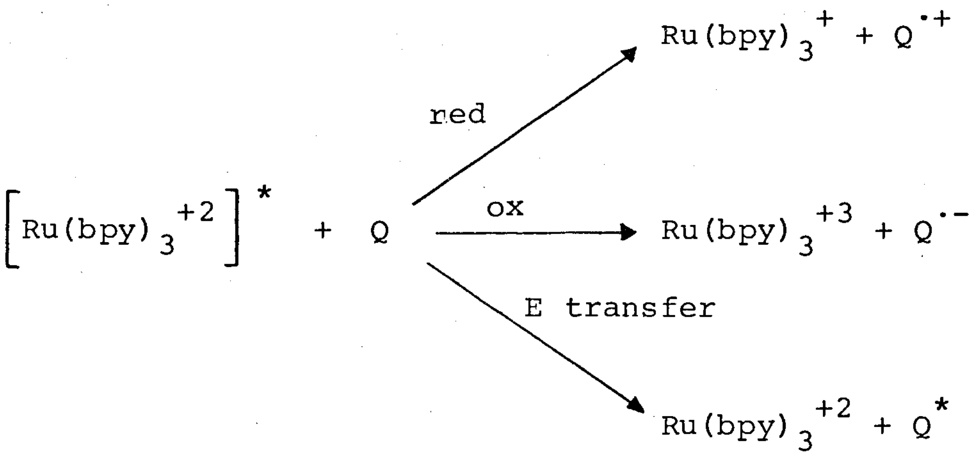
$R^2 = OEt, CH_3$
$R^1 = R^3 = CH_3$

the ligands (at ~320 nm) shifts the thermodynamic equilibrium similar to the photoisomerization described for the ligands (32).

1-5 Sensitized Reactions in Metal Complexes

The quenching of an excited molecule by metal complexes can occur in three fundamental ways: i) energy transfer to generate the excited state of the metal complex, ii) electron transfer leading to radical ions via exciplexes (excited state complex), and iii) ligand substitution reactions. Since the substitution is generally too slow to compete with intramolecular decay, it follows that the two most important bimolecular quenching processes are electron transfer and electronic energy transfer (33).

Although there have been many investigations on the mechanism of sensitized reactions of metal complexes (34), most of these studies have been focussed on polypyridine ruthenium(II) complexes (35-38), in particular $Ru(bpy)_3^{+2}$. The quenching of its emission by various types of substrates has been the subject of extensive studies. These studies have shown that the quenching may proceed by an energy transfer mechanism, or by oxidation or reduction of the complex, that is the complex can act as electron donor as well as acceptor depending on the nature of the quenchers.



Scheme 1-3

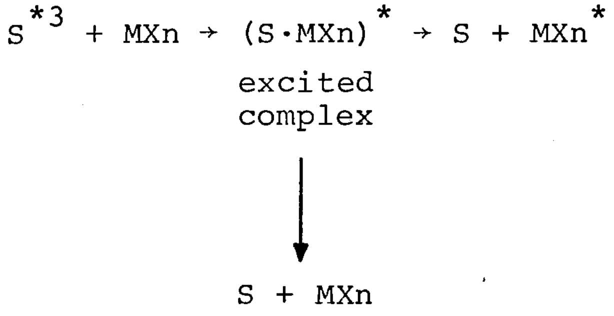
In spite of all the work done on the quenching of triplet states of organic compounds by coordination complexes, its mechanism is still imperfectly understood. Most of the evidence seems to indicate that energy transfer is the predominant mechanism of quenching. However, due to the lack of spectroscopic studies available on the number and nature of energetically accessible excited states in transition metal complexes, other mechanisms cannot be ignored.

1-6 Quenching of Triplet States by Metal β-Diketonates

In 1963, Bell and Linschitz (39) reported that Fe(acac)$_3$ and Fe(dpm)$_3$ were very efficient quenchers of triplet benzophenone and triplet 1-naphthaldehyde, with rate constants close to those expected for diffusion controlled reactions. Later, Hammond and Foss (40), using a static quenching method, found that dipivaloylmethanato complexes were consistently less efficient quenchers of triplet benzophenone than the corresponding acetylacetonate complexes and they attributed this to steric effects.

Wilkinson and co-workers (41) reported the bimolecular rate constants (k_q) for quenching of the triplet states of sixteen different organic molecules (Table 1-2) by iron(III), aluminum(III) and ruthenium(III) β-diketonate complexes in benzene solution. From a correlation of their quenching rate constant measurements with spectroscopically determined energy levels of the complexes they concluded that the mechanism of quenching involves electronic energy transfer (42).

However, from results of kinetic flash photolysis experiments, Hammond (43) earlier had reported that some transition metal β-diketonate complexes quench the triplet state of eight different organic compounds efficiently in benzene solution, but found very little dependence on the triplet energy of the sensitizers (Table 1-3). For example, the triplet state of anthracene, whose energy is very low (42.6 kcal/mol), was still very efficiently quenched by all the complexes investigated. He concluded that either the complexes have very low-lying states to which they can be promoted by energy transfer or with these compounds quenching does not involve energy transfer. Since they did not find any evidence for formation of excited states of the chelates, they suggested that the results are equally compatible with either one of the following two mechanisms:



$$\begin{tikzcd} S^{*3} + MXn \arrow[r] & \underset{\text{excited complex}}{(S\cdot MXn)^{*}} \arrow[r] \arrow[d] & S + MXn^{*} \\ & S + MXn & \end{tikzcd}$$

Scheme 1-4

Table 1-2 Rate Constants for Quenching of Triplet States of Several Organic Compounds by $Fe(acac)_3$, $Fe(dpm)_3$ and $Ru(acac)_3$ (1)

Donor (analyzing λ/nm)	E_T (kcal/mole) (2)	$kq/10^9\ M^{-1}\ sec^{-1}$		
		$Fe(acac)_3$	$Fe(dpm)_3$	$Ru(acac)_3$
Xanthone (610)	74.0	5.0	1.6	-
Benzophenone (535)	69.2	3.2	0.87	4.8
Phenanthrene (489)	62.0	-	1.1	4.5
2-Acetonaphthone (428)	59.4	3.2	0.98	4.7
Chrysene (560)	57.3	3.2	1.0	-
Pyrene (416)	48.1	2.5	0.32	2.4
1,2-Benzanthracene (490)	47.0	-	-	2.2
Acridine (440)	46.0	0.73	0.16	$\leqslant 0.07$
Anthracene (425)	42.6	0.76	0.15	$\leqslant 0.08$
Naphthacene (459)	29.4	0.53	0.085	-
Pentacene (498)	22.9	0.055	-	-

1. From Ref. 41
2. Lowest triplet energies of donors.

Table 1-3 Rate Constants for Triplet Quenching of Various Sensitizers by Cu(II), Cr(III), Ni(II) and Fe(III) β-Diketonates (kq, M^{-1} sec^{-1} × 10^{-9})[1]

Sensitizer (E_T)[2]	Fe(AA)$_3$	Cu(AA)$_2$	Cr(AA)$_3$	Ni(DPM)$_2$	Cu(DPM)$_2$
Triphenylene (66.6)	-	1.3	3.8	-	-
Phenanthrene (62.2)	3.3	-	-	-	-
Naphthalene (60.9)	1.8	-	-	-	-
2-Acetonaphthone (59.3)	1.9	1.9	1.1	-	0.5
Benzil (53.7)	2.7	1.7	0.4	0.3	-
Fluorenone (53.3)	1.2	1.0	1.1	-	-
Benzanthrone (47.0)	1.0	2.3	1.3	-	-
Anthracene (42.6)	0.7	0.6	1.3	-	0.3

1. From Ref. 43

2. Lowest triplet energies of the sensitizers (in kcal/mole).

1-7 Research Proposal

Preliminary experiments carried out by Chow (44) showed that the photoreduction of $Cu(acac)_2$ in methanol is greatly accelerated in the presence of benzophenone. It was also

$$Cu(acac)_2 + Ph_2CO \xrightarrow[CH_3OH]{h\nu\ (>300\ nm)} Cu^0 + 2acacH$$

reported, while this research was underway, that benzophenone and acetophenone sensitize the photodecomposition of polyfluorinated copper β-diketonates (45), but no mechanism was proposed.

In order to gain more insight into the mechanism of quenching of organic sensitizers by metal complexes, we decided to re-examine the sensitized photochemistry of metal β-diketonate complexes. We have chosen bis-(2,4-pentanedionato)copper(II) for study for the following reasons:

a) It is thermally stable (it sublimes at atmospheric pressure) (46) and simple to prepare.

b) Its physical properties have been widely investigated (1,47) and its structure has been determined by x-ray crystallography (48).

c) It shows a high reactivity towards sensitization by a variety of different compounds (43,44).

d) It is photochemically stable when irradiated at λ >280 nm (23).

e) Its potential use in photocatalyzed reactions of different substrates.

The aim of this research can be outlined as follows:

1. To establish the general reaction pattern of the photodecomposition of $Cu(acac)_2$ in the presence of different sensitizers and/or solvents and to determine the overall quantum efficiency under these conditions.

2. To stabilize the reduction intermediate Copper(I) species with suitable ligands and investigate its catalytic reactivity.

3. To investigate the acetylacetonyl radical reactions.

4. To investigate the kinetics and mechanism of the sensitization process by using static quenching methods and flash photolysis experiments.

5. To look at the possible applications of the sensitized reaction, particularly in the field of olefin isomerization.

CHAPTER 2

Results

2-1 Photolysis of $Cu(acac)_2$

In preliminary experiments, methanol solutions of $Cu(acac)_2$ in the absence of sensitizers were irradiated in a conventional immersion type photocell (Apparatus III). This apparatus was clearly unsatisfactory because of the deposition of black precipitates and metallic copper mirrors, both of which obstructed the incident light. Nevertheless, several features of the photodecomposition reported earlier were confirmed: i) the blue color of the $Cu(acac)_2$ solution disappeared slowly under nitrogen to form black precipitates when photolyzed in a quartz but not in a Pyrex photocell; ii) the photolysate, on exposure to the air was slowly converted to a blue solution of $Cu(acac)_2$; and iii) on irradiation under oxygen, the Cu(II) complex was irreversibly decomposed. In order to circumvent the deposition problems, an apparatus was designed (Apparatus I) in which the solution was irradiated from overhead. $Cu(acac)_2$ in alcohol solutions absorbs light strongly at λ_{max} 293 nm (ε 23,500) (Fig. 2-1) which tails to the 370 nm region with $\varepsilon \sim 600$ at 330 nm. In sensitized photolysis, the concentration of the sensitizers were adjusted so that they absorb most of the incident light.

Figure 2-1 Uv Spectra of Cu(acac)$_2$ and Benzophenone in Methanol.

a) 2×10^{-5} M Cu(acac)$_2$
b) 5×10^{-4} M Cu(acac)$_2$
c) 5×10^{-3} M Benzophenone

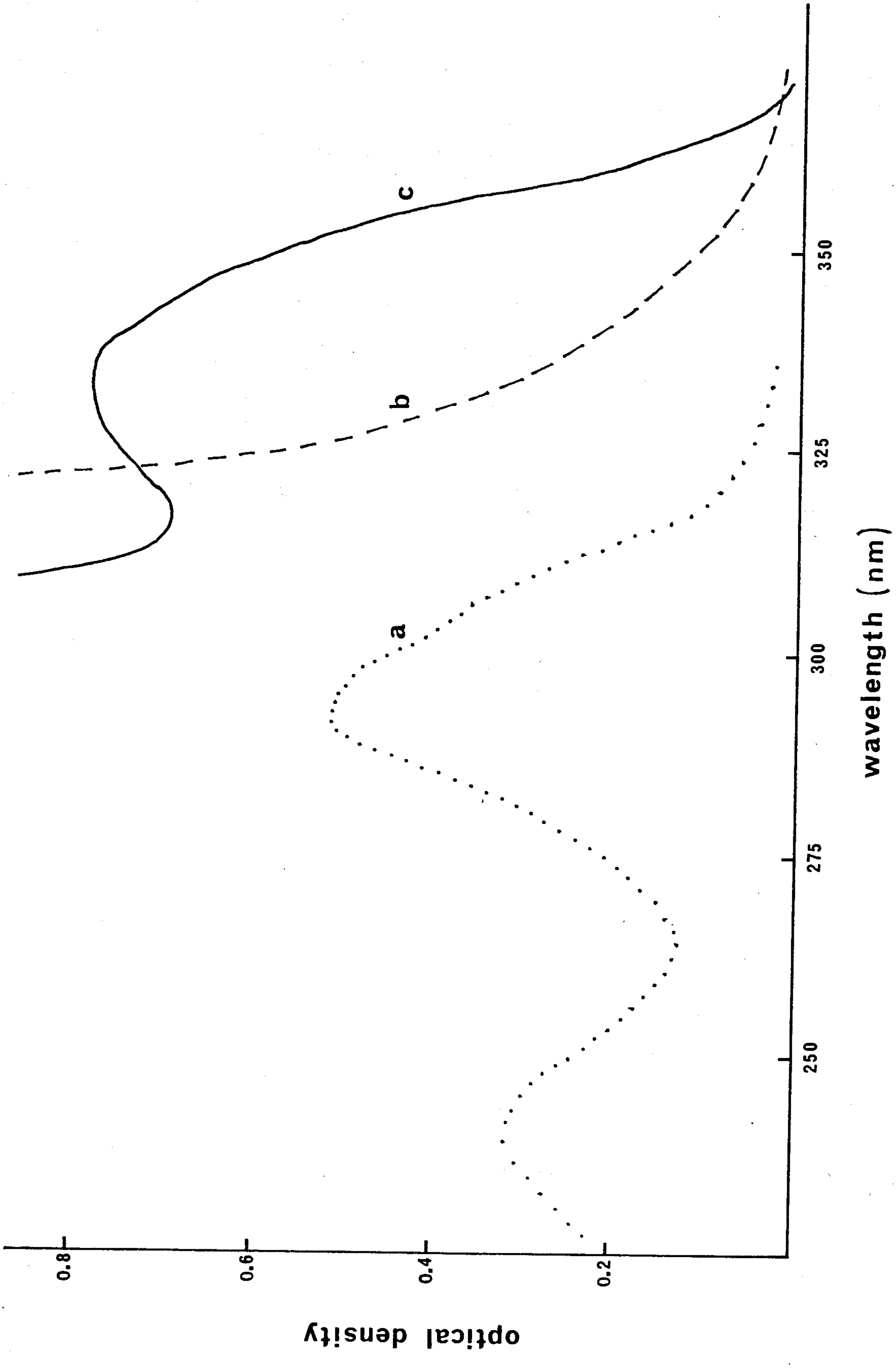

optical density
0.2
0.4
0.6
0.8
wavelength (nm)
250
275
300
325
350
a
b
c

Table 2-1 UV Data of Sensitizers[a]

Sensitizer	λ_{nm} (log ε)
Benzophenone	252(4.25), 333(2.18)
Acetophenone	240(3.85), 278.5(2.79)
Anthrone	263(4.47), 307(3.76), 316(3.49), 333(3.25)
Biacetyl	290(1.40)
Benzil	259(4.31)
Xanthone	237(4.58), 260(4.07), 283(3.59), 336(3.84)
Phenothiazine	254(4.63), 317(3.67)
2-Acetonaphthone	246(4.70), 282(3.98), 290(3.93), 338.5(3.22)
1-Cyanonaphthalene	224(4.59), 296(3.84), 308.5(3.70), 322(3.35)
p-Methoxyacetophenone	271(4.20)
Carbazole	244(4.35), 257(4.27), 392(4.23), 322(3.57), 335(3.54)
Fluorenone	249(4.8), 256(4.9), 285(3.4), 293.5(3.6), 307(3.3), 314(3.2), 321(3.1), 329(3.0), 379(2.5), 293(2.4)
Phenanthrene	245(4.7), 251(4.8), 275(4.1), 281(4.0), 293(4.1), 309(2.4), 315(2.6), 323(2.5), 331(2.5), 339(2.5), 347(2.5), 357(2.1), 375(2.1)
Pyrene	306(4.1), 319(4.4), 334(4.7), 350(2.8), 356(2.6), 360(2.5)

Table 2-1 (Cont'd)

Sensitizer	λ_{nm} (log ε)
Perylene	251(4.20), 368(3.68), 387(4.08), 406(4.42), 434(4.56)
Anthracene	252(5.3), 296(2.7), 311(3.1), 324(3.5), 340(3.7), 357(3.92), 374(3.91)

[a] in methanol

2-2 Benzophenone Sensitization

Irradiation of a methanol solution of $Cu(acac)_2$ (5.7 mmol) containing 6.3 mmol of benzophenone under nitrogen gave a suspension of black precipitate in 3 h with concurrent discharge of the original blue color. On continued irradiation, the suspension changed to lustrous copper particles in a colorless solution, or gave a copper mirror in certain cases. The progress of the reaction was monitored by following the decrease of the absorption band of $Cu(acac)_2$ at 630 nm.

The yield of copper in the photolysis was determined by colorimetry to be nearly quantitative. The colorless solution contained acetylacetone in 78% yield as determined by high pressure liquid chromatography (HPLC) and uv spectroscopy (λ_{max} 273 nm). Formaldehyde, in ~50% yield, was detected as its 2,4-dinitrophenylhydrazone derivative. Benzophenone was quantitatively recovered and the absence of benzopinacol was ascertained.

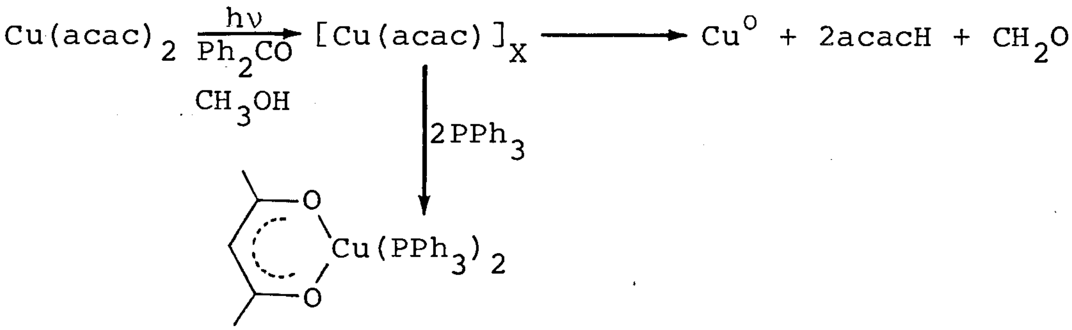
$$Cu(acac)_2 \xrightarrow[CH_3OH]{h\nu,\ Ph_2CO} Cu^0 + 2acacH + CH_2O$$

The metallic copper suspension, obtained after photolysis, was stable under nitrogen. However, on exposure to air it dissolved slowly and reverted quantitatively to give $Cu(acac)_2$ with the original concentration as shown by uv spectroscopy. This occurred more rapidly under oxygen purging. β-Diketones, e.g., acetylacetone, with a large enol content, are known to react with metals (among them copper) in the presence of oxygen (49,50). When metallic copper (5 mmol) was treated with a solution of acetylacetone (10 mmol) in methanol and left at room temperature for 24 h, a blue solution of $Cu(acac)_2$ was obtained.

$$Cu^{0} + 2acacH \xrightarrow[24\ h,\ r.t.]{CH_3OH} Cu(acac)_2$$

As the primary photodecomposition product for the reaction in alcohols was the black precipitate, its identity was investigated. It was observed that the suspension of the black precipitate in the transparent solution reverted quantitatively to $Cu(acac)_2$ under oxygen and to one-half of the original $Cu(acac)_2$ concentration under nitrogen as determined by uv spectroscopy; metallic copper was also deposited in the latter case. This disproportionation of the black precipitate appeared to be similar to the behaviour of a black Cu(I) acetyl acetonate ($Cu(acac)\cdot 2.5\ NH_3$) prepared by Nast (51), which readily decomposes to metallic copper and $Cu(acac)_2$.

Black precipitates were also obtained in the direct photolysis of $Cu(acac)_2$ in alcohols and have been assumed to be Cu(acac)(ROH)$_X$, where ROH is the alcohol solvent (23). However, all the black precipitates obtained in the sensitized photolysis in various alcohols and tetrahydrofuran showed identical infrared spectra and did not show any absorption band characteristic of an alcohol. In fact the spectrum was very similar to the ir spectrum of Cu(acac)$_2$ except for a few additional peaks. Furthermore, when the black precipitates were treated with alcohol solutions of triphenylphosphine under nitrogen a white crystalline compound identified as Cu(acac)(PPh$_3$)$_2$ was obtained (52):



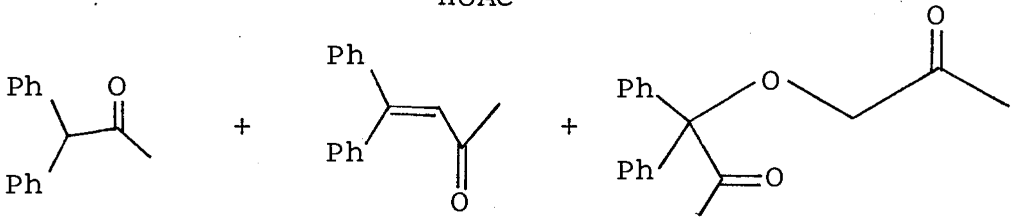
The solvent dependence of the reaction was investigated. The sensitized photodecomposition of Cu(acac)$_2$ in ethanol caused appearance of the black precipitate within 30-40 min and in isopropanol within ~15 min. In both cases copious amounts of the black suspension were rapidly formed as the irradiation proceeded. This suspension was transformed into metallic copper (100% and 98%, respectively) after 3 h and 1 h of irradiation, respectively. The yields of acetylacetone were analyzed to be 84% and 76%, and the oxidation products from the solvents, acetaldehyde and acetone, were determined (as the 2,4-DNPH derivatives) to be 38% and 62%, respectively. Benzophenone was recovered in high yields in both cases.

Under similar conditions, the sensitized reaction of $Cu(acac)_2$ in tetrahydrofuran solution followed the same pattern; i.e., disappearance of the 630 nm band with formation of a black precipitate after 1.5 h and complete reduction to Cu^0 in ~6 h. However, oxidation products from THF could not be isolated.

In chloroform solution the photodecomposition occurred very slowly but the color of the solution changed to deep green. A similar pattern has been observed by Lintvedt in the direct photolysis of $Cu(acac)_2$ in chloroform (23), in which the resulting product appears to be a polymeric cuprous chloride salt. He suggested that since it is known that chloroform undergoes a photodecomposition with production of chlorine atoms, the observed reaction may result from these atoms attacking the reactant or metallic copper. In benzene solution, no photodecomposition of $Cu(acac)_2$ was observed after 16 h of irradiation. However, when 1:1 mixtures of benzene-methanol or chloroform-methanol were used as solvents, the patterns of photochemical changes were the same as those observed in the alcohol solutions.

The benzophenone sensitized photoreduction of $Cu(acac)_2$ in acetic acid induced slow deposition of copper metal and the formation of acetylacetone, 1,1-diphenylacetone, 2-1 (8%), 1,1-diphenyl-1-buten-3-one, 2-2 (4%) and the diketoether, 2-3 (11%).

$$Cu(acac)_2 + Ph_2CO \xrightarrow[HOAc]{h\nu,\ N_2} Cu^0 + acacH +$$



2-1 2-2 2-3

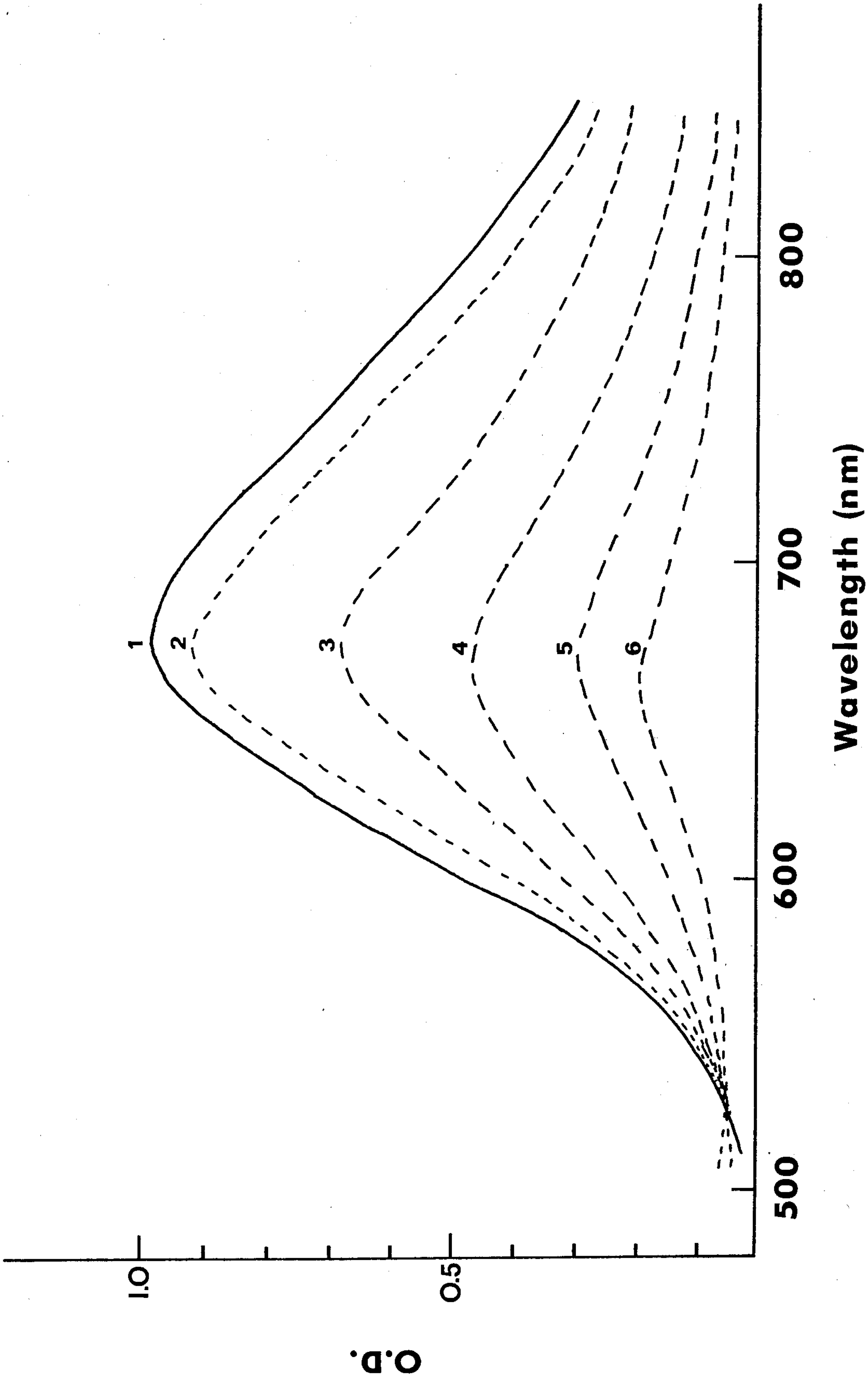
In acetic acid solution, $Cu(acac)_2$ is in equilibrium with $Cu(OAc)_2$ and acetylacetone. The formation of the latter pair is strongly favored as indicated by the uv absorption (λ_{max} 675 nm, ε 200) of a 1×10^{-3} M $Cu(acac)_2$ solution (Fig. 2-2).

$$Cu(acac)_2 + 2HOAc \rightleftharpoons Cu(OAc)_2 + 2acacH$$

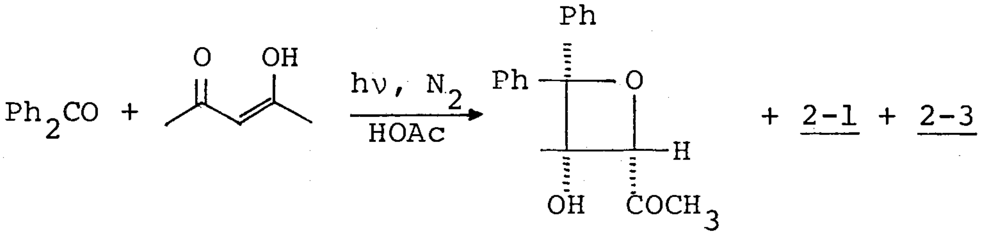
The photolysis of benzophenone in acetic acid in the presence of acetylacetone (λ_{max} 273 mm, ε 6800) under nitrogen with a Pyrex filter caused slow disappearance of both substrates to give cis-2,2-diphenyl-3-hydroxy-3-methyl-4-acetyloxetane, 2-4 (24%), 2-1 (6%) and the diketoether, 2-3 (14%). On the basis of one proton singlet

Figure 2-2 Visible Spectrum of $Cu(acac)_2$ (1×10^{-3} M) in Acetic Acid in the Presence of Different Concentrations of Acetylacetone.

Spectrum	$Cu(acac)_2$	: acacH
1	1	0
2	1	1
3	1	5
4	1	10
5	1	15
6	1	20

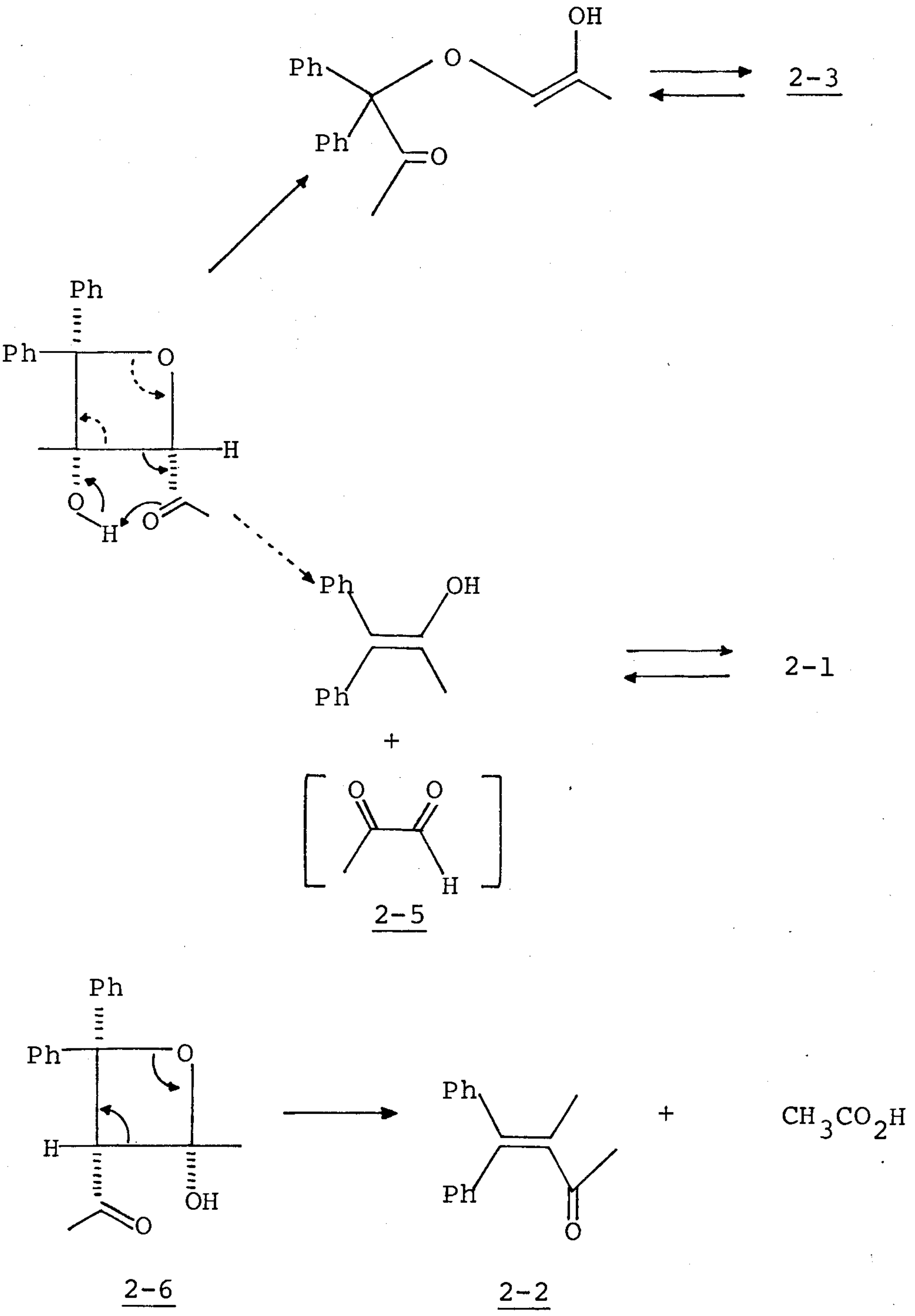

O.D.
1.0
0.5
500
600
700
800
Wavelength (nm)
1
2
3
4
5
6

at 4.92 ppm and a sharp intramolecular hydrogen bond absorption at 3550 cm^{-1} in CCl_4 solution, a cis configuration for the oxetane 2-4 was assigned (Scheme 2-1).



2-4

The formation of the diketo ether 2-3 was rationalized by a retro aldol reaction of oxetane 2-4. In gc analysis the oxetane 2-4 readily underwent a thermal rearrangement to give the ketone 2-1, a known compound (53). Since the diketo ether 2-3 is thermally stable, it is rather unlikely that 2-1 is formed by thermolysis of 2-3. The small amount of 1,1-diphenyl-1-buten-3-one 2-2, formed in the sensitized photolysis of $Cu(acac)_2$ could be explained by the formation of an unisolated oxetane, 2-6, and its subsequent thermal cycloreversion to give 2-2 (Scheme 2-1).


OH
Ph
O
Ph
O
2-3
Ph
Ph
O
H
O
H
O
Ph
OH
Ph
2-1
+
O
O
H
2-5
Ph
Ph
O
H
O
OH
Ph
Ph
O
+
CH_3CO_2H
2-6
2-2

Scheme 2-1

2-3 Other Sensitizers

The photodecomposition of Cu(acac)$_2$ in the presence of several sensitizers was investigated and the results are summarized in Table 2-2.

The photodecomposition could be sensitized by anthrone (54), biacetyl (55), benzil, xanthone (56,57), acetophenone and 2-acetonaphthone in that order of decreasing efficiency. In all these sensitized decompositions the black precipitate, metallic copper and acetylacetone were formed in nearly stoichiometric yields and the sensitizers were recovered almost quantitatively. Vpc analysis of the recovered anthrone, biacetyl and benzil showed small peaks that were assumed to be minor photoproducts of the sensitizers as they are known to decompose photolytically (54,55,58).

The decomposition of Cu(acac)$_2$ was also sensitized by phenyl alkyl ketones. The photolysis in the presence of butyrophenone, valerophenone and γ-methylvalerophenone gave, in addition to metallic copper, products derived from the Norrish II type photo process as shown by vpc and nmr analysis (59-63).

Table 2-2 Sensitized Photodecomposition of $Cu(acac)_2$ ($3.0-0.5 \times 10^{-3}$ M)

Sensitizer (ε at 330 nm)[a]	Concentration ($M \times 10^3$)	Solvent	E_T[b]	Result	ΔG[c]
Anthrone (291)	3.8	EtOH, MeOH	72.0	+	-25.5
Benzophenone (155)	6.4	EtOH, MeOH IPA, THF	69.1	+	- 9.9
Biacetyl (11)	470	EtOH	54.9	+	- 8.5
Xanthone (5980)	12.7	MeOH	74.2	+	-19.4
Acetophenone (24)	120	MeOH	74.1	+	-10.7
Benzil (210)	29.8	MeOH	53.7	+	+ 1.8
2-Acetonaphthone (1600)	3.5	MeOH	59.3	+	+ 1.7
γ-Methylvalerophenone (50)	100	MeOH		+	
Valerophenone (45)	108	MeOH	74.5	+	
Butyrophenone (40)	118	MeOH	74.7	+	
Fluorenone (1000)	5.5	MeOH, IPA	53.3	-	- 7.2
1-Cyanonaphthalene (192)	6.5	MeOH, EtOH THF	57.5	-	+23.8
Anthracene (3980)	5.6	MeOH	42.0	-	+30.1
Pyrene (50000)	4.2	EtOH	48.0	-	+27.9
Perylene (1580)	0.33	EtOH	35.0	-	+31

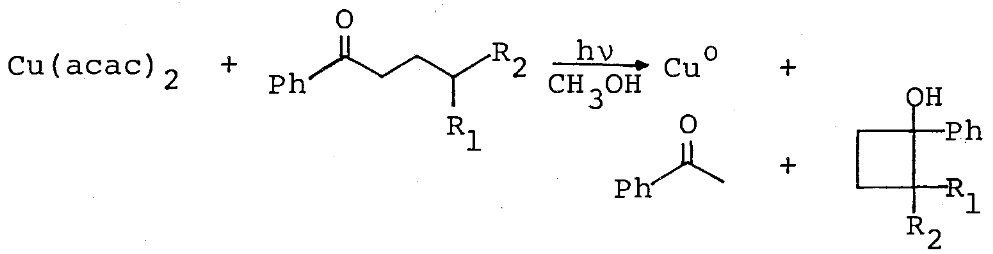
Table 2-2 (Cont'd)

Sensitizer (ε at 330 nm)[a]	Concentration ($M \times 10^3$)	Solvent	E_T[b]	Result	ΔG[c]
Carbazole (1258)	5.0	EtOH	70.0	-	
Phenothiazine (3800)	5.0	EtOH		-	
Phenanthrene (316)	11.4	EtOH	62.2		+21.8
p-Methoxy-Acetophenone		MeOH	71.7	-	- 9.3

[a] Molar extinction coefficient at λ 330 nm calculated from the uv spectra in methanol.

[b] Lowest triplet state energies of the sensitizers in kcal/mole taken from Ref. 64, 65 and 66.

[c] Free energy change (in kcal/mole) for electron transfer reactions according to Weller's equation (see P.80)



$R_1 = R_2 = H$	3%	0%
$R_1 = H_1, R_2 = CH_3$	41%	8%
$R_1 = R_2 = CH_3$	63%	11%

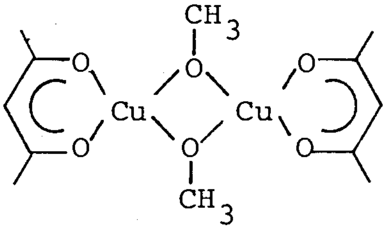
Other sensitizers shown in Table 2-2 failed to photodecompose $Cu(acac)_2$ as indicated by uv and visual observation. Except for a few cases to be described below, the sensitizers were recovered quantitatively and no acetylacetone or black precipitate was obtained. Fluorenone (67) failed to sensitize the photodecomposition of $Cu(acac)_2$ in methanol or isopropyl alcohol on prolonged irradiation. Although in the latter solvent the absorption maximum at 630 nm was shown to shift to ~680 nm, no product other than the starting materials was recovered from the photolysate in either solvent.

The photolysis in the presence of anthracene in methanol immediately precipitated the anthracene dimer (68). On prolonged irradiation the dimer was obtained in 70% yield while 60% of $Cu(acac)_2$ was recovered. Trace amounts of other products were also detected by vpc but no acetylacetone was obtained.

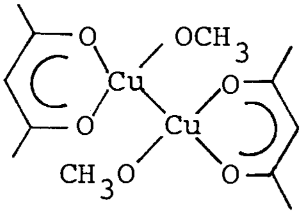
In the phenothiazine sensitized photodecomposition only

60% of $Cu(acac)_2$ was recovered and trace amounts of other products were detected by tlc. While prolonged photolysis gave a dark brown solution, phenothiazine was completely recovered.

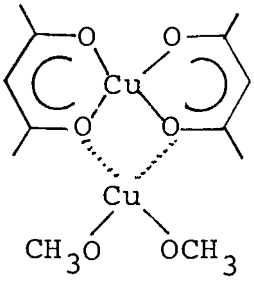
An attempted sensitization with 1-cyanonaphthalene did not cause the formation of the black precipitate, but showed instead a 15% decrease in the $Cu(acac)_2$ absorption at 630 nm with deposition of a small amount of a blue solid (15%). The ir and melting point were identical with $[Cu(acac)(CH_3O)]_n$, which has been obtained by the reaction of $Cu(acac)_2$ with methanolic KOH, and for which structure 2-8 has been assigned (69-72).



2-8



2-9



2-10

The ir spectrum of the solid showed, in addition to the ir bands of $Cu(acac)_2$, absorptions at 2820, 1070 and 560 cm^{-1}

(but no absorption above 3000 cm^{-1}), indicating the presence of a methoxide moiety. The mass spectrum showed m/e peaks at 386, 355, 324 and 261 (100%) corresponding to M^+, M^+-[OCH_3], M^+-2[OCH_3] and M^+-[$Cu(OCH_3)_2$], respectively. The fragmentation pattern below m/e 261 was very similar to that of $Cu(acac)_2$ (73). From these data, structures 2-8, 2-9 and 2-10 could be suggested for the compound. However, 2-10 appears to satisfy the mass spectral data better than the others. Furthermore, a chloroform solution of the blue solid when evaporated, gave a residue which showed an identical ir (KBr) spectrum to that of $Cu(acac)_2$ (74).

2-4 Photolysis of $Cu(acac)_2$ in the Presence of Various Ligands

The benzophenone sensitized photolysis of $Cu(acac)_2$ in the presence of different ligands did not form, in most cases, the black precipitate.

The photoreaction in the presence of triphenylphosphine in ethanol gave a colorless, clear solution from which $Cu(acac)(PPh_3)_2$ (52), 2-7 (94%), acetylacetone (80%) and acetaldehyde (42% as 2,4-DNPH) were obtained.

$$Cu(acac)_2 + 2PPh_3 \xrightarrow[Ph_2CO]{h\nu,\ ROH} \underset{\underline{2-7}}{(acac)Cu(PPh_3)_2} + acacH$$

The photolysis in the presence of ligands other than PPh_3, gave air sensitive solutions, usually colored, except when carbon monoxide or olefins were used in which cases colorless solutions were obtained. These solutions exhibited different stability toward air oxidation with visual lifetimes ranging from 10-20 sec to ~20 min on exposure to the air. For example, red solutions derived from the reactions with α,α-bipyridyl and 1,10-phenanthroline were oxidized back to the original blue $Cu(acac)_2$ solution in 15-20 min, while it took only a few seconds for the yellow solutions derived from the reactions with 2,5-dithiahexane and ethylenediamine. The colorless solutions obtained in the photolysis in the presence of carbon monoxide and olefins, such as styrene, 1,5-cyclooctadiene and norbornadiene, were oxidized within 2-3 min on exposure to the air.

Most of the solutions reacted readily with triphenylphosphine to give the stable $Cu(acac)(PPh_3)_2$. This indicates the presence of Cu(I) complexes in these solutions. The sensitized photolysis in the presence of cyclohexene or 1,3-pentadiene gave the black precipitate which indicated that copper(I) complexes were not formed with these olefins.

On continuing irradiation of the solutions of the Cu(I) complexes, metallic copper was formed with various efficiency. For example, while the red solutions of the copper(I) complexes of α,α-bipyridyl and 1,10-phenanthroline formed metallic copper only after prolonged irradiation for 15-20 h, for the reactions in the presence of carbon monoxide and ethylenediamine, metallic copper was formed almost immediately after the blue color of $Cu(acac)_2$ disappeared. In the case of styrene, copper metal was formed even while the blue color still persisted. The same was observed for the reaction in the presence of diglyme.

$$\begin{tikzcd}
Cu(acac)_2 + xL \arrow[r, "h\nu", "Ph_2CO"'] & Cu(acac)Lx + acacH \arrow[d, "h\nu"] \\
 & Cu^o + xL + acacH
\end{tikzcd}$$

By running the photolysis in the presence of ligands in 1 cm uv cells, it was possible to determine the absorption maxima of the copper(I) complexes quantitatively at the stationary state of photolysis (Table 2-3). Due to the instability of the colorless solution formed in the photolysis under carbon monoxide, attempts to take the ir spectrum of the photolysate were only rewarded with a weak absorption at ~2100 cm^{-1}. Although these spectral data did not reveal the structure of the Cu(I) complexes, they probably have molecular formulae of $Cu(acac)L_x$, where $x = 1$ or 2 depending on the ligands (bidentate or monodentate).

Table 2-3 Spectral Data of Copper(I) Acetylacetonate Complexes Derived from $Cu(acac)_2$ Photolysis in the Presence of Several Ligands.

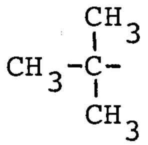
Ligand[a]	Complex	Data
bpy	Cu(acac)(bpy)	427 nm (ε ~2500) 550 nm (sh)
o-phen	Cu(acac)(o-phen)	430 nm (ε 7600) 570 nm (ε 2600)
DTH	Cu(acac)(DTH)	575 nm (ε 146)
CO	$Cu(acac)(CO)_2$	~2100 cm^{-1} (w)
PPh_3	$Cu(acac)(PPh_3)_2$	Ref (52)

[a] bpy = α,α'-bipyridyl; o-phen = 1,10-Phenanthroline; DTH = 2,5-dithiahexane.

2-5 Benzophenone Sensitized Photoreaction in the Presence of Acetylenes

The benzophenone sensitized photolysis of Cu(acac)$_2$ in methanol in the presence of 1-hexyne or phenylacetylene gave yellow precipitates of Cu(I) acetylides in good yields. From the organic layer benzophenone was recovered quantitatively and acetylacetone was obtained. The reaction in the presence of t-butylacetylene gave an orange solution from which the Cu(I) t-butylacetylide was separated, as an orange solid.

$CuC\equiv CR$

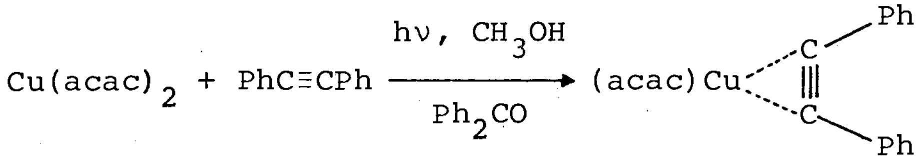
R-	% Yield	ir (cm^{-1})	mp (°C)	Ref.
Ph-	72%	1930 (w)	230° d	75,76
$CH_3(CH_2)_3$-	90%	1927 (m)	145-185° d	77
 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-$	37%	2000 (w)	82° d	78,79

As these acetylides are very insoluble and non-crystalline solids, they were identified by the coupling with iodobenzene (77) to give substituted phenylacetylenes which were easily identified by spectroscopic methods.

$$\begin{tikzcd}[column sep=small] \mathrm{Cu(acac)_2} & + & \mathrm{RC{\equiv}CH} \arrow[r, "h\nu", "\mathrm{Ph_2CO}"'] & \mathrm{CuC{\equiv}CR} \arrow[d, "\mathrm{PhI}\ \mathrm{pyr}"] & + & \mathrm{2acacH} \\ & & & \mathrm{Ph{-}C{\equiv}CR} & & \end{tikzcd}$$

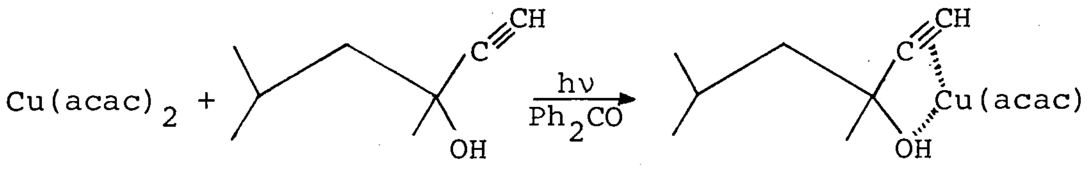
The photoreaction in the presence of 1,5-hexadiyne gave a dark orange amorphous solid of bis-acetylide 2-11 (67%). Treatment of 2-11 with iodobenzene in hot pyridine afforded crystals of 1,6-diphenyl-1,5-hexadiyne, 2-12 (44%), which was characterized by nmr and ms (80).

The sensitized photolysis in the presence of diphenylacetylene in methanol readily deposited fine white needles of Cu(acac)(PhC≡CPh), 2-13 (29%), which showed an ir band at 1975 cm^{-1} and molecular ion peak at m/e 340 (1%). On continued irradiation, a brown precipitate and a colorless solution were obtained. The crystals decomposed rapidly in solution at room temperature, even under nitrogen and could not be purified. However, the nmr of a decomposed solution in a sealed tube (in distilled $CDCl_3$) showed the methyl signal for acetylacetone at 2.02 and 2.30 ppm and the aromatic proton signal for diphenylacetylene at 7.40 ppm in a ratio of 6:10.



2-13

A similar photolysis in the presence of 3,5-dimethyl-1-hexyn-3-ol afforded a yellow-brown solution which rapidly oxidized to Cu(acac)$_2$ when exposed to the air. After the usual work-up only the unchanged starting materials were recovered. Treatment of the yellow-brown solution with triphenylphosphine under nitrogen gave the stable Cu(acac)(PPh$_3$)$_2$. This suggested the structure 2-14 for the Cu(I) complex as shown below.



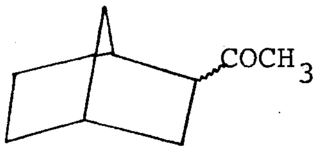
2-14

2-6 Benzophenone Sensitized Photoreaction in the Presence of Olefins

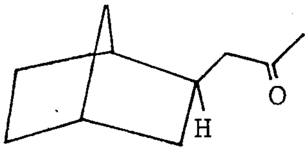
In order to investigate the formation of organic free radicals in the benzophenone sensitized photoreaction of Cu(acac)$_2$, the photolysis was carried out in the presence of olefins with no abstractable hydrogens in solvents such as acetic acid and acetonitrile.

2-6-1 Norbornene

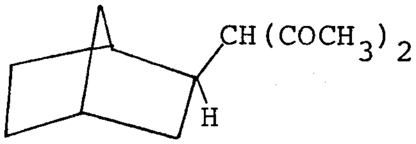
The photoreaction of Cu(acac)$_2$ in the presence of norbornene in acetic acid gave metallic copper and a yellow photolysate after 16 h of irradiation. The photolysate gave after separation by column chromatography, 2-acetylnorbornane, 2-15 (4%), 2-exo-norbornylacetone, 2-16 (11%), 3-exo-(2-norbornyl)acetylacetone, 2-17 (30%) in addition to products from the reaction of benzophenone with acetylacetone, 2-1 (19%), 2-2 (9%) and 2-3 (20%).



2-15



2-16



2-17

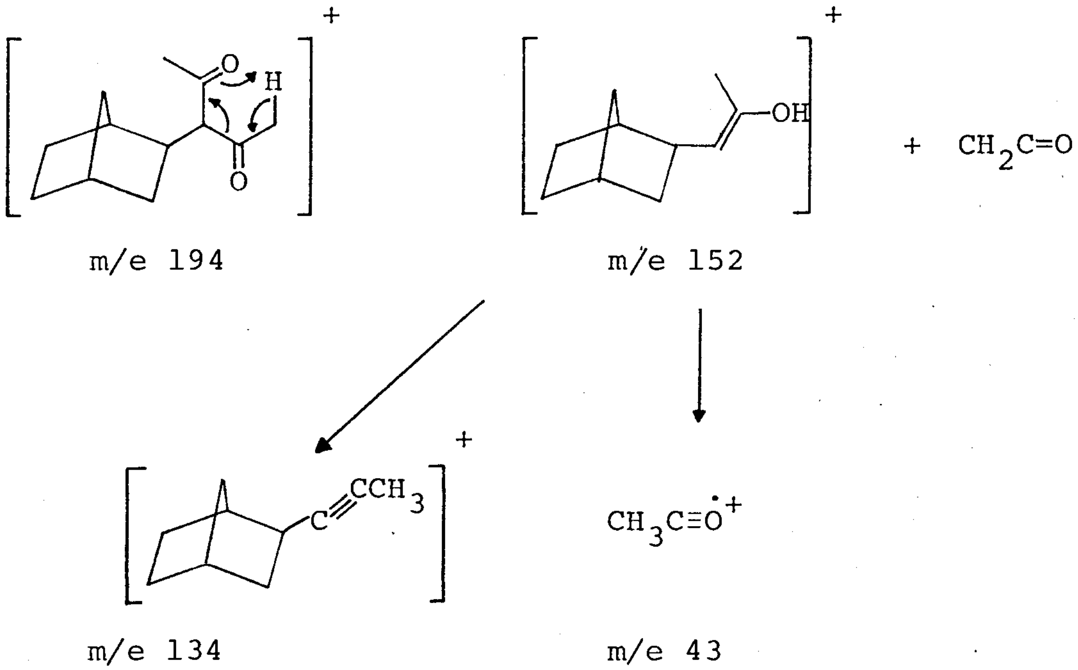
The basic hydrolysis of 2-17 afforded the ketone 2-16 quantitatively. This ketone has been prepared by photolysis of norbornene in acetone (81). The reaction gives stereospecifically the exo-compound as shown by chromic acid oxidation of 2-16 to give the 2-exo-norbornylcarboxylic acid.

The structure of 2-17 was also determined by spectroscopic methods. It was shown by elemental analysis and high resolution mass spectrum to have the molecular formula $C_{12}H_{18}O_2$. Its infrared spectrum showed bands at 2960, 2880 and 1700 (C = 0) cm^{-1}. The ^{13}C nmr spectrum showed two carbonyl singlets at 203.8 and 203.5 ppm and doublet at 76.0 for the C_3 carbon of the diketone. The 400 MHz ^1H nmr spectrum[1] also showed two non-equivalent CH_3 groups at 2.17 and 2.13 ppm. On heating up to 100°C the two methyl signals did not collapse. A doublet at 3.46 ppm (J = 11.0 Hz) was assigned to the methine proton of the diketone moiety. Decoupling experiments indicated that the β-diketonyl group must be attached to the C_2 carbon. On irradiation of the doublet at 3.46 the multiplet at 2.32 for the C_2-proton was modified to a double doublet (J = 8.2 and 5.4 Hz). The doublet at 3.46 collapsed to a singlet upon irradiation of the signal at 2.32. The

---

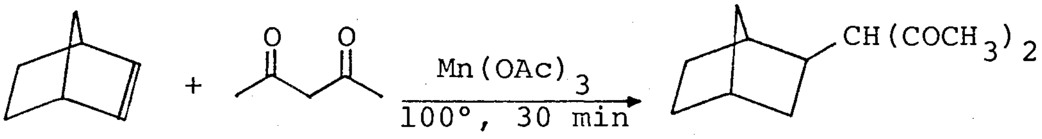
[1] We are grateful to Dr. W. Ayer from the University of Alberta for the 400 MHz ^1H nmr spectrum.

large coupling constant for the C_2-proton obviously showed its endo-orientation (82); therefore, the acetylacetonyl group must have an exo-orientation. The absence of exchangeable protons indicated that the diketone exists mainly in the keto form. It is known that 3-alkyl substituted β-diketones normally show a low enol content (83). The mass spectrum for 2-17 exhibited a molecular ion peak at m/e 194 and mass peaks that might be derived from a fragmentation pattern as shown in Scheme 2-2.



Scheme 2-2

The diketone 2-17 was also obtained by oxidative addition of acetylacetone to norbornene in the presence of manganese triacetate in acetic acid.

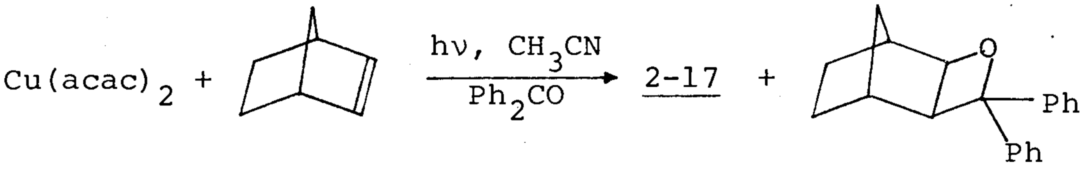


2-17

This reaction has been proposed to involve the generation of the acetylacetonyl radical by Mn(III) oxidation and the subsequent addition of the radical to olefins (84-87).

A similar photolysis of $Cu(acac)_2$ in the presence of norbornene in acetonitrile afforded norbornene, diketone 2-17 (17%) and oxetane 2-18 (88) without acetylacetone adducts 2-1, 2-2 and 2-3.

The reaction after 28 h of irradiation showed small amounts of metallic copper while the original blue color of the solution still persisted.

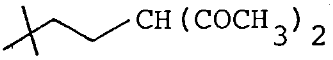


2-18

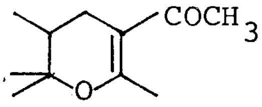
A photolysis in acetonitrile under similar conditions, but in the presence of an excess of acetylacetone gave 2-17 in 14% yield. Benzhydrol (<5%), 2-1 (16%), 2-2 (6%), 2-3 (32%) and 2-18 (18%) were also obtained.

2-6-2 Neo-hexene

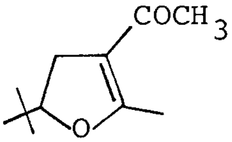
The photolysis of an acetic acid solution of Cu(acac)$_2$, benzophenone and neo-hexene under nitrogen gave after 12 h metallic copper and a yellow solution. The photolysate afforded 3-acetyl-6,6-dimethyl-2-heptanone, 2-19 (35%), 3-acetyl-2,5,6,6-tetramethyldihydropyran, 2-20 (11%) and a mixture of two compounds tentatively identified as 2-21 and 2-22 (~30%).



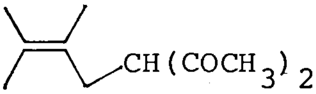
2-19



2-20

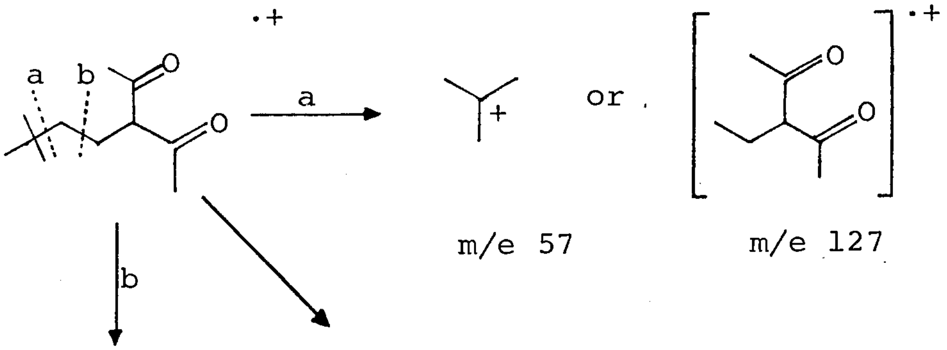


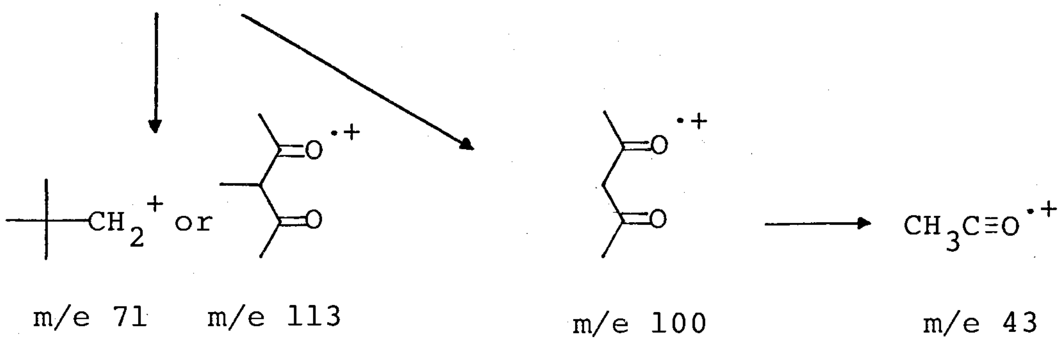
2-21



2-22

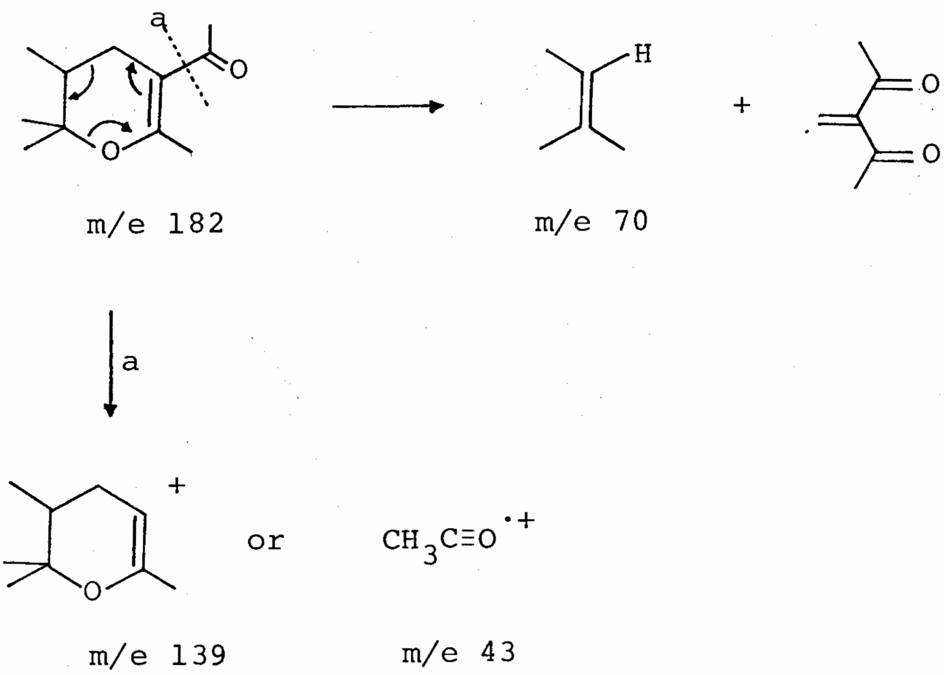
The structure of 2-19 was determined by spectroscopic methods. Its infrared spectrum showed absorptions at 1730, 1703 and 1600 cm^{-1} indicative of the keto and enol forms of a β-diketone (89). The ^1H nmr spectrum showed an enolic signal at 16.47 ppm, the methine proton at 3.54(t,J=6.5 Hz) and two methyl signals at 2.17 (keto) and 2.12 (enol) as well as two t-butyl groups at 0.96 and 0.90. The enol content was determined by ^1H nmr to be 22% in $CDCl_3$ solution. The ^{13}C nmr spectrum showed two lines at 205.1 (C = 0, keto) and 191.3 (CO, enol) as well as two lines for the C_3 carbon, at 111.0 (singlet, enol) and 70.2 (doublet, keto). Its mass spectrum exhibited a molecular ion peak at m/e 184. A fragmentation pattern to explain the other mass peaks is proposed below (Scheme 2-3).





Scheme 2-3

The infrared spectrum of compound 2-20 showed a strong absorption band at 1670 cm^{-1}, characteristic of an α,β-unsaturated ketone. Its ^{13}C nmr spectrum showed a carbonyl signal at 199.5, which is lower than values normally observed in saturated ketones (90). In conjugated systems, the α,β-double bonds shift the ketone carbonyl absorption upfield by ~ 5 to 7 ppm (91). Two lines at 164.1(s) and 109.3(s) were assigned to the C_2 and C_3 carbons by comparison with the ^{13}C spectrum of unsubstituted dihydropyran (C_2: 144.9, C_3: 100.5) (92). The observed shifts to lower fields for 2-20 are those expected upon introduction of a methyl group at the α-position and of an acetyl group at the β-position (92). The mass spectrum exhibited a molecular ion peak at m/e 182 in addition to major peaks at m/e 139, 70 and 43 (Scheme 2-4).



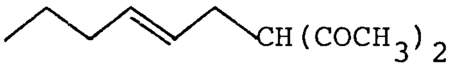
Scheme 2-4

Several attempts to separate 2-21 and 2-22 were unsuccessful. Their structures were suggested based on ir, ms (gc-ms) and ^1H nmr of the mixture. The infrared spectrum showed absorption bands for a diketone at 1720 cm^{-1} (C = 0), a C=C double bond stretching at 1605 cm^{-1} (enol) and an α,β-unsaturated ketone and/or a trisubstituted double bond at 1675 cm^{-1}. The ^1H nmr spectrum showed an enolic proton at δ 16.41 as well as a triplet at δ 4.23(J=10 Hz) assigned to the C_5 proton of 2-21, but no olefinic proton signals. The mass spectrum of both compounds (gc-ms) exhibited a molecular ion peak at m/e 182. The base peak at m/e 125 for 2-21 can be explained by the loss of t-butyl group (-57). This fragmentation is not observed in the mass spectrum of 2-22 suggesting that the t-butyl group has undergone rearrangement. A possible mechanism is discussed in Chapter 3.

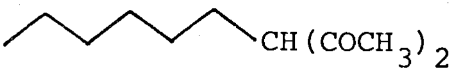
The reaction in CH_3CN in the presence of acetylacetone. afforded neohexene, diketone 2-19, pyran 2-20 and the corresponding oxetane. The acetylacetone adducts 2-1 and 2-3 were obtained in a 2 : 1 ratio.

2-6-3 1-Hexene

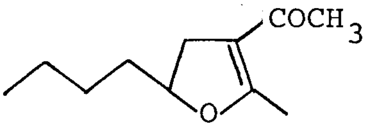
The photolysis of $Cu(acac)_2$ in the presence of 1-hexene in acetic acid gave after 3 h of irradiation metallic copper and a yellow solution. Column chromatography of the photolysate followed by preparative vpc afforded a mixture of 3-acetyl-5-nonen-2-one, 2-23 (4%) and 3-acetyl-2-nonanone, 2-24 (16%), and 3-acetyl-5-(n-butyl)-2-methyldihydrofuran, 2-25 (12%), in addition to small amounts of the benzophenone adducts to acetylacetone, 2-1, 2-2 and 2-3.



2-23



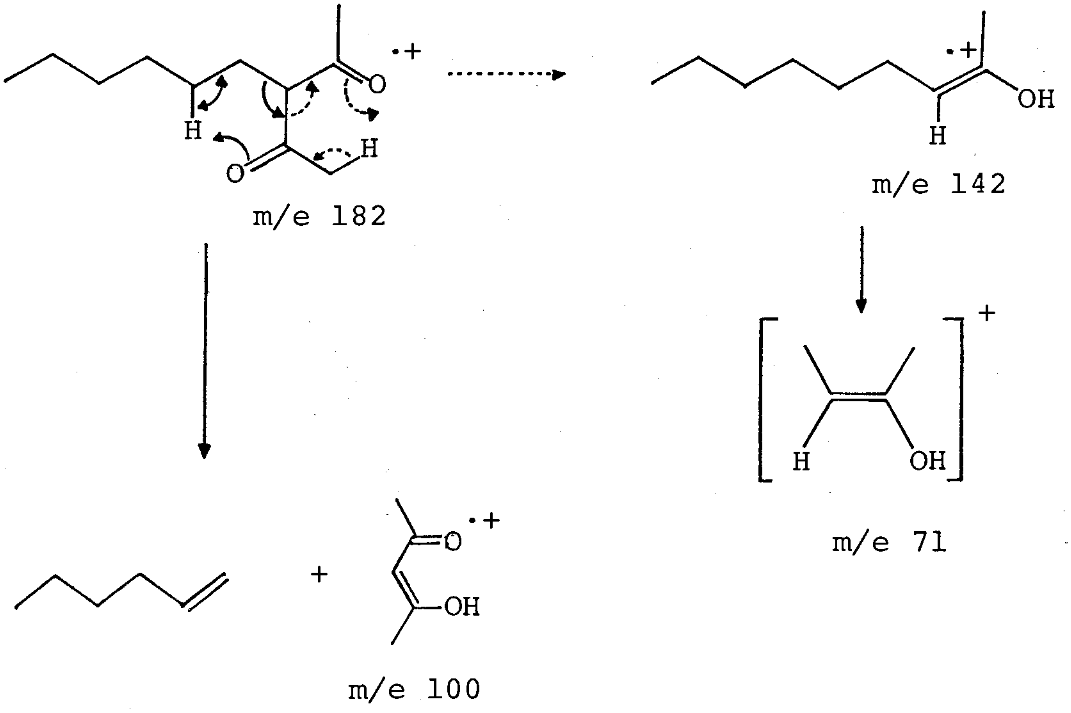
2-24



2-25

The infrared spectrum for the mixture of 2-23 and 2-24 showed absorption bands at 1728, 1680 and 1610, typical for an acetylacetone group (89), and 969(CH=CH) cm^{-1}. The ^1H nmr spectrum indicated the presence of an enolic proton (δ 16.62) and olefinic protons (δ ~5.4). Also observed in the spectrum were two distinct triplets at δ 3.70(J=7.2 Hz) and δ 3.63(J=7.5 Hz) assigned to the C_3 hydrogens. The ^{13}C nmr spectrum exhibited two carbonyl signals at 205.0 and 204.5 ppm. The presence of a CH=CH group was indicated by the two doublets at 134.3 and 126.0 ppm.

Two doublets at 69.5 and 69.2 were assigned to the α-carbons to the carbonyls. The mass spectrum (gc-ms) for 2-24 showed a molecular ion peak at m/e 184 with major mass peaks at m/e 142, 100, 85, 71 and 43 (Scheme 2-5).



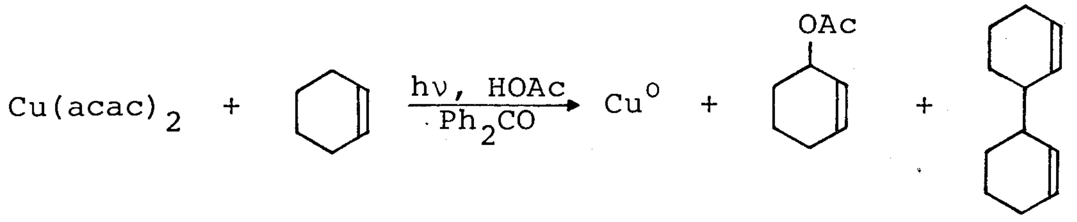
Scheme 2-5

The mass spectrum of 2-25 exhibited a molecular ion at m/e 182, which coupled with elemental analysis was in agreement with a molecular formula of $C_{11}H_{18}O_2$. Its infrared spectrum showed absorption bands at 1670 and 1602 for an α,β-unsaturated ketone. The ^1H nmr spectrum showed a multiplet at δ 4.62 for the C_5 proton. The methyl signals appeared at δ 2.18, while the C_4 protons appeared as a multiplet at δ 2.6-3.1. In the ^{13}C nmr spectrum the carbonyl peak appeared at 195.1 which indicated conjugation with a double bond (90). The signals at 168.5(s) and 112.5(s) for the C_2 and C_3 carbons, respectively, are in agreement with typical carbon resonances for substituted dihydrofurans (93).

The photoreaction in acetonitrile afforded after 14 h of irradiation a yellow-green solution and traces of metallic copper. Vpc and gc-ms analyses indicated the presence of 2-24 and small amounts of an oxetane (94).

2-6-4 Cyclohexene

The photolysis of Cu(acac)$_2$ in the presence of cyclohexene in acetic acid gave metallic copper after 4 h of irradiation. Vpc and gc-ms analyses indicated the formation of Δ'-cyclohexenyl-3-acetate, 2-26 (58%), showing a molecular ion peak at m/e 140 and a base peak at m/e 79, and bicyclohexenyl, 2-27 (8%). An authentic sample of 2-26 was synthesized by acetoxylation of cyclohexene with mercuric acetate (95,96).



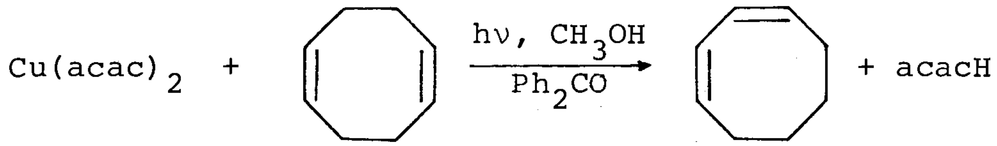
2-26 2-27

The photoreaction in acetonitrile afforded metallic copper after 2 h of irradiation. Vpc and gc-ms analyses showed the formation of 2-27 (~12%) and the oxetane (~25%) derived from benzophenone and cyclohexene (163).

2-7 Benzophenone Sensitized Photoreaction in the Presence of Polyenes

2-7-1 1,5-Cyclooctadiene (1,5-COD)

The sensitized photolysis of $Cu(acac)_2$ in methanol in the presence of 1,5-cyclooctadiene was carried out to give after 16 h a colorless solution which turned blue in a few seconds on exposure to the air. Further irradiation caused the formation of metallic copper. Chromatography on silica gel afforded 1,5-COD and 1,3-COD in a 46 : 54 ratio in addition to acetylacetone and traces of oxetane 2-28 as shown by gc-ms.

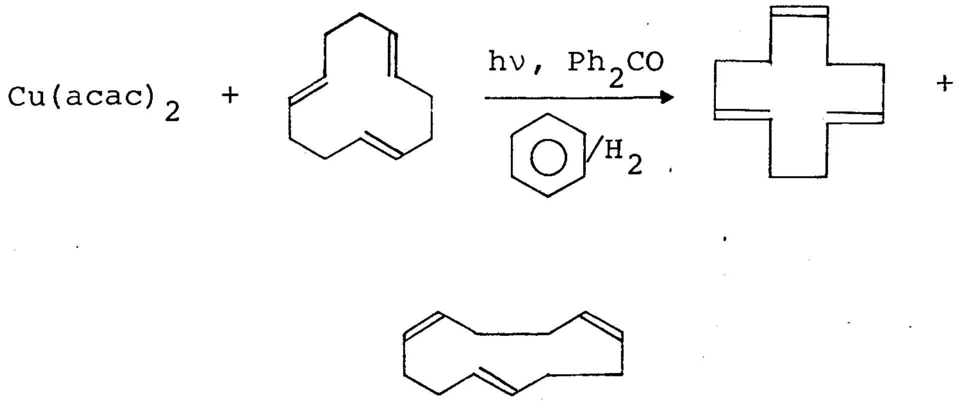


The two isomers were identified by nmr and mixed injection with authentic samples on vpc. The ^1H nmr spectrum showed signal at δ 1.50(CH_2-CH_2), 2.25(CH_2C=CCH_2) and 5.77(olefinic protons) for 1,5-COD (97) and at 2.38(CH_2) and 5.58(olefinic protons) for 1,3-COD (98). The photolysate from this reaction was also left under nitrogen for 48 h and no change was observed in the % yield of the isomers as shown by vpc.

A photolysis of benzophenone and 1,5-COD under similar conditions afforded, after 10 h, benzhydrol (25%) and oxetane 2-28 (~39%) (99) in addition to small amounts of unidentified products. However, no isomerization of the 1,5-diene was observed.

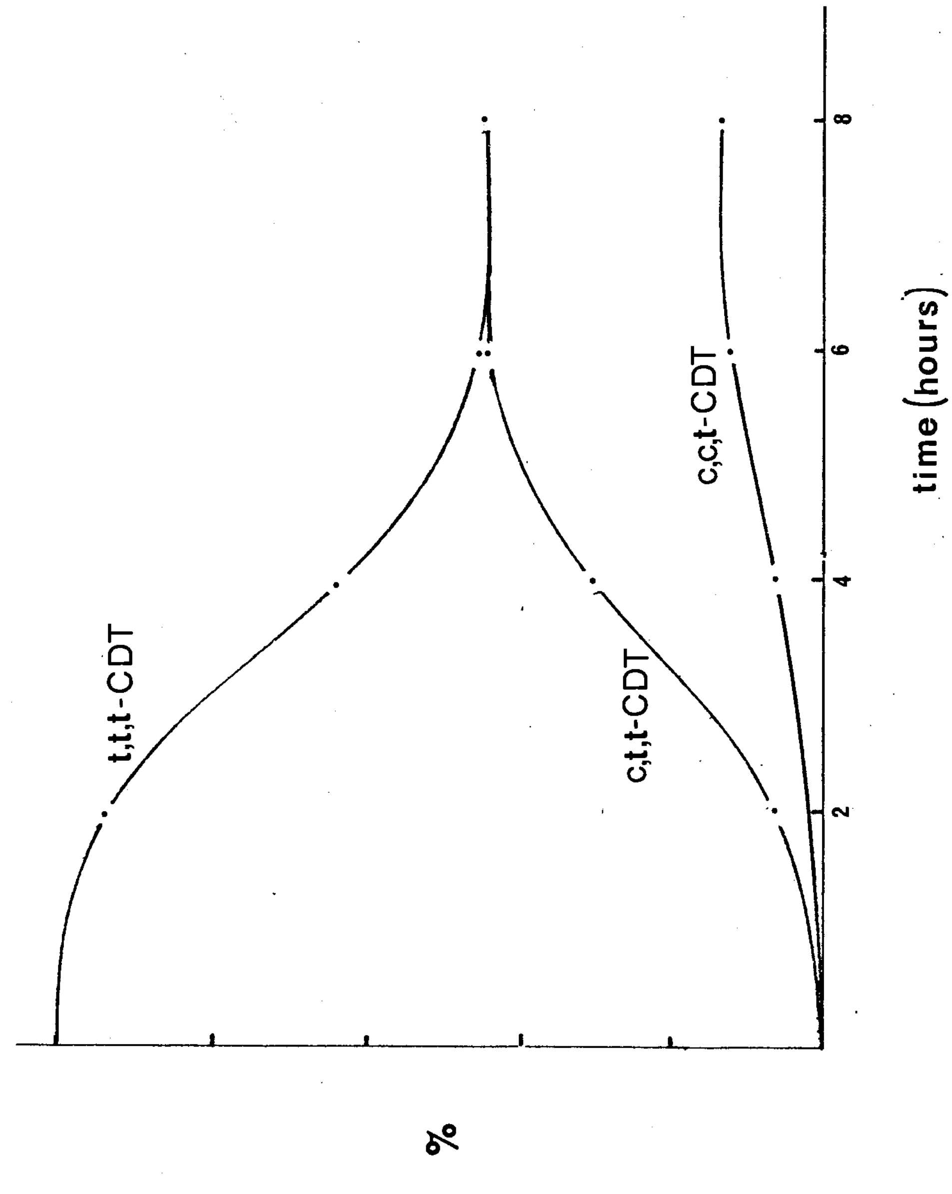
2-7-2 t,t,t-1,5,9-Cyclododecatriene (t,t,t-CDT) and c,t,t-CDT

The photoreaction of Cu(acac)$_2$ in the presence of t,t,t-CDT in benzene under hydrogen was carried out to give after 8 h a yellow solution which turned blue in a few seconds on exposure to air. The gc analysis (gc-ms) indicated the formation of cis,trans,trans-CDT (~45%) and another isomer which was assumed to be cis,cis,trans-CDT (~12%) as it is known that c,c,t-CDT has a longer gc retention time than the other two isomers (100).



The progress of the reaction was also monitored by gc analysis and the relative yields of isomerization determined to give the following results (Fig. 2-3).

Figure 2-3 Variation of t,t,t-CDT during photolysis.


%
t,t,t-CDT
c,t,t-CDT
c,c,t-CDT
2
4
6
8
time (hours)

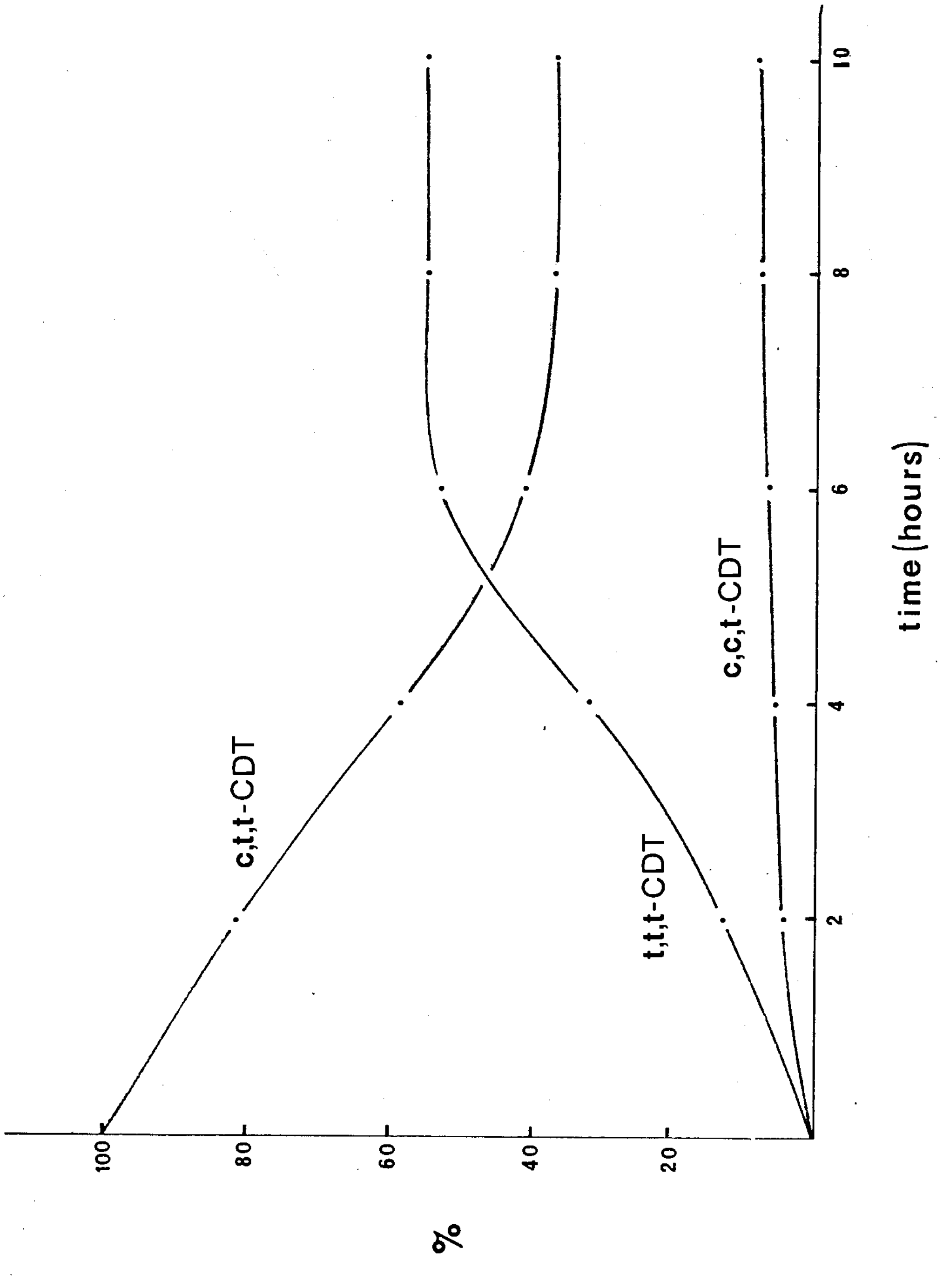
time (h)	t,t,t	c,t,t	c,c,t
0	100%	0%	0%
2	94.1%	5.9%	0%
4	64.2%	29.8%	6.0%
6	44.8%	43.5%	11.7%
8	44.5%	43.5%	11.9%

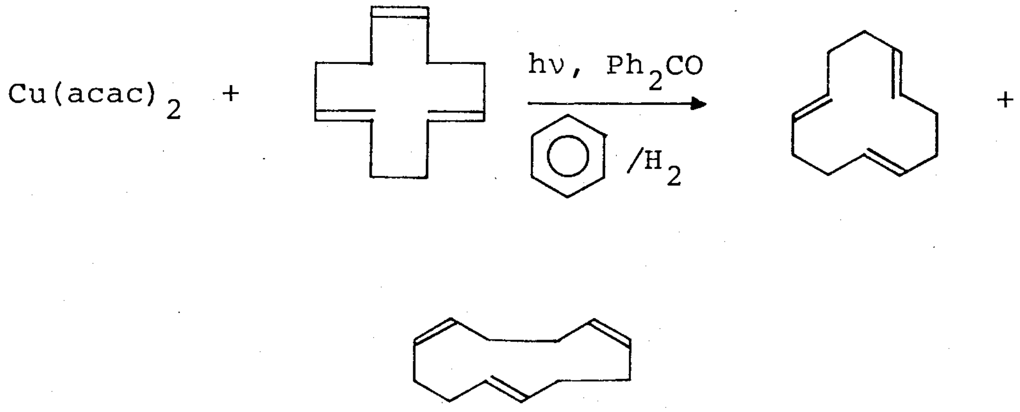
The isomerization of t,t,t-CDT was shown to reach a photostationary state in 6-8 h. The photolysate was also left under hydrogen in the dark for 24 h but no change was observed in the ratio of isomers.

A similar photolysis in acetonitrile under hydrogen for 8 h afforded only 4% of c,t,t-CDT. No photoreduction of Cu(acac)$_2$ seemed to have occurred as indicated by the blue-green color of the photolysate. The photolysis in methanol under nitrogen gave metallic copper after 1 h of irradiation but no isomerization. When a solution of benzophenone and t,t,t-CDT in benzene under hydrogen was irradiated for 6 h, 10% isomerization to c,t,t-CDT was observed (100).

The photolysis of Cu(acac)$_2$ in the presence of c,t,t-CDT in benzene under hydrogen gave a yellow solution after 10 h. Vpc analysis of the photolysate indicated the formation of t,t,t-CDT (~56%) and c,c,t-CDT (~8%).

Figure 2-4 Variation of c,t,t-CDT during photolysis.


%
100
80
60
40
20
c,t,t-CDT
t,t,t-CDT
c,c,t-CDT
2
4
6
8
10
time (hours)



The progress of the reaction was also monitored every 2 h by vpc to give the following results (Fig. 2-4).

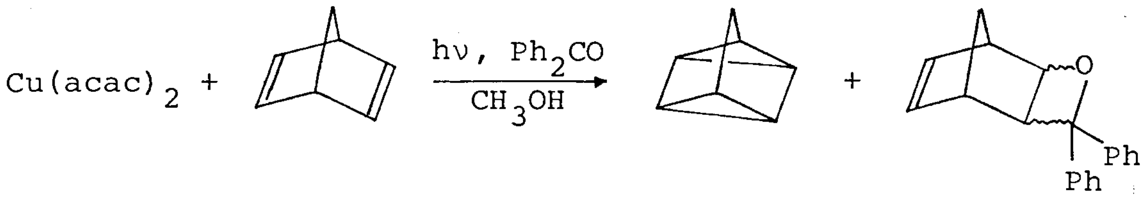
time (h)	t,t,t	c,t,t	c,c,t
0	0%	100%	0%
2	13.7%	81.6%	4.8%
4	32.0%	59.2%	5.3%
6	52.7%	41.4%	5.9%
8	55.3%	37.1%	7.6%
10	55.6%	36.7%	7.6%

A photostationary state was reached after 8-10 h of irradiation, and did not change when the photolysate was left under hydrogen in the dark for 24 h.

A similar photolysis in methanol under nitrogen did not show any isomerization products. Metallic copper and acetylacetone were formed and the triene was recovered unchanged. The photolysis of c,t,t-CDT in the presence of benzophenone in benzene under hydrogen showed 12% isomerization to t,t,t-CDT (100) after 10 h of irradiation.

2-7-3 Norbornadiene

The photoreaction of $Cu(acac)_2$ in the presence of norbornadiene in methanol under nitrogen gave a yellow solution which turned blue in seconds on exposure to air, or gave metallic copper and $Cu(acac)_2$ when left under nitrogen for 48 h. Preparative vpc afforded quadricyclene (101) and oxetanes (~20%) as shown by nmr and gc-ms.



The progress of the reaction was also followed by vpc analysis and the relative yields of norbornadiene (NBD) and quadricyclene (QC) determined from peak areas to give the following results.

t (min)	NBD	QC	
0	100%	0%	
90	83.1%	16.9%	
180	73.1%	26.9%	
300	72.3%	27.7%	
390	62.3%	37.7%	
24 h	68.9%	31.1%	in the dark
48 h	76.2%	23.8%	

The isomerization of NBD was shown to reach a photostationary state in ~6.5 h. The photolysate was also left under nitrogen in the dark for 48 h to show a decrease in the relative yield of QC.

The photolysis of NBD in the presence of benzophenone in methanol under nitrogen was carried out and the progress of the NBD→QC isomerization monitored as above to give the following results.

t (min)	NBD	QC
0	100%	0%
15	91%	9%
30	88.1%	11.9%
90	68.5%	31.5%
180	54.9%	45.1%
300	45.4%	54.6%
390	51%	49%

A photostationary state was reached in about 3 h. It is known that NBD and QC undergo photointerconversion in the presence of certain aromatic ketones triplet sensitizers (103-105).

2-8 Quantum Yield Determinations

2-8-1 Quantum yields of $Cu(acac)_2$ disappearance

a) benzophenone sensitization

Taking advantage of the thermal as well as photostability of $Cu(acac)(PPh_3)_2$, the quantum yields of $Cu(acac)_2$ disappearance (Φ_C) and that of benzophenone disappearance (Φ_B) were determined in the presence of triphenylphosphine. This allowed the photolysate to be analyzed spectroscopically at 630 nm for $Cu(acac)_2$ and/or by gas and liquid chromatography for benzophenone, without the interference of the black precipitate formed in the absence of triphenylphosphine.

Quantum yields were determined in methanol solutions (unless otherwise specified) containing proper concentrations of materials on a merry-go-round apparatus. The light intensity (I_o) was determined by the benzophenone (0.05 M)-benzhydrol (0.1 M) actinometer in benzene for which a quantum yield of 0.74 has been assumed (106).

Corrections for the light absorbed by $Cu(acac)_2$ at 330 nm (ε 330~600) were made using the following equation:

$$I_a = I_o \frac{A^S_{330}}{A^Q_{330} + A^S_{330}} \quad \text{Einstein } l^{-1}t^{-1} \qquad (2\text{-}1)$$

where: I_a = light intensity absorbed by sensitizer.

I_o = light intensity determined from actinometer.

A^S_{330} = optical density of sensitizer at λ 330 nm.

A^Q_{330} = optical density of $Cu(acac)_2$ at λ 330 nm.

The quantum yield of Cu(acac)$_2$ disappearance, Φ_C, in methanol in the presence of benzophenone and PPh$_3$ was determined at various concentrations of Cu(acac)$_2$ (Table 2-4). The quantum yield (Φ_C) was shown to increase steadily with Cu(acac)$_2$ concentration (0.6-6.0 X 10^{-3} M range) to reach a nearly constant value of ~0.25 at 10^{-2} M. The quantum yields of Cu(acac)$_2$ disappearance, Φ_C, under comparable conditions, in methanol, ethanol and isopropanol were found to increase in the same order, indicating that Φ_C increased as the hydrogen donating power of the solvent increased (Table 2-5).

b) <u>other sensitizers</u>

In order to evaluate the nature of the quenching of triplet sensitizers by Cu(acac)$_2$ the quantum yields of Cu(acac)$_2$ disappearance were determined in the presence of several sensitizers (Table 2-6). For these experiments the concentrations of the sensitizers were adjusted so that >98% of the incident light was absorbed by the sensitizers. Biacetyl was an exception in which absorbed only 68% of the light. In this case the Cu(acac)$_2$ disappearance was determined by normalizing the light absorbed to 100% according to Equation 2-1, and Φ was calculated accordingly.

Table 2-4 Quantum Yields of $Cu(acac)_2$ Disappearance Sensitized by Benzophenone in Methanol (at 20°C)[a].

$[Cu(acac)_2] \times 10^3$ M	Φ_C[b]	$1/[Cu(acac)_2]$	$1/\Phi_C$
0.6	0.09	1670	10.8
0.8	0.11	1250	8.80
1.0	0.14	1000	6.40
2.0	0.17	500	5.90
4.0	0.18	250	5.70
6.0	0.23	167	4.35
8.0	0.23	125	4.35
10.0	0.25	100	3.97

[a] Solutions were irradiated for 5-30 min to cause 10-18% decomposition of $Cu(acac)_2$. The concentration of benzophenone and triphenylphosphine were 0.04 M and 0.01 M, respectively.

[b] Estimated error = ± ~20%.

Table 2-5 Quantum Yields of $Cu(acac)_2$ (2×10^{-3} M) Disappearance Sensitized by Benzophenone (0.1 M) in Alcohols[a,c].

solvent	I (einsteins)	Φ_{av}[b]
methanol	1.89×10^{-5}	0.23
ethanol	9.20×10^{-6}	0.40
isopropanol	9.15×10^{-6}	0.52

[a] Concentration of PPh_3 was 4×10^{-3} M.

[b] Averaged values from three sets of experiments. Error was estimated to be ± 10%.

[c] Solutions were irradiated for 10 min to cause 30-50% decomposition of $Cu(acac)_2$.

Table 2-6 Quantum Yields of $Cu(acac)_2$ Disappearance in the Presence of Various Sensitizers in CH_3OH[a].

	Sensitizer	Concentration (M)	E_T (kcal/mol)[b]	Φ_C[c]
1.	Anthrone	0.1	72.0	0.29[d]
2.	Benzophenone	0.1	68.5	0.23[d]
3.	Xanthone	0.1	74.0	0.16
4.	Benzil	0.1	54.3	0.067
5.	Acetophenone	1.0	74.1	0.057
6.	Biacetyl	0.5	54.9	0.023
7.	2-Acetonaphthone	0.1	59.3	0.013
8.	Fluorenone	0.1	55.3	0.00

---

[a] Concentration of $Cu(acac)_2$ was 2×10^{-3} M and that of PPh_3 4×10^{-3} M.

[b] Triplet energies quoted from Ref. 64.

[c] Values from one set of experiments. Estimated errors = 10-15%.

[d] Due to high % conversion (50-70%) error could be as large as ± 50%.

2-9 Quenching Rate Constants (k_q) Determinations

2-9-1 Quenching of triplet benzophenone by PPh_3 in methanol

In order to determine quantitatively the contribution of triphenylphosphine to the quenching of benzophenone triplet state, the quantum yields of benzophenone disappearance (Φ_B) were determined in the presence of various concentrations of PPh_3 in methanol (Table 2-7).

A Stern-Volmer plot of Φ^o_B/Φ_B against PPh_3 concentration (Fig. 2-5) gave a straight line with a slope of 92.93 M^{-1} (correlation coefficient = 0.9917) calculated by the least-squares method. The quenching rate constant (k_b) was then calculated by the equation:

$$\frac{\Phi_B{}^o}{\Phi_B} = 1 + k_b\ \tau_o\ [PPh_3] \qquad 2\text{-}2$$

where Φ^o_B = quantum yield of Ph_2CO disappearance in the absence of PPh_3.

Φ_B = quantum yield of Ph_2CO disappearance at different concentrations of PPh_3.

τ_o = lifetime of triplet benzophenone in CH_3OH.

The decay rate constant of benzophenone triplet state (k_d) in methanol has been measured by flash photolysis to be 3.8×10^6 sec^{-1} (or $\tau_o = 2.6 \times 10^{-7}$ sec) (107). Using this value, k_b for the quenching of triplet benzophenone by PPh_3

Table 2-7 Quenching of Triplet State Benzophenone[a] by Triphenylphosphine in Methanol (at 20°C)[b].

$[PPh_3] \times 10^3$ M	Φ_B[c]	Φ^o_B/Φ_B	τ_B ($\times 10^7$ sec)
0.0	0.79	1.00	2.6
2.5	0.79	1.00	2.12
5.0	0.65	1.21	1.79
7.5	0.59	1.35	1.54
10.0	0.50	1.59	1.36
15.0	0.34	2.34	1.10
20.0	0.27	2.95	0.92
25.0	0.25	3.15	0.79
30.0	0.22	3.56	0.70
35.0	0.20	4.00	0.62

[a] Concentration of Ph_2CO was 0.05 M.

[b] Solutions (4 ml) were irradiated for 55 min; % conversion of Ph_2CO ranged from 8 to 35%.

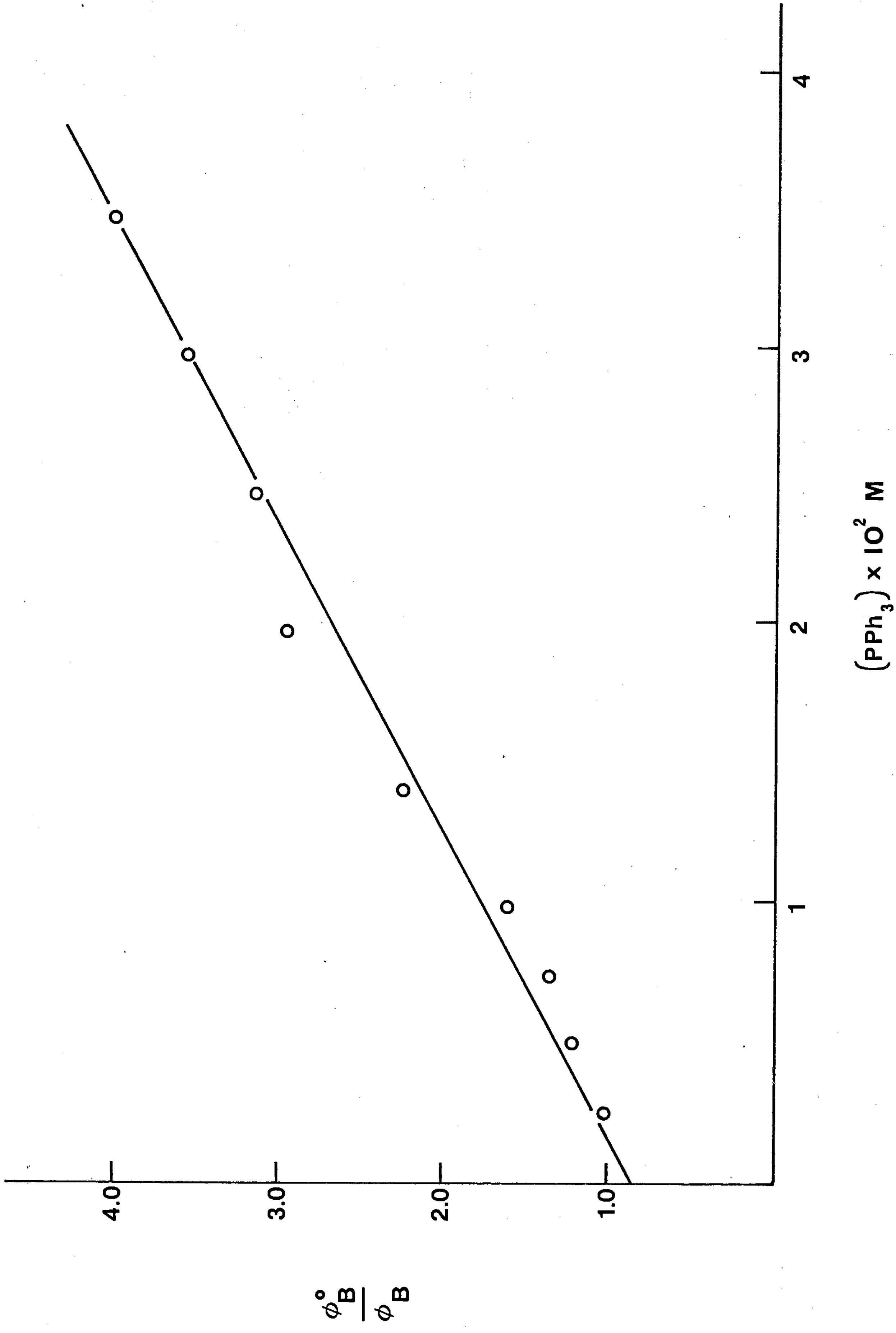
[c] Average values from two sets of experiments. Estimated error = ± 12%.

Figure 2-5 Stern-Volmer Plot of Φ^{0}_{B}/Φ_{B} versus $[PPh_3]$ for Quenching of Triplet Benzophenone by PPh_3 in Methanol.

slope = $92.93\ M^{-1}$

corr. coeff. = 0.9917

k_b = $(3.5 \pm 0.4) \times 10^{8}\ M^{-1}\ S^{-1}$



ϕ°_B / ϕ_B
1.0
2.0
3.0
4.0
1
2
3
4
$(PPh_3) \times 10^2$ M

was calculated to be 3.5 × 10^8 M^{-1} sec^{-1}. This k_b value was used to calculate the lifetime of triplet benzophenone (τ_B) in methanol at different concentrations of triphenylphosphine (Table 2-7) by the equation

$$\frac{1}{\tau_B} = \frac{1}{\tau_o} + k_b\ [PPh_3] \qquad \underline{2\text{-}3}$$

2-9-2 Quenching of triplet benzophenone by $Cu(acac)_2$ in methanol

The efficiency of quenching of triplet benzophenone by $Cu(acac)_2$ in methanol was evaluated by measuring the quantum yields of benzophenone disappearance, Φ_B, at different concentrations of $Cu(acac)_2$ in the presence of triphenylphosphine (Table 2-8). A Stern-Volmer plot of $\Phi_B{}^o/\Phi_B$ against concentration of $Cu(acac)_2$ (Fig. 2-6) gave a straight line with a slope of 9.65 × 10^2 M^{-1} (correlation coefficient = 0.9854). The rate constant for quenching of triplet state benzophenone (k_q) was then calculated to be (6.89 ± 1.0) x 10^9 M^{-1} s^{-1} according to equation

$$\frac{\Phi_B{}^o}{\Phi_B} = 1 + k_q\ \tau_B\ [Cu(acac)_2] \qquad 2\text{-}4$$

where $\Phi_B{}^o$ = Quantum yield of Ph_2CO disappearance in the absence of $Cu(acac)_2$.

Φ_B = Quantum yield of Ph_2CO disappearance at different concentrations of $Cu(acac)_2$

Table 2-8 Quenching of Triplet State Benzophenone[a] by $Cu(acac)_2$ in Methanol (at 21°C)[b]

$[Cu(acac)_2] \times 10^3$ M	Φ_B[d]	Φ_B^o/Φ_B
10	0.110	9.91
6	0.144	7.71
5	0.201	5.52
2	0.418	2.66
1	0.418	2.66
0.8	0.729	1.52
0.5	1.07	1.04
0.0	1.11[c]	1.00

[a] Concentration of benzophenone was 0.05 M and that of PPh_3 was 0.01 M.

[b] Solutions (5 ml) were irradiated for 15 min. Benzophenone decomposition ranged from 3 to 9%.

[c] This value was taken as Φ_B^o for Stern-Volmer calculations.

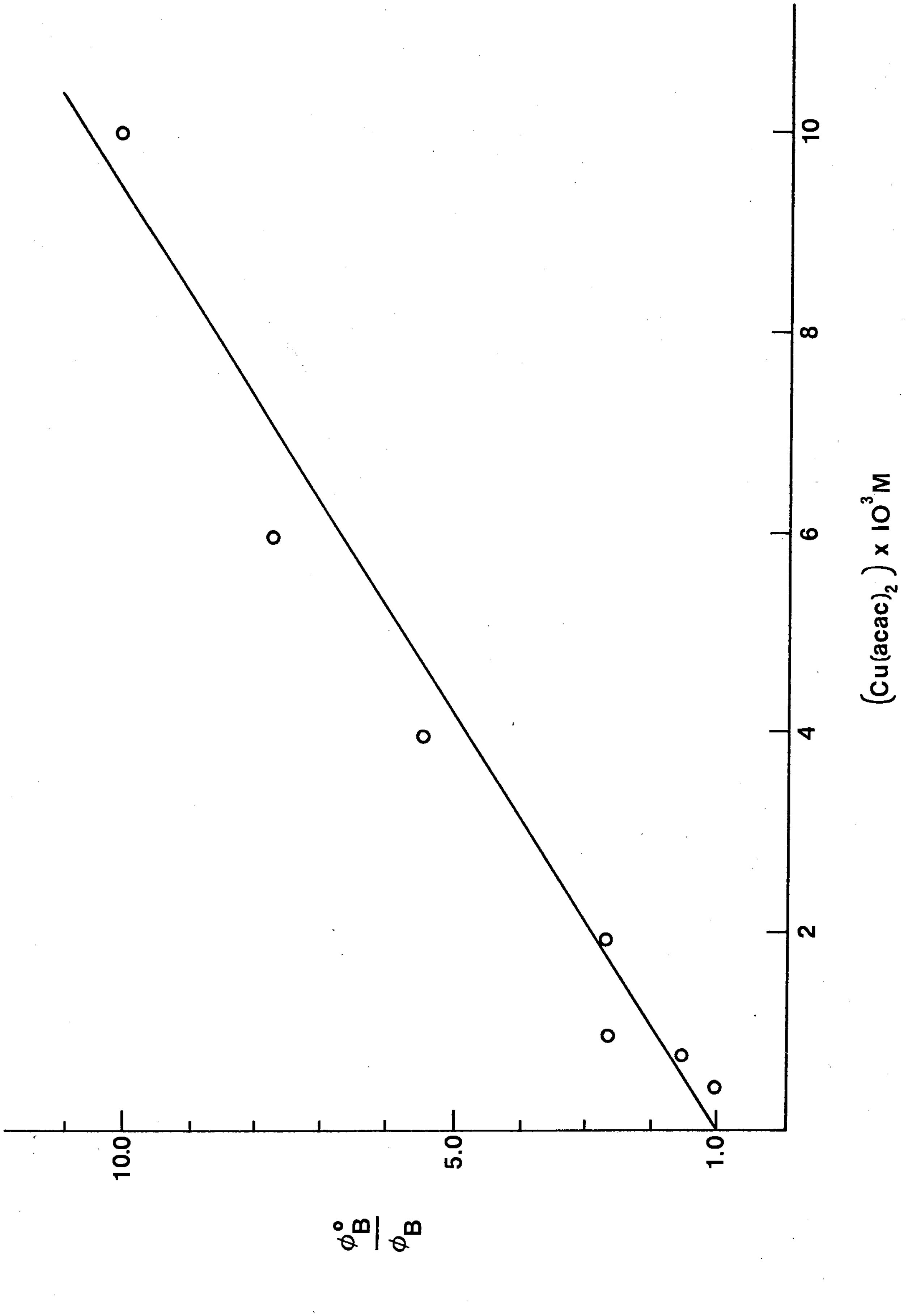
[d] Average values from two sets of experiments. Estimated error = 15%.

Figure 2-6 Stern-Volmer Plot of Φ^{o}_{B}/Φ_{B} versus $[Cu(acac)_2]$ for Quenching of Triplet Benzophenone by $Cu(acac)_2$ in Methanol.

slope = 9.65×10^{2} M^{-1}

corr. coeff. = 0.9854

k_q = $(6.89 \pm 1.0) \times 10^{9}$ M^{-1} s^{-1}


$\frac{\phi_B^\circ}{\phi_B}$
10.0
5.0
1.0
2
4
6
8
10
$(Cu(acac)_2) \times IO^3 M$

τ_B = Lifetime of triplet Ph_2CO in the presence of 0.01 M PPh_3 (1.36 x 10^{-7} s) (Table 2-7).

2-9-3 Flash photolysis studies

These studies were carried out by Miss Carol Beddard at N.R.C. in Ottawa.

Taking advantage of the fact that the triplet state absorption spectra of several compounds are well known, the rate constants for the quenching of triplet sensitizers by $Cu(acac)_2$ in methanol could be determined directly without being encumbered by the presence of triphenylphosphine or any follow-up reactions.

By using a nitrogen laser pulsed flash photolysis apparatus (337.1 nm, 8 nsec,10 mJ), the lifetimes of the triplet state decay of the sensitizers were measured in the absence ($\tau_o = 1/k_o$) and in the presence ($\tau_{exptl} = 1/k_{exptl}$) of various concentrations of $Cu(acac)_2$ (10^{-3} - 10^{-5} M) (Table 2-9). The concentration of the sensitizers as well as the monitoring wavelength are given in the table. In each case, the decays of the triplet signals were analysed by fitting of the corresponding time profiles from which the pseudo-first order decay patterns were ascertained and their rate constants, k_{exptl}, determined. The quenching rate constants were obtained from plots of pseudo-first order rate constant for triplet

Table 2-9 Quenching Rate Constants of Triplet Sensitizers by $Cu(acac)_2$ in Methanol as Determined by Flash Photolysis

No.	Sensitizers (λ^a)	Concentration[b]	E_T[c]	E_{A/A^-}[d]	$-E_T-E_{(A/A^-)}$	$k_q \times 10^{-9}$ M^{-1} s^{-1}
1	Anthrone (435)	0.001	72.0	-18.6	-53.4	-[e]
2	Benzophenone (535)	0.008	69.1	-31.3	-37.8	3.6
3	Xanthone (610)	0.005	74.2	-26.9	-47.3	5.6
4	Benzil (480)	0.005	53.7	-27.6	-26.1	0.95
5	2-Acetonaphthone (430)	0.019	59.3	-33.1	-26.2	1.86
6	Fluorenone (-)	0.015	53.3	-18.2	-35.1	-[f]
7	Propiophenone (365)	0.04	74.6	-35.9	-38.7	7.6
8	p-MeO Acetophenone (390)	0.05	71.7	-39.1	-32.6	5.4
9	Duroquinone (430)	0.002	53.0	-19.3[g]	-33.7	3.8

Table 2-9 (Cont'd)

No.	Sensitizers (λ^a)	Concentration[b]	E_T (kcal/mol)[c]	E_{A/A^-}[d]	$-E_T-E_{(A/A^-)}$	$k_q \times 10^{-9}$ M^{-1} s^{-1}
10	Anthracene (435)	0.0005	42.0	-44.2[g]	+ 2.2	1.2
11	Phenanthrene (483)	0.002	62.2	-56.1[g]	- 6.1	2.2
12	Pyrene (520)	0.001	48.0	-48.1[g]	+ 0.1	1.9

[a] Monitoring wavelength (nm) of the triplet state decay.

[b] Molar concentrations of the sensitizers.

[c] Triplet energies of the sensitizers quoted from Ref. 64 (in kcal/mole)

[d] Half-wave reduction potentials of the sensitizers (in kcal/mol) as determined by cyclic voltammetry (1 eV = 23.1 kcal/mol).

[e] The correlation of K_{obs} with $[Cu(acac)_2]$ was poor.

[f] The transient signal was too weak.

[g] Values quoted from C.K. Mann and K.K. Barnes, "Electrochemical Reactions in Non-Aqueous Solutions", M. Dekker, New York, N.Y., 1974.

decay as a function of $Cu(acac)_2$ concentration according to Eq. 2-5.

$$k_{exptl} = k_o + k_q [Cu(acac)_2] \qquad 2\text{-}5$$

In Fig. 2-7, log k_q were plotted against the lowest triplet state energies of the sensitizers (E_T) and a poor correlation could be observed (corr. coeff. = 0.856). A similar correlation (corr. coeff. = 0.855) was obtained when log k_q was plotted against $-E_T-E_{(A/A^-)}$ (Fig. 2-8), the free energy available for an electron transfer quenching, according to Weller's equation (108). $E_{(A/A^-)}$, the reduction potentials of the sensitizers were determined by Mr. Peter Hoang of this department and the results are shown in Table 2-9.

The free energy associated with an electron transfer process within an encounter complex can be estimated from the oxidation potential of the donors, $E_{(D/D^+)}$, the reduction potential of the acceptors, $E_{(A/A^-)}$, a Coulombic attraction term, C, and the sensitizer excited state energy, E_{0-0}, according to Weller's equation as shown below (108, 142-144).

$$\Delta G(\text{kcal/mol}) \cong E_{0-0} + [E_{(D/D^+)} - E_{(A/A^-)}] + C$$

Figure 2-7 Plot of log k_q for Quenching of Triplet Sensitizers by $Cu(acac)_2$ in Methanol versus E_T, the Lowest Triplet Energies of the Sensitizers.

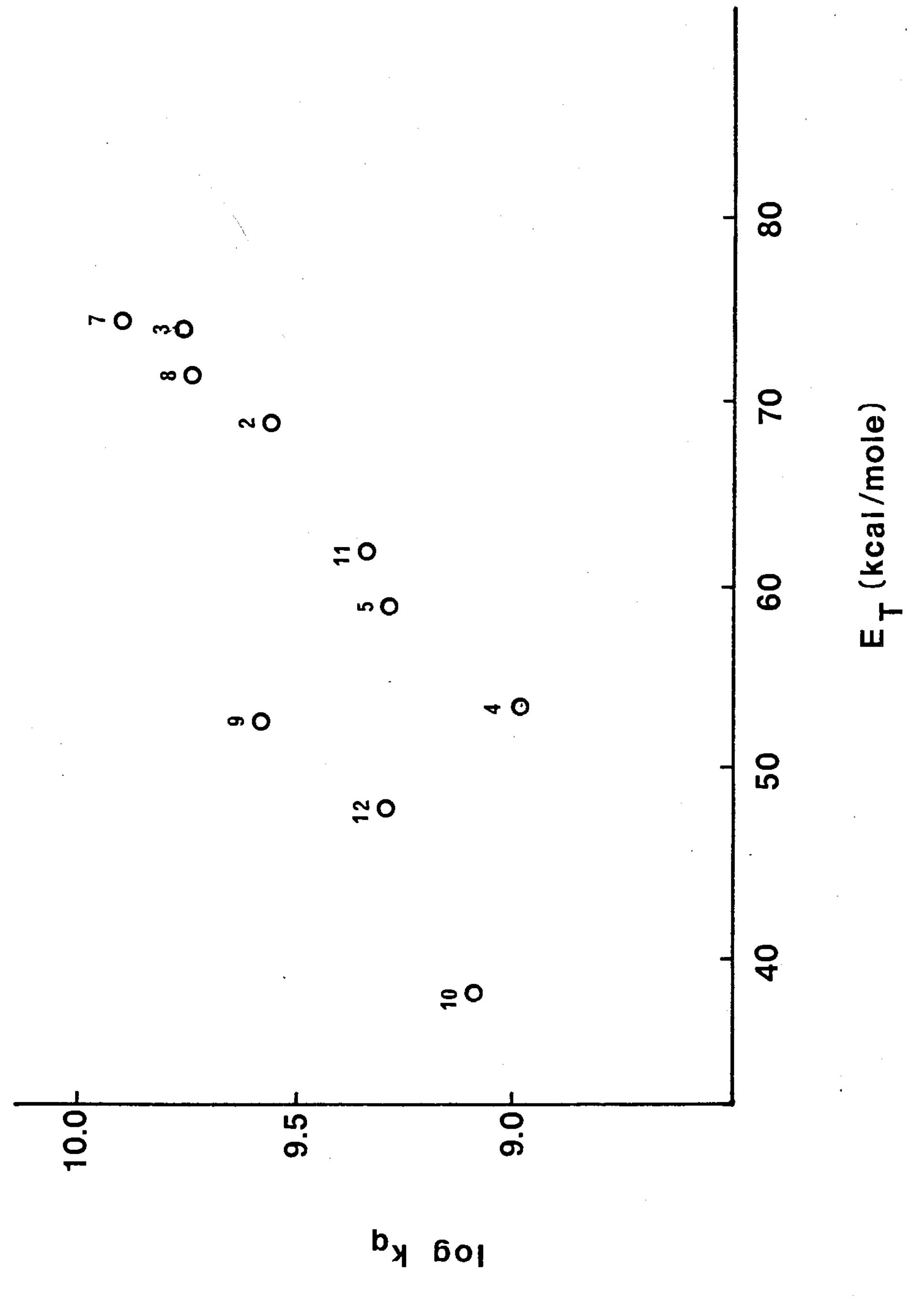
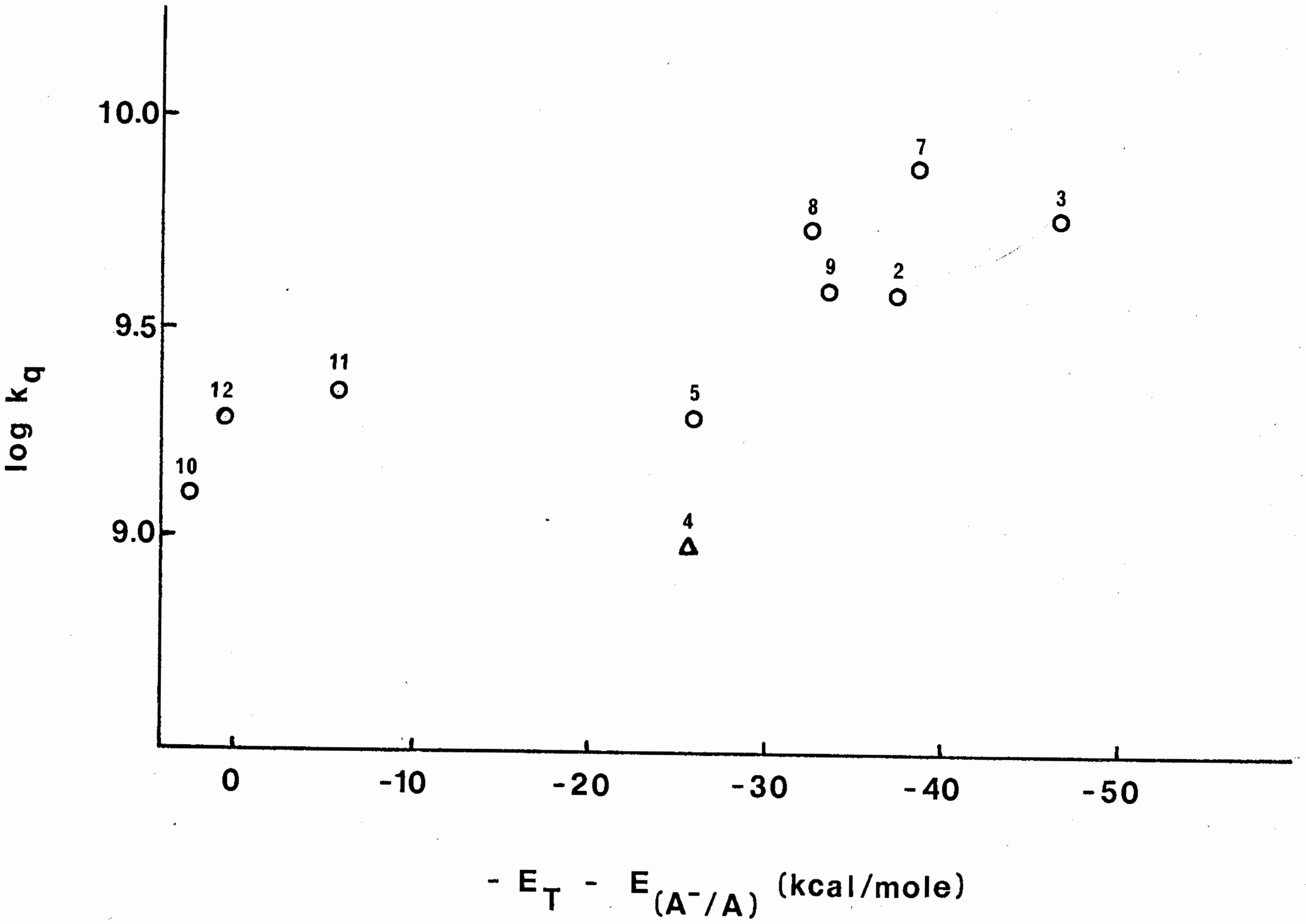

log k_q
10.0
9.5
9.0
40
50
60
70
80
E_T (kcal/mole)
10
12
9
4
5
11
2
8
3
7

Figure 2-8 Plot of log k_q for Quenching of Triplet Sensitizers by Cu(acac)$_2$ in Methanol versus $-E_T-E_{(A^-/A)}$, According to Eq. 3-16.


log k_q
10.0
9.5
9.0
0
-10
-20
-30
-40
-50
$- E_T - E_{(A^-/A)}$ (kcal/mole)
10
12
11
5
4
8
9
2
7
3

The free energy, ΔG, can be regarded as the stabilization gain arising from the contribution of charge transfer resonance forms. The term in brackets represents the energy required fro the electron transfer while E_{0-0} is the energy available to promote the process.

The ΔG calculations for several sensitizers used in this investigation are shown in Table 2-2. The Coulombic attraction term in a polar medium with encounter distance of *ca*. 7 Å is small and therefore omitted in the calculation. The oxidation potential, $E_{(D/D^+)}$ of Cu(acac)$_2$ is calculated from its ionization potential (IP = 7.75 ev).

2-9-4 Kinetic Analysis

On the basis of the general pattern observed for the benzophenone sensitized reduction of Cu(acac)$_2$, a mechanistic scheme (Scheme 2-6) was devised for the kinetic analysis of the reaction.

It is assumed in this scheme that the species formed after the interaction of the triplet state sensitizer with Cu(acac)$_2$ which is referred to as complex C, for the moment, must be partitioned into a successful reduction (Eq. 2-11) yielding Cu(I)acac, benzophenone, acetylacetone and the $\cdot CH_2OH$ radical on one hand, and an unsuccessful reduction (Eq. 2-12) in which the complex C reverts to benzophenone and $Cu(acac)_2$ on the other. The successful reduction involves an irreversible hydrogen abstraction from methanol the rate constant of which contains the terms of fixed concentration of methanol. The equations derived from this kinetic scheme are also shown where [C] = concentration of complex, [Q] = concentration of $Cu(acac)_2$, [BP*] = concentration of triplet benzophenone and α = fraction of intersystem crossing (for benzophenone, $\alpha = 1$).

$$Ph_2CO \xrightarrow[I_a]{h\nu} Ph_2CO(\text{singlet}) \xrightarrow[\alpha]{} Ph_2CO(\text{triplet}) \qquad \alpha I_a \tag{2-6}$$

$$\overset{*}{Ph}_2CO + CH_3OH \xrightarrow{k_r} Ph_2\dot{C}OH + \cdot CH_2OH \qquad k_r[BP^*] \tag{2-7}$$

$$\overset{*}{Ph}_2CO + PPh_3 \xrightarrow{k_b} \text{Products} \qquad k_b[BP^*][PPh_3] \tag{2-8}$$

$$\overset{*}{Ph}_2CO \xrightarrow{k_c} Ph_2CO + h\nu(\Delta) \qquad k_c[BP^*] \tag{2-9}$$

$$\overset{*}{Ph}_2CO + Cu(acac)_2 \xrightarrow{k_q} [\text{Complex}] \qquad k_q[BP^*][Q] \tag{2-10}$$

$$[\text{complex}] + CH_3OH \xrightarrow{k_p} \text{Cu(acac)} + \text{acacH} + \cdot CH_2OH + Ph_2CO \qquad k_p[C] \qquad 2\text{-}11$$

$$[\text{Complex}] \xrightarrow{k_d} \text{Cu(acac)}_2 + Ph_2CO \qquad k_d[C] \qquad 2\text{-}12$$

Scheme 2-6

Using steady state approximations:

$$\alpha I_a = (k_r + k_b[PPh_3] + k_c + k_q[Q])[BP^*] \qquad 2\text{-}13$$

and $$k_q[BP^*][Q] = (k_p + k_d)[C] \qquad 2\text{-}14$$

By definition:

$$\Phi_C = \frac{k_q[BP^*][Q] - k_d[C]}{I_a} \qquad 2\text{-}15$$

$$\Phi_C = \frac{\alpha(k_q[BP^*][Q] - k_d[C])}{(1/\tau_B + k_q[Q])[BP^*]} \qquad 2\text{-}16$$

where $1/\tau_B = k_r + k_c + k_b[PPh_3]$

$$\Phi_C = \frac{\alpha k_p[C]}{(1/\tau_B + k_q[Q])[BP^*]} \qquad 2\text{-}17$$

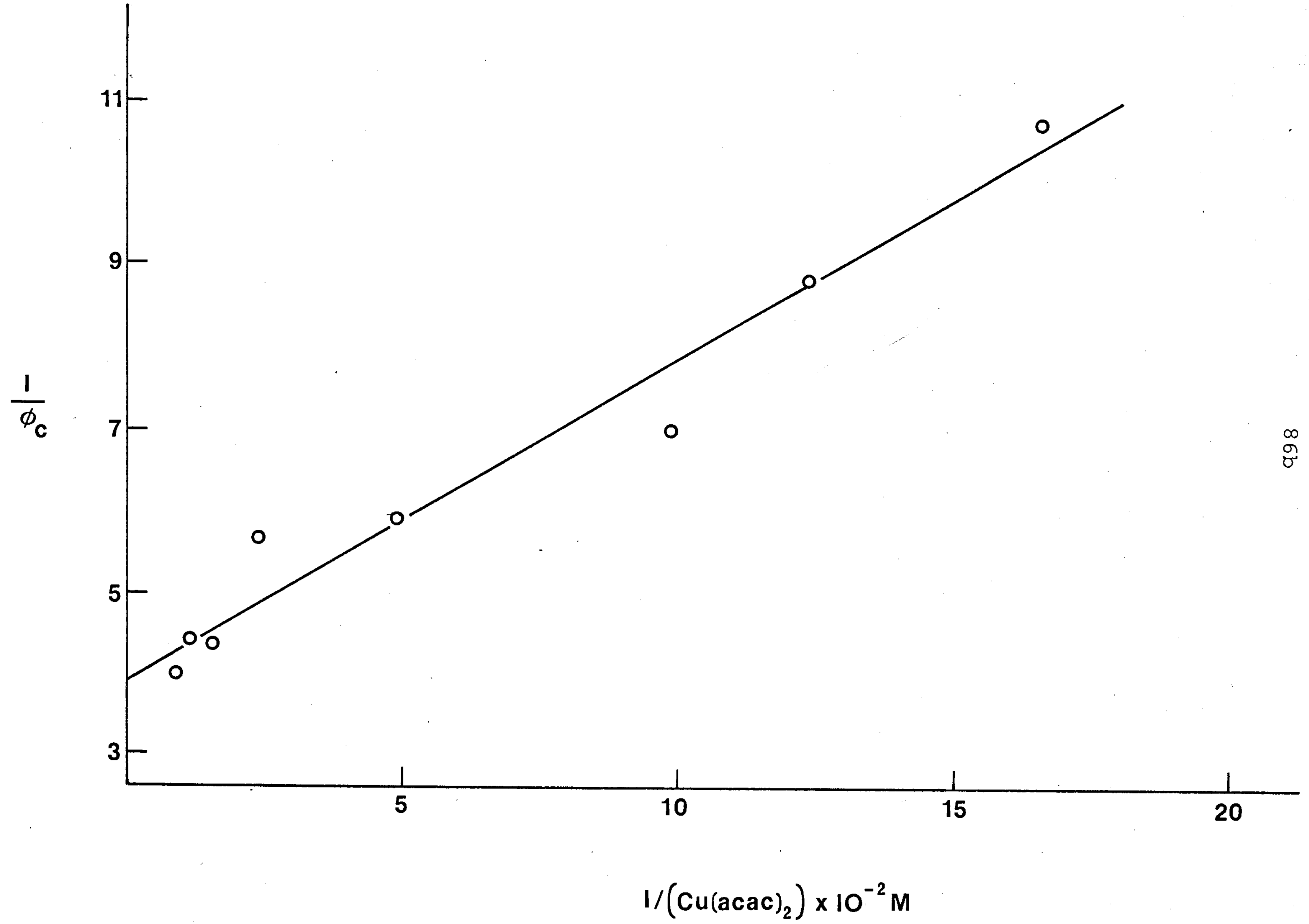
Figure 2-9 Plot of $1/\Phi_C$ for the Benzophenone Sensitized Photoreduction of $Cu(acac)_2$ in Methanol versus $1/[Cu(acac)_2]$.

slope = 3.91×10^{-3}

intercept = 3.86

corr. coeff. = 0.9763

k_q = $(7.35 \pm 1.4) \times 10^9\ M^{-1}\ s^{-1}$


$\frac{1}{\phi_c}$
11
9
7
5
3
5
10
15
20
1/(Cu(acac)$_2$) x 10^{-2} M

$$= \frac{\alpha k_q}{1/\tau_B + k_q[Q]} \; \frac{k_p[Q]}{k_p + k_d} \qquad 2\text{-}18$$

$$\Phi_C = \frac{\alpha\beta k_q[Q]}{1/\tau_B + k_q[Q]} \qquad 2\text{-}19$$

where $\beta = k_p/(k_p + k_d)$

$$\frac{1}{\Phi_C} = \frac{1}{\alpha\beta} + \frac{1}{\alpha\beta\tau_B k_q[Q]} \qquad 2\text{-}20$$

The quantum yields of Cu(acac)$_2$ disappearance, Φ_C, obtained in methanol (Table 2-4) were used to plot $1/\Phi_C$ vs. 1/[Cu(acac)$_2$] according to Eq. 2-20 as shown in Fig. 2-9. This plot gave a straight line with a correlation coefficient of 0.9763, from which the slope (= $1/\beta\tau_B k_q$) 3.91×10^{-3} and intercept (= $1/\beta$) 3.86 were obtained. From these data, k_q was calculated to be $(7.35 \pm 1.4) \times 10^9$ M^{-1} sec^{-1}. The intercept of 3.86 also showed that the limiting Φ_C in the benzophenone sensitized Cu(acac)$_2$ decomposition in methanol is ca. 0.25 and k_d/k_p was calculated to be ca. 2.9.

2-9-5 Quenching of Triplet 2-Acetonaphthone by $Cu(acac)_2$ in Methanol.

The quantum yields of $Cu(acac)_2$ disappearance for 2-acetonaphthone sensitized reduction were determined in the presence of triphenylphosphine (Table 2-10). For two sets of experiments the plot of $1/\Phi_c$ *vs.* $1/[Cu(acac)_2]$ gave straight lines with correlation coefficients of 0.9888 and 0.9933, slopes of 0.0813 and 0.0768 and intercepts of 54.21 and 74.06, respectively. The lifetime of triplet 2-acetonaphthone in methanol has been determined to be 36×10^{-6} s (167). The quenching rate constants, k_q, were calculated according to Eq. 2-20 to be $(1.85 \pm 0.28) \times 10^{7}\ M^{-1}s^{-1}$ and $(2.68 \pm 0.40) \times 10^{7}\ M^{-1}s^{-1}$, respectively: the average value of k_q was $(2.27 \pm 0.27) \times 10^{7}\ M^{-1}s^{-1}$. Because of the lack of photochemical reaction of 2-acetonaphthone in methanol the quantum yield of the ketone disappearance could not be determined.

Table 2-10 Quantum Yields of $Cu(acac)_2$ Disappearance Sensitized by 2-Acetonaphthone in Methanol.[a]

$[Cu(acac)_2] \times 10^3$ M	$\Phi_{c(1)}$[b]	$\Phi_{c(2)}$[b]
0.6	0.0053	0.0050
0.8	0.0063	0.0057
1.0	0.0125	0.0066
1.2	0.0087	0.0075
1.4	0.0083	0.0079
1.6	0.0073	0.0080
1.8	0.0100	0.0087
2.0	0.0110	0.0088

[a] Solutions (5 ml) were irradiated for 1 h and the % conversions of $Cu(acac)_2$ ranged from 8 to 18%. The concentrations of 2-acetonaphthone and triphenylphosphine were 0.05 and 0.001 M respectively.

[b] Estimated error = ± 15%

CHAPTER 3

DISCUSSION

3-1 General Reaction Pattern

The results described in Chapter 2 showed that the sensitized photodecomposition of $Cu(acac)_2$ is much more efficient than direct photodecomposition. In both cases the product patterns are the same; i.e., acetylacetone and a black precipitate assumed to be a copper(I)acetylacetonate complex. The latter disproportionates to Cu^o and $Cu(acac)_2$ under nitrogen or is oxidized to $Cu(acac)_2$ under oxygen. The formation of the known $Cu(acac)(PPh_3)_2$ when the black precipitate is treated with triphenylphosphine provides strong evidence that a copper(I) complex is the primary photoproduct. In addition to metallic copper, the protonated ligand as well as oxidation products from the alcohol solvents have been isolated and identified.

These experimental observations can be explained by a reaction scheme as shown below, in which S^* represents the triplet state sensitizer.

[3-1] $Cu(acac)_2 + S^* \longrightarrow Cu(acac) + acac\cdot + S$

[3-2] $2Cu(acac)_2 \xrightarrow{N_2} Cu(acac)_2 + Cu^0$

[3-3] $Cu(acac) + 2PPh_3 \longrightarrow Cu(acac)(PPh_3)_2$

[3-4] $acac\cdot + R_2CHOH \longrightarrow acacH + R_2\dot{C}OH$

[3-5] $2R_2\dot{C}OH \longrightarrow R_2C{=}O + R_2CHOH$

[3-6] $Cu(acac) + acac\cdot \longrightarrow Cu(acac)_2$

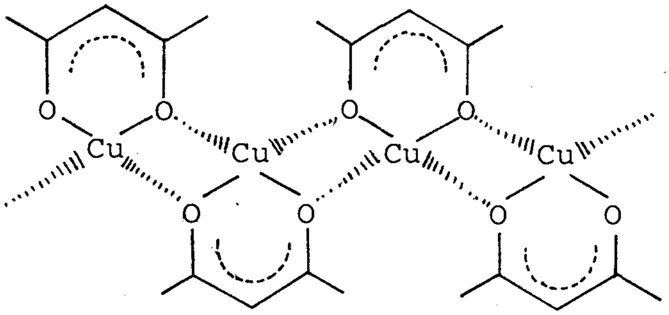
Since disproportionation of the copper(I) complex as in Equation [3-2] is rather slow in the solvents used in comparison to the photodecomposition of $Cu(acac)_2$ (Equation [3-1]), the black precipitate always appears first, followed by the slow appearance of metallic copper. In ethanol or iso-propanol reaction [3-1] occurs much faster as seen by the rapid disappearance of the blue color of the $Cu(acac)_2$ solution and the immediate deposition of the black precipitate.

Stoichiometrically, the reduction of copper(II) to copper(O) via copper(I) must be coupled with the oxidation reaction of alcohols to carbonyl compounds. At the same time, the mechanism of oxidation must be related to the way an acetylacetonato ligand acquires a hydrogen to form acetylacetone. This must occur by hydrogen abstraction from alcohols since the quantum yields of $Cu(acac)_2$ disappearance are in the order of the ability of the alcohols to donate hydrogen atoms.

3-2 Structure and Reactivity of the Copper(I) Intermediate

While adequate information could not be obtained to assign a structure owing to its instability, it is certain that the amorphous black precipitate formed in the sensitized photoreduction, as well as in the direct photolysis in alcohols, is not Cu(acac)(ROH)$_2$ as assumed before (23). This is indicated by the identical infrared spectrum obtained for the precipitates in alcohols as well as tetrahydrofuran.

The insolubility and non-crystallinity of the black precipitate suggests that it might be a polymeric Cu(acac) for which a tentative structure is shown below.



3-1

This type of polymeric structure is not uncommon for copper (I) complexes. For example, the x-ray structure analysis of the chloro(2,5-dithiahexane)copper(I) complex showed that each copper atom has distorted tetrahedral configuration: two to the sulphur atoms of the ligand, one to the terminal chlorine atom and one to the sulphur atoms of the ligand of a neighbouring molecule (112). The Cu(DTH)Cl moieties are thus formed into polymeric chains through Cu-S links. Copper also forms many compounds in which the Cu-Cu distances are short enough to indicate significant metal-metal interaction, but in no case is there an actual bond (109). The high reactivity of the black precipitate towards different ligands suggests the presence of weak Cu-O and Cu-Cu interactions.

This transient Cu(acac) species forms complexes readily with various ligands to give Cu(acac)L_x, where x = 1 for bidentate ligands and x = 2 for monodentate ligands (Table 2-3). With the exception of Cu(acac)$(PPh_3)_2$ which is known to possess a tetrahedral configuration around the Cu atom (110), the structures of these Cu(acac) complexes cannot be decided due to their instability under the ambient conditions. Although a definite structure cannot be assigned, a tetrahedral configuration can also be assumed for the Cu(acac) complexes with 1,10-phenanthroline, α,α-bipyridyl and carbon monoxide.

Most of the Cu(acac)L_X complexes are stable under inert atmosphere but very sensitive to air oxidation, regenerating Cu(acac)$_2$ in the presence of acetylacetone. It is also observed that the chelating ligands are readily displaced under mild conditions by triphenylphosphine. The stability of these complexes is thought to depend on the extent of back donation of electrons through π-overlap between the copper-ligand bond. Both bipyridyl and 1,10-phenanthroline (weak σ-donors) can function very effectively as π-acceptors as shown by their ability to stabilize low oxidation states (112a). Back bonding seems to be less important in the stabilization of the Cu(acac) complex with 2,5-dithiahexane.

Copper(I) carbonyl complexes have been rarely investigated mainly due to their extreme lability and ready disproportionation. The same characteristics are observed in the Cu(acac) complex with carbon monoxide. The reduction in the carbonyl frequency (ν 2100 cm^{-1}) observed for this complex, compared with that of free carbon monoxide (ν 2143 cm^{-1}), suggests some degree of back donation of copper 3-d electrons to CO π-anti-bonding orbitals. Such a back donation in Cu(acac) complexes of simple olefins, alkylamines and ethers is not significant as seen by their instability to air oxidation.

An interesting observation is that these Cu(acac)L_x complexes can also undergo benzophenone sensitized photoreduction in alcohols to give copper metal. While the Cu(I) complexes of bpy, o-phen and DTH are more stable towards photolysis, other complexes of olefins and ethers are just as easily photoreduced as Cu(acac)$_2$ under the sensitization conditions. As the complexes could not be isolated for investigation of their photolytic behavior, the reduction mechanism could not be clarified.

The transient Cu(acac) species can also be intercepted by terminal or disubstituted acetylenes to form σ or π copper(I) acetylene complexes. A reasonable mechanism for the formation of the σ bonded Cu(I) acetylides may involve the interception of the transient Cu(acac) by the acetylene to form a π-acetylene complex as in Eq. 3-7. The π donation

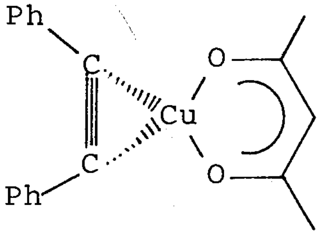
[3-7] $\mathrm{Cu(acac)} + \mathrm{RC{\equiv}CH} \longrightarrow \mathrm{Cu(acac)(RC{\equiv}CH)}$

[3-8] $\mathrm{Cu(acac)(RC{\equiv}CH)} \longrightarrow \mathrm{CuC{\equiv}CR} + \mathrm{acacH}$

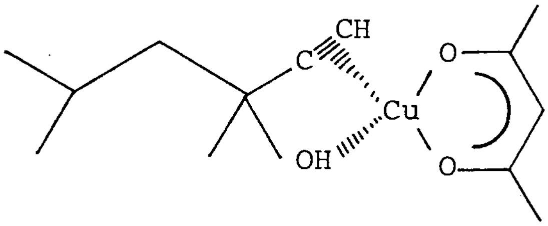
of electrons to the copper center conceivably increases the acidity of the acetylenic hydrogens and facilitates proton transfer from the acetylene to the acetylacetonate ligand (Eq. 3-8).

A π-acetylene complex may also be formed in the photolysis of $Cu(acac)_2$ in the presence of 3,5-dimethyl-3-hydroxy-1-hexyne. However, in α-hydroxyacetylenes the OH groups may form weak bonds with the metal (as shown below), hence the acetylene-hydroxyls could act as bidentate ligands (115). Such a ligand may have prevented proton transfer to the acetylacetonate ligand required to form the σ-type complex.

The number of mononuclear metal complexes which contain a π-coordinated acetylene remains surprisingly small in view of the extensive coordination chemistry which is known for other alkyne derivatives (116, 117). For the isolated Cu(acac)diphenylacetylene, structure <u>2-13</u> is assumed based on infrared and nmr data as well as its reactivity towards triphenylphosphine. Diphenylacetylene forms a series of stable complexes with Pt, W, Pd and Ir among others and x-ray studies have shown that the phenyl groups are bent (30° - 40°) out of the C-C axis (115). It is known that acetylenes can behave as monodentate (two-electron donor) or bidentate (four-electron donor) ligands (115). However, acetylenes as four-electron donors in monomeric complexes are not common, even though acetylenes as four-electron donor in binuclear complexes have been prepared, e.g. $Co_2(RC{\equiv}CR)(CO)_6$ and $(\pi\text{-}C_5H_5)_2Ni_2(RC{\equiv}CR)$ (118). Copper (I) being a d^{10} ion requires four



2-13

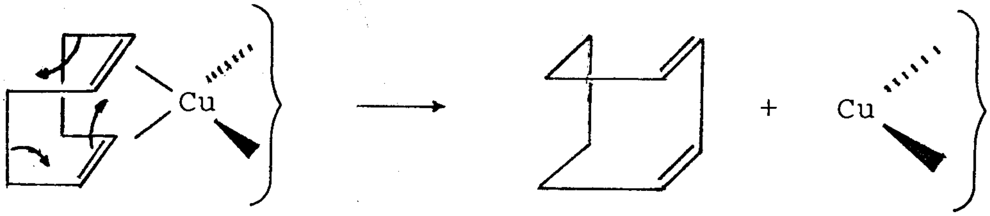


2-14

classical two-electron donors to attain the noble gas configuration. Since acetylacetonate ligand is considered a four-electron donor, it is expected that the diphenylacetylene ligand is also acting as a four-electron donor.

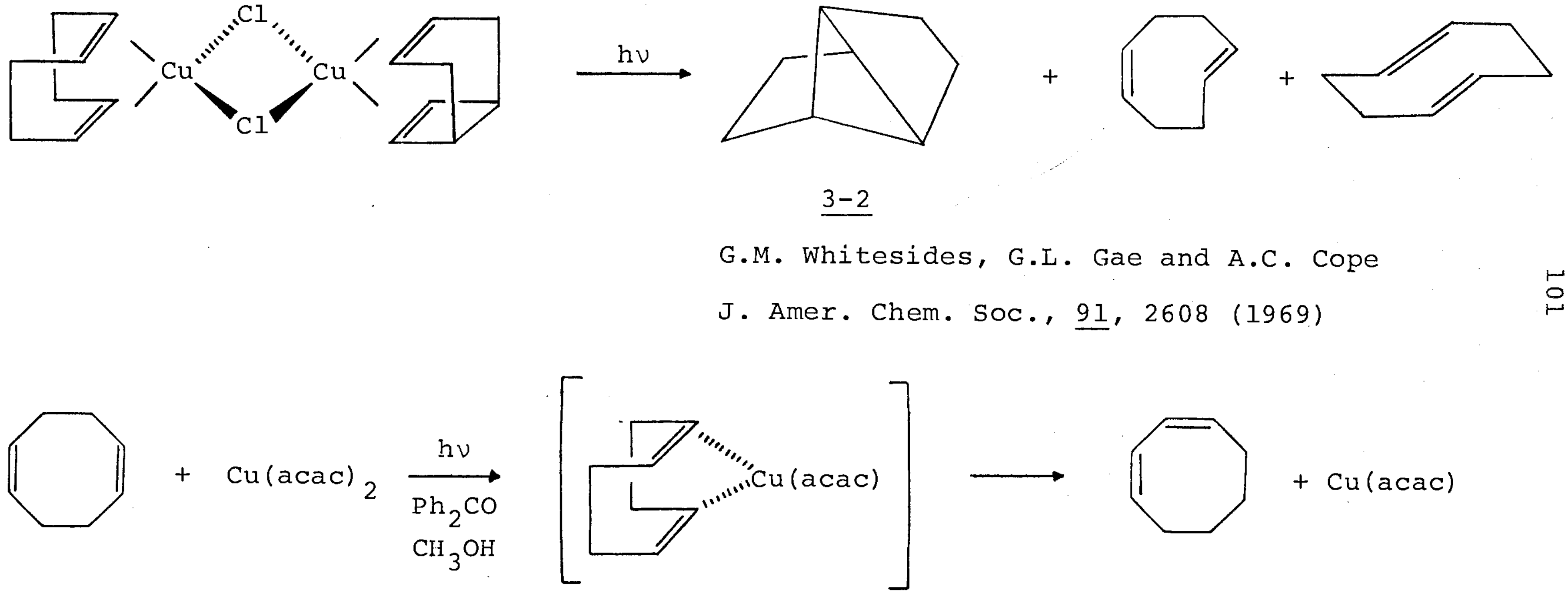
Although only preliminary experiments were carried out, the potential use of the benzophenone-Cu(acac)$_2$ system in photocatalytic reactions was demonstrated by the reactions in the presence of certain polyenes. Numerous studies have been reported on copper(I)-promoted photoreactions of olefins (119). These involve photodimerization of cyclic alkenes (120-122) and photocyclization and/or photoisomerization of dienes (123-127) among others. These studies have also shown that the reactions catalyzed by copper are generally quite different from those catalyzed by other transition metals and have no analogies in thermal processes. For example, in contrast to rhodium which catalyzes allylic hydrogen migration (123,128), copper(I) chloride catalyzes the intramolecular photocycloaddition of 1,5-cyclooctadiene to give the tricyclooctane <u>3-2</u> as the major product of photorearrangement (123,124) (Scheme 3-1). Cis,trans- and trans,trans-isomers have also been isolated and implicated as intermediates in the formation of <u>3-2</u> (128).

The benzophenone sensitized photoreaction of Cu(acac)$_2$ in the presence of 1,5-COD causes clean isomerization to 1,3-COD, and may proceed through an unstable copper(I)-acac-diene complex intermediate, 3-3 (Scheme 3-1). The formation of 1,3-COD can be visualized to involve a series of bond shifts as proposed before for the Rh(I) photocatalyzed isomerization of 1,5-COD. The catalytic cycle is obviously interrupted when the complex 3-3 undergoes disproportionation to Cu^0 and $Cu(acac)_2$.



3-3

A Cu(acac)-diene complex is also thought to be formed in the sensitized isomerization of norbornadiene. As benzophenone is known to sensitize the interconversion of norbornadiene and quadricyclene (104, 105), without kinetic studies it cannot be sure if the Cu(I)NBD complex is participating in the interconversion under the photolysis conditions. Our results showed that quadricyclene is formed faster in the absence of $Cu(acac)_2$ which indicates that the complex could be acting as an inhibitor of the interconversion. The rate constants for quenching of triplet benzophenone by NBD and Q in benzene have been determined to be $9.7 \times 10^8\ M^{-1}s^{-1}$ and $8.3 \times 10^8\ M^{-1}s^{-1}$ respectively



3-2

G.M. Whitesides, G.L. Gae and A.C. Cope

J. Amer. Chem. Soc., 91, 2608 (1969)

Scheme 3-1

(129). This shows that both NBD and Cu(acac)$_2$ (see Table 2-9) would be competing for the quenching of triplet state benzophenone.

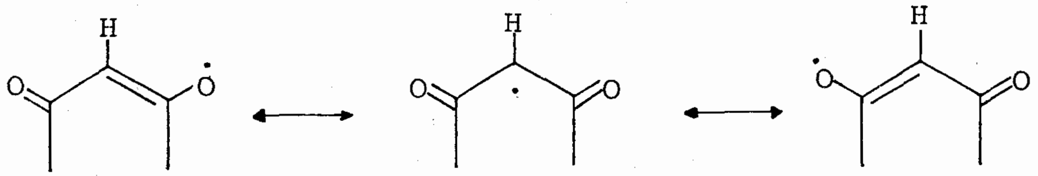
Benzophenone and copper halides have been shown to sensitize the photoisomerization of twelve-membered cyclic olefins such as 1,5,9-cyclododecatriene (100). The benzophenone/Cu(acac)$_2$ photolysis in benzene under hydrogen obviously caused the formation of a Cu(I) complex with benzene or the polyene. This complex proved to be much more effective in catalysing the cis-trans isomerization of the trienes. Only 6-8 hours of irradiation were required to reach a photostationary state compared with 200-300 hours for the benzophenone (or copper halides) sensitization (100). It is proposed that copper(I)acac-benzene mediates the isomerization, and certainly a complex of CDT must be involved. A similar photolysis in benzene under nitrogen did not promote the isomerization of trienes nor was Cu(acac)$_2$ photoreduced. Hydrogen therefore must be acting as the hydrogen atom donor.

3-3 Reactivity of the Acetylacetonyl Radical

That the redox process in the sensitized photodecomposition of Cu(acac)$_2$ takes place by a radical mechanism is suggested by the following observations. First, poor hydrogen donor solvents such as benzene and chloroform do not promote the photoreduction. Secondly, the rate of formation of the black precipitate as well as the quantum yields of Cu(acac)$_2$ disappearance (Table 2-5) indicates that the sensitized photoreduction occurs in alcohols with a decreasing order of efficiency of i-PrOH>EtOH>MeOH. This order coincides with the efficiency order in which these alcohols donate an α-hydrogen (but not a hydroxy hydrogen) by a radical mechanism (130). Therefore, the acetylacetonyl radical might be suggested as the reactive intermediate in the oxidation reaction by abstraction of an α-hydrogen from the alcohol. Since this radical is a neutral species, it may diffuse away from the solvent cage rapidly to enter into independent radical reactions.

On the basis of its resonance stabilization forms, this type of radical could react as a carbon or as an oxygen radical. However, esr studies have shown that this type of resonance stabilization in β-diketone radicals appears to be of little importance (131). It has been predicted that more than 75% of the unpaired spin resides on the C$_3$

carbon.

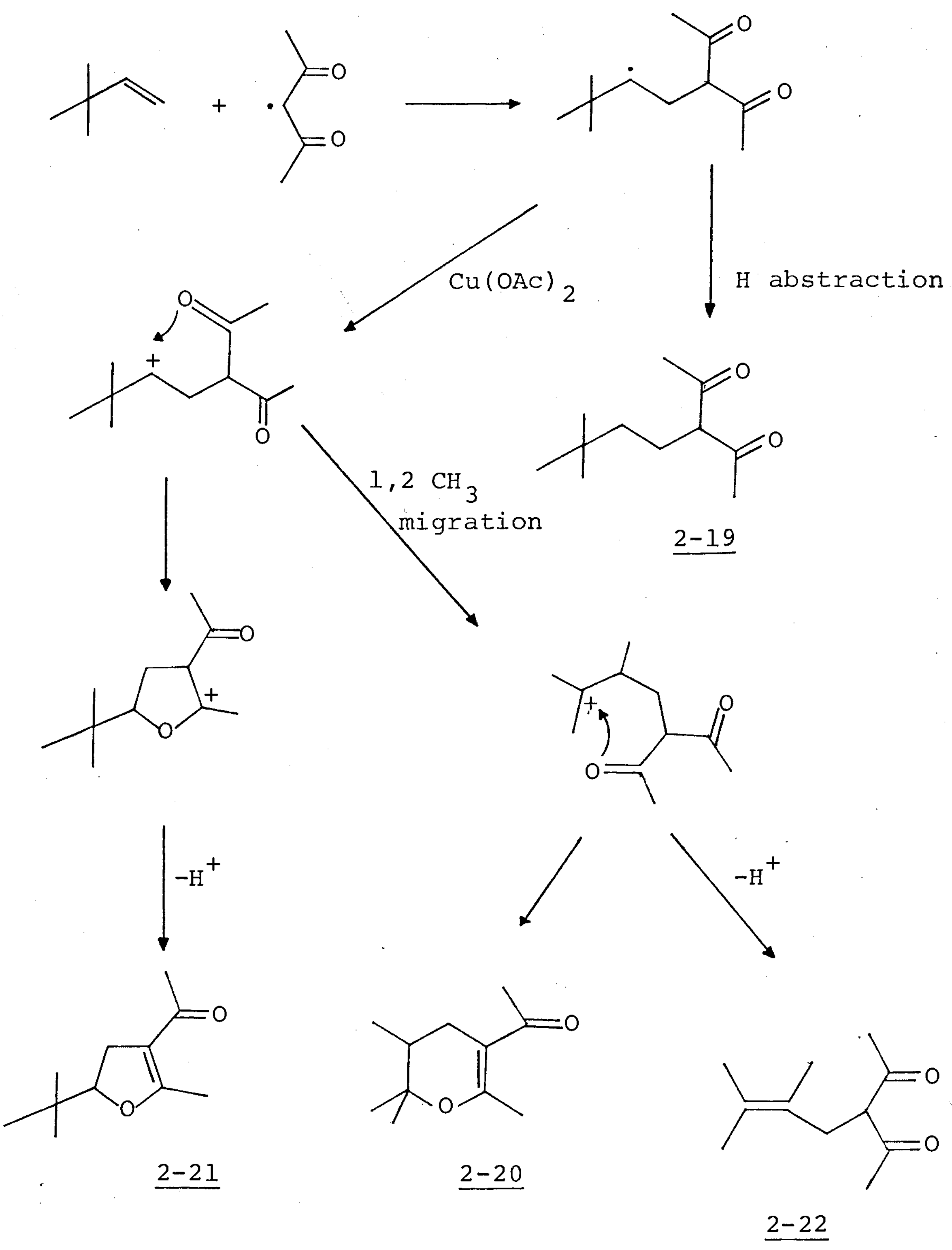


The acetylacetonyl radical has been generated by electrolytic (132), chemical (Ce^{4+}, Mn^{+3}) (131,87) or radical (amino, hydroxyl) (133) oxidation, and is reported to add to terminal olefins (84-87). The benzophenone sensitized photolysis of $Cu(acac)_2$ in the presence of olefins in solvents such as acetic acid or acetonitrile gives addition products which can be explained by the reaction of the acetylacetonyl radical intermediate with olefinic π-bonds. A direct photochemical reaction between free acetylacetone in solution and the olefins can be ruled out since all the incident light is being absorbed by the sensitizer. Furthermore, published reports show that the benzophenone triplet state does not sensitize the cycloaddition of acetylacetone to olefins (134).

The reaction in the presence of norbornene gives mainly one product, that is, (3-norborn-2-yl)-2,4-pentadione, 2-17. Since basic or acid hydrolysis of 2-17 gives exo-2-norbornylacetone, 2-16, its formation during the photolysis probably arises from hydrolysis under the conditions.

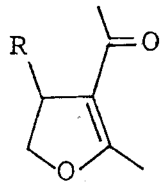
The reaction with non-cyclic olefins such as neo-hexene and 1-hexene gives several types of addition products. For the addition to neo-hexene, a mechanism as shown in Scheme 3-2 can be assumed which involves the rearrangement of the tert-butyl group. This is a definite proof of carbonium ion participation in the reaction. When the reaction is run in acetonitrile as solvent, the yield of the dihydropyran 2-20 decreases considerably while the compounds 2-21 and 2-22 are not formed at all. These results can be related to the oxidative capacities of $Cu(OAc)_2$ and $Cu(acac)_2$. It has been shown that the oxidative power of Cu(II) towards carbon radicals decreases drastically when the acetate ligands in $Cu(OAc)_2$ are replaced by acetylacetonate (84). As $Cu(acac)_2$ in acetic acid is in equilibrium with $Cu(OAc)_2$, the latter oxidizes the carbon radical intermediate more rapidly than the former.

Similar results are obtained in the reaction of the radical with 1-hexene. The major products are the saturated ketone 2-24 and the substituted dihydrofuran 2-25, in addition to small amounts of the γ,δ-unsaturated ketone 2-23. A similar mechanism can be written for the addition to 1-hexene (Scheme 3-3). The reaction in acetonitrile only afforded the saturated

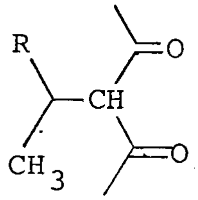


Scheme 3-2

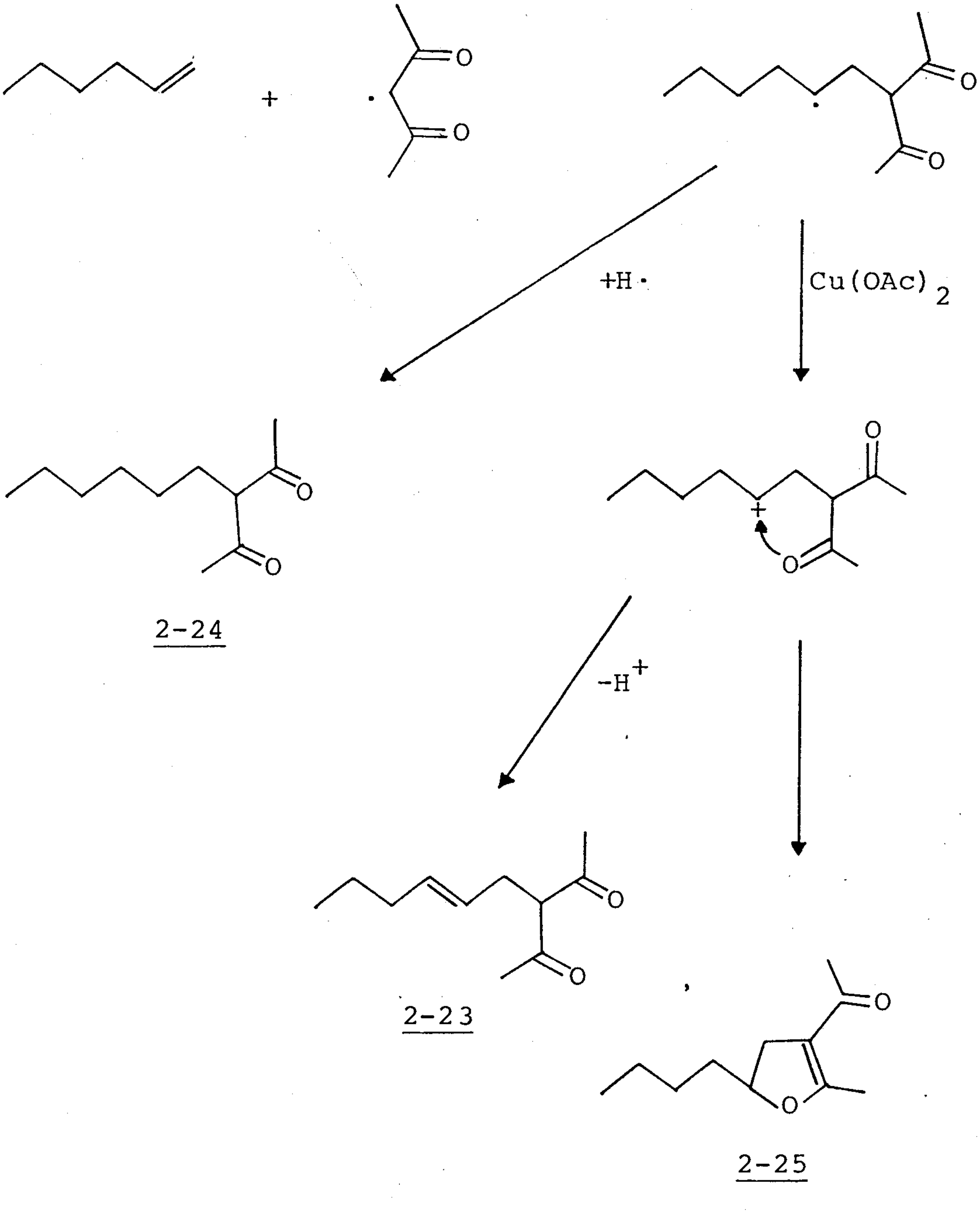
ketone 2-24, which again indicates the inability of Cu(acac)$_2$ to oxidize carbon radicals. These results also emphasize the fact that β-diketone radicals behave only as carbon radicals in addition reactions to olefins. The absence of such products as 3-4 and 3-5 shows that O-radical addition does not occur.



3-4



3-5



Scheme 3-3

3-4 General Mechanism

The proposed general mechanism (P. 84) appears to agree with the kinetic analysis for benzophenone sensitized photoreduction. The plots of Φ^{o}_{B}/Φ_{B} against $[Cu(acac)_2]$ (Fig. 2-4) and $1/\Phi_C$ vs. $1/[Cu(acac)_2]$ (Fig. 2-7) give straight lines, and the calculated k_q values from these plots are in reasonable agreement with that obtained by flash photolysis within experimental errors. The higher value obtained from static quenching experiments may be attributed to the presence of triphenylphosphine. It is not inconceivable that triphenylphosphine participates in some way to facilitate the photoreduction process. It must be pointed out, though, that $Cu(acac)_2$ is not photoreduced in the presence of PPh_3 but absence of benzophenone, nor is it thermally reduced by PPh_3 in the dark.

The kinetic analysis suggests that the limiting quantum yield of $Cu(acac)_2$ disappearance, Φ_C, observed in the benzophenone sensitized photoreduction arises from the partition of the complex between a successful reduction (Eq. 3-9) and an unsuccessful one (Eq. 3-10) (k_d/k_p was calculated to be 2.86).

$$[3\text{-}9] \qquad [\text{Complex}] + CH_3OH \xrightarrow{k_p} Cu(acac) + acacH + Ph_2CO + \cdot CH_2OH$$

[3-10] $$[\text{Complex}] \xrightarrow{k_d} \text{Cu(acac)}_2 + \text{Ph}_2\text{CO}$$

This conclusion is supported by the following evidence. First, it was observed that the quantum yields, Φ_C, at the same concentration of Cu(acac)_2, increase in better hydrogen donor solvents as shown in Table 2-5; e.g., Φ_C increased in the solvents MeOH<EtOH<2-PrOH. Secondly, the relatively invariable k_q values for different sensitizers (Table 2-9), as opposed to the wide variation of Φ_C (Table 2-6), requires that the efficient quenching process must be modified by a partition scheme to account for product patterns. This argument is admissible on the assumption that in the absence of triphenylphosphine the variations of Φ_C are in the same order of arrangement and magnitude as shown in Table 2-6.

3-5 Sensitization Mechanism

The direct photodecomposition of $Cu(acac)_2$ has been speculated to occur by an internal redox process arising from the excitation of the charge transfer band (ligand-to-metal band, CTLM) at 243 nm (E ~119 kcal/mol) based on which the acetylacetonyl radical has been proposed as the intermediate (23). Since $Cu(acac)_2$ shows no emission, the energy levels of its excited states remain unclear. The sensitized photodecomposition might be assumed to proceed from a yet undefined excited state of $Cu(acac)_2$ by an internal redox mechanism similar to that for direct photolysis. However, no evidence can be found in favor of a classical energy transfer mechanism from the excited states of the sensitizers to the ground state of $Cu(acac)_2$. For example, the order of reaction efficiency; i.e., anthrone> benzophenone>xanthone>benzil>acetophenone>biacetyl>2-acetonaphthone, does not agree with the order of the lowest triplet energies of the sensitizers. It is also apparent, none of these ketones has a triplet state energy high enough to succesfully activate the CTLM band of $Cu(acac)_2$ at 240 nm.

A majority of photoreactions of carbonyl compounds involve either electron or hydrogen transfer to their triplets (135 - 137). A hydrogen atom transfer leading to the reduction of $Cu(acac)_2$ by ketyl radicals such as $Ph_2\dot{C}OH$

as shown in Eq. 3-11 and 3-12, also deserves some consideration. In fact, this mechanism has been invoked to explain the photolytic dehydrogenation of cyclohexane in the presence of Cu(II) pivalate (138).

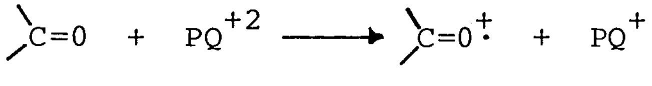
[3-11] $$Ph_2CO^* + RCH_2OH \longrightarrow Ph_2\dot{C}OH + R\dot{C}HOH$$

[3-12] $$Ph_2\dot{C}OH + Cu(acac)_2 \longrightarrow Ph_2CO + Cu(acac) + acacH$$

Although this mechanism would explain why certain ketones which do not undergo photoreduction in alcohols, failed to effectively sensitize the photoreduction of $Cu(acac)_2$, it still would not explain the high quenching rate constants observed with most the compounds studied. Also on the basis of the results obtained with benzophenone, it is unlikely that a hydrogen transfer mechanism is operating. First of all, since triplet state benzophenone is almost totally quenched at $Cu(acac)_2$ concentrations above 10^{-2} M and the limiting quantum yield for $Cu(acac)_2$ disappearance at these concentrations is far below unity ($\Phi_c = 0.25$), one would still observe photoreduction products of benzophenone if Eq. 3-11 was the only quenching pathway. The photoreduction of benzophenone is virtually reduced to insignificant amounts when $[Cu(acac)_2] > 10^{-2}$ M, which contradicts the hydrogen abstraction mechanism. Secondly, the quenching rate constant for reaction 3-9, that is, the unimolecular rate constant for the hydrogen abstraction by triplet benzophenone from alcohols, has been determined to be $3.8 \times 10^6 s^{-1}$ in MeOH, $12.0 \times 10^6 s^{-1}$ in EtOH, and $23.0 \times 10^6 s^{-1}$ in 2-propanol (107). Considering the value of $k_q = 3.6 \times 10^9 M^{-1}s^{-1}$ for reaction 3-11 in MeOH, as determined by monitoring the triplet state decay by flash photolysis, the hydrogen abstraction by triplet state benzophenone from MeOH would not be competitive unless the concentration of $Cu(acac)_2$ is 10^{-2} M or lower.

There is evidence to believe that sensitization of $Cu(acac)_2$ photoreduction takes place by an electron transfer mechanism. A direct electron transfer to the copper(II) metal center from the triplet state benzophenone is unlikely since it would involve high energy species such as the benzophenone cation radical, $[Ph_2CO]^{+\cdot}$. Although there are many examples of electron transfer to carbonyl triplets (135, 139), only one recent study concerning possible electron transfer from carbonyl triplets has been reported (140). This involves the photoreduction of paraquat (PQ^{+2} = 1,1"-dimethyl-4,4'-bipyridylium) through electron transfer from a number of aromatic carbonyl triplets.

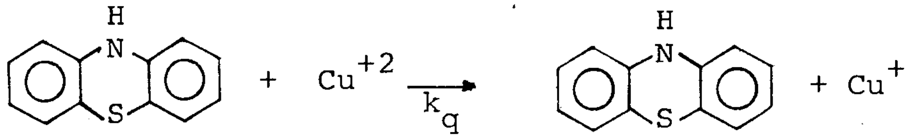
[3-13]



The radical cations derived from the carbonyl triplets could not be detected because they either have relatively short lifetimes or very weak absorption in the spectral region investigated (140).

Another indication against this type of electron transfer (to the metal center) is provided by the failure of phenothiazine to photolytically reduce Cu(acac)$_2$. In methanol solutions, the phenothiazine triplet state has been shown to be quenched by electron transfer to metal ions to give the phenothiazine cation radical and the reduced metal ion, provided the reduction potentials of the latter are favorable. The quenching rate constant of phenothiazine by Cu^{+2} ion was determined to be 6.0 x 10^{9} M^{-1}s^{-1} in methanol (141). The inefficacy of phenothiazine

[3-14]



as well as p-methoxyacetophenone in sensitizing the photoreduction of Cu(acac)$_2$ suggest that reduction of the complex by direct electron transfer to the metal does not occur.

It is believed that the quenching of triplet sensitizers by Cu(acac)$_2$ takes place by electron transfer from the ligand of Cu(acac)$_2$ to the excited state of the sensitizer via an unspecified encounter complex (and/or exciplex) which might be represented as 3-4 or 3-5.

$$Ph_2CO^* + Cu(acac)_2 \longrightarrow [Ph_2CO^{\overline{\cdot}}---(acac)^{\overset{+}{\cdot}}Cu(acac)]$$

3-4

$$[Ph_2CO^{\overline{\cdot}}---(acac)^{+}Cu---acac\cdot] \longrightarrow Ph_2CO + Cu(acac) + acac\cdot$$

3-5

The formulation assumes a loose association between Cu(acac)$^+$ and the acetylacetonyl radical which may undergo irreversible hydrogen abstraction from the solvent as in Equation 3-4, or addition reactions in the presence of reactive olefins. The overall process might be regarded as an electron migration from the ligand to the copper center, as proposed for the direct photolysis (23), but with the triplet state benzophenone acting as the electron carrier. The deviation of the quantum yield of photoreduction Φ_c from unity could be a result of back electron transfer, following the formation of complex 3-4 or 3-5 in the solvent cage. It is not understood precisely at what stage the back electron transfer can occur within the complex 3-4 → 3-5. One may perceive that the dissociation of the complex is rapid owing to the instability of Cu(acac)$_2^{\overset{+}{\cdot}}$. While the back electron transfer in complex 3-4 is straightfroward, that in complex 3-5 may instead involve electron transfer from the ketyl anion radical to the acetylacetonyl radical which is in competition with the irreversible hydrogen abstraction of the radical from methanol.

The calculations of the free energy change (ΔG) associated with the electron transfer according to Weller's equation (Table 2-2) show that the electron transfer to the triplet state of some ketones is energetically favorable, but to other sensitizers is not. This is in general agreement with the observed results in qualitative experiments.

Furthermore, from Weller's semi-empirical correlations (145) the bimolecular rate constants for electron transfer quenching, k_q, can also be related to ΔG as shown in Eq. 3-16.

$$[3\text{-}16] \qquad \log k_q \sim \Delta G \cong -E_{0-0} + [E_{(D/D^+)} - E_{(A^-/A)}]$$

Observation of the correlation implied by Eq. 3-16 usually provides support for an electron transfer mechanism (145). The reasonably good linear correlation (except for the point due to benzil) found between $\log k_q$ and $-E_{0-0} - E_{(A^-/A)}$, as shown in Fig. 2-8, supports the proposal that the triplet states of the sensitizers are quenched by $Cu(acac)_2$ by an electron transfer mechanism. Previous studies have noted that the quenching of triplet state benzil by metal complexes and other quenchers is an exception with uniquely low rate constatnts (43, 140, 146). This is probably due to the sensitizer undergoing unwanted side reactions.

3-6 Conclusions and Research Proposals

Although this investigation provides strong evidence in favor of an electron transfer mechanism for the quenching of triplet sensitizers by $Cu(acac)_2$, the validity of this proposal can be tested further if transient species formed during the reaction can be detected by flash excitation techniques. One of these species, the benzophenone anion radical, $Ph_2\dot{C}\bar{O}$, absorbs strongly at ~630 nm (ε ~5000) in acetonitrile solution (147). Therefore, if detected, its decay kinetics could be studied.

The fast rate constants (k_q ~$3.6-7.3 \times 10^9$ M^{-1} s^{-1}) of quenching of triplet state benzophenone suggest that the process may involve the formation of encounter complexes and/or exciplexes. Although many singlet exciplexes are strongly fluorescent, triplet-derived exciplexes do not usually luminesce, and as a result their direct characterization is more difficult. However, evidence for the intermediacy of exciplexes in the quenching of triplet benzil by triethylamine has been reported (148). A similar study for the benzophenone (and other sensitizers) $Cu(acac)_2$ system could also be carried out to look for exciplex formation.

Provided the acetylacetonyl radical has an absorption in a transparent region, flash techniques could also be used to study its decay kinetics in the presence of various substrates.

The behaviour and reactivity of different β-diketonyl radicals ($R_1CO\dot{C}HCOR_2$) can be investigated by carrying out the sensitized photoreduction of various Cu(II) β-diketonate complexes under the conditions used in this research. This would reveal electronic and steric effects of the R_1 and R_2 groups on the electrophilic addition to olefins or hydrogen abstraction reactions.

The transient copper(I) acetylacetonate Cu(acac) can coordinate with a variety of ligands, such as olefins, phosphines, amines and sulfides to give $Cu(acac)L_X$ complexes. These complexes are, in most cases, spontaneously and rapidly oxidized by air to regenerate $Cu(acac)_2$ in the presence of acetylacetone.

$$[3\text{-}17] \qquad Cu(acac)L_X + acacH + O_2 \longrightarrow Cu(acac)_2 + {}_xL + H_2O$$

The repetitive photoreduction and recycling by air oxidation of the copper(II) acetylacetonate complex could result in a catalytic reaction of a substrate, such as oxidation (alcohols), isomerization or dimerization (olefins), etc.

Also, the potential catalytic properties of the benzophenone-Cu(acac)$_2$ system in a benzene-hydrogen medium towards isomerization and/or hydrogenation of olefins, may deserve a more extensive study.

CHAPTER 4

Experimental

4-1 General Techniques

Unless specified otherwise the following experimental conditions prevailed. Melting points (mp) were determined on a Fisher-Johns apparatus and were uncorrected. Infrared spectra (ir) were obtained with a Perkin-Elmer 457 or a Perkin-Elmer 599B spectrophotometer as a nujol mull, KBr pellet, liquid film or CCl_4 solution. Ultraviolet and visible spectra were recorded on a Unicam SP8000 or a Cary 17 spectrophotometer. Nuclear magnetic resonance (nmr) spectra were recorded on a Varian A56/60, EM-360 or a Varian XL-100 spectrometer in $CDCl_3$ solution using TMS as internal standard. Chemical shifts for proton nmr spectra are reported in δ values and coupling constants (J) in Hz. The coupling patterns of nmr signals are presented as s (singlet), d (doublet), t (triplet), q (quartet), d,d (double doublet), m (multiplet) and b (broad). D_2O exchangeable protons are indicated by "D_2O exch". In ^{13}C nmr spectra, chemical shifts are reported in ppm relative to TMS and the splitting patterns from off-resonance decoupling (ord) are indicated in parenthesis. Mass spectra (ms) and gas chromatography mass spectra (gc-ms) were obtained on a

Hitachi-Perkin Elmer RMU-6E mass spectrometer or on a Hewlett-Packard 5985 gc-ms system. The gas chromatographic mass spectra used a 20% SE-30 (10 ft × 1/8 in) column in a Varian 1400 or a SE-30 capillary column (J & W, 45 ft × 0.28 mm) in a Hewlett-Packard 5840 gc which were coupled to the mass spectrometer. High resolution mass spectra (hrms) were performed at the University of British Columbia mass spectrometric services. Vapour phase chromatographic analyses (vpc) were performed on a Varian 1200 (FID) with a 10% SE-30 (6 ft × 1/8 in) column or a Varian 1400 (FID) with a SE-30 capillary column (J & W, 45 ft × 0.28 mm). Preparative runs were executed on a Varian 1700 (thermal conductivity detector) using a 10% SE-30 (10 ft × 1/4 in) column. Retention times (rt) are reported in minutes (min). Thin layer chromatographic analyses (tlc) were performed on silica gel impregnated with uv indicator or on alumina, and were then developed with iodine. Separations by column chromatography were carried out using neutral alumina (Brockman activity I, Fischer, 80-200 mesh) or silica gel (Baker analyzed, 60-200 mesh). For high pressure liquid chromatography (hplc) two types of system were used. One was a Varian Model LC-4010-1 using a Porasil C-4000 (37-75 m) column. The other was constructed with a LDC Model 711 solvent delivery system, a Rheodyne Model 7120 syringe loading sample injector, a Partisil PXS 10/25 Whatman analytical column and a LDC Model 1203 uv monitor (254 nm). Preparative HPLC separations were carried out on a Varian Model 5020 using a PAC-Magnum 9 Whatman column. Elemental analyses were performed by Mr. M.K. Yang on a Perkin Elmer 240 microanalyzer.

4-2 Chemicals

Solvents were reagent grade and distilled before use. Benzene (distilled from H_2SO_4) was stored over sodium ribbon; acetonitrile (distilled over P_2O_5), methanol (distilled from Mg), chloroform and methylene chloride (distilled over $CaCl_2$) were all kept over molecular sieves. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride and stored over sodium. Concentrated nitric acid and hydrochloric acid were supplied by Baker, concentrated sulfuric acid by CanLab and glacial acetic acid by BDH Chemicals. Nitrogen and hydrogen gas (Union Carbide) were purified by scrubbing through a Fieser solution followed by concentrated sulfuric acid and KOH pellets. Carbon monoxide (C.P., Union Carbide) was scrubbed through KOH pellets before use.

$Cu(acac)_2$ was prepared by the known method (149) and recrystallized from benzene. Acetylacetone (Fischer) was distilled before use. Commercially obtained sensitizers[1] were purified by recrystallization, vacuum sublimation or a combination of both. Biacetyl (Eastman) was distilled and stored under nitrogen. 1-Cyanonapthalene was provided by Dr. T. Koyanagi, Kyoto University. Olefins, dienes and acetylenes were commercially available (Aldrich), and distilled or recrystallized before use. Trienes were purified by a previously described method (150). A sample of 2,5-dithiahexane was provided by Dr. R.K. Pomeroy.

4-3 Photolysis Apparatus

Three different types of apparatus were used.

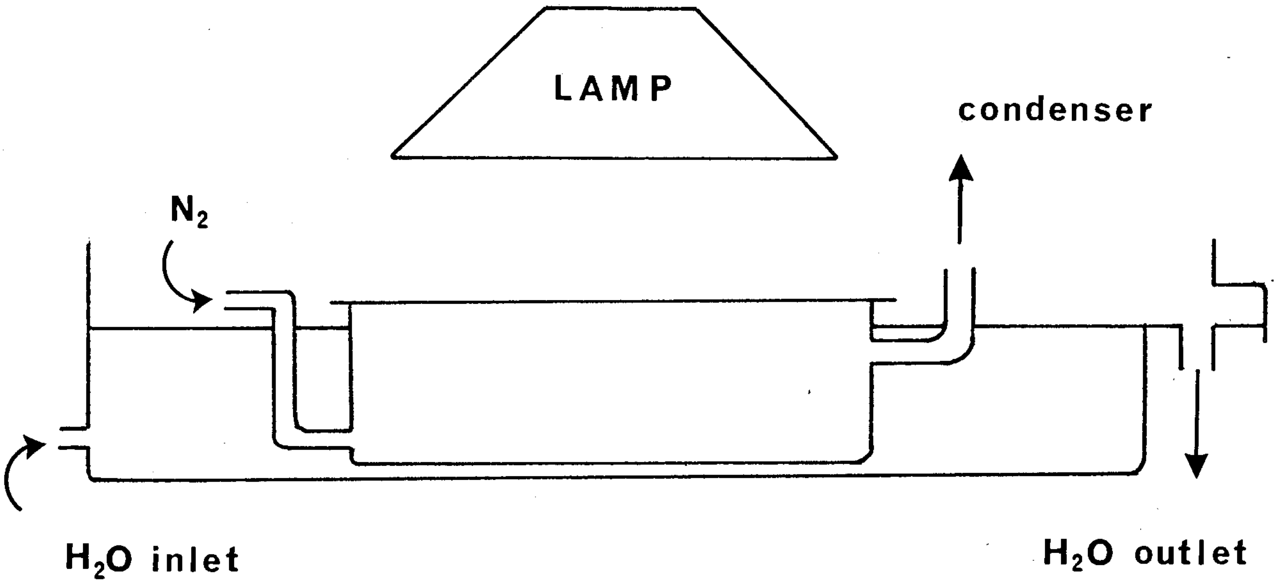
Apparatus I

This apparatus (Fig. 4-1) (151) consisted of a cylindrical vessel fitted with a condenser, a Pyrex (o quartz) plate cover and a gas inlet tube. An air trap was also fitted on top of the condenser allowing only the gas inside the apparatus to escape. The whole vessel was immersed in running tap water for cooling purposes. This apparatus was normally used in conjunction with a 140-Watt Hanovia mercury lamp (SH 616 A 1030) which was placed at a distance of ~2 cm from the plate cover. This type of overhead irradiation has the advantage of diminishing the obstruction of the incident light when insoluble precipitates are formed.

---

[1] Samples of butyrophenone, valerophenone and γ-methylvalerophenone were kindly provided by Dr. J.C. Scaiano.

Figure 4-1 Photolysis Apparatus I.


LAMP
condenser
N_2
H_2O inlet
H_2O outlet

Apparatus II

This apparatus consisted of a flat cylindrical vessel (Pyrex glass) fitted with a condenser, a side arm (gas inlet) and a Teflon stopcock with a sintered glass filter in order to separate insoluble precipitates from the rest of the photolysate solution. The light source was generally a 200-Watt Hanovia medium pressure mercury lamp (654 A 36) inserted into a quartz cooling jacket.

Apparatus III

This apparatus was a normal immersion type photocell which has been previously described (152). The light source was a 200-Watt or a 450-Watt (679 A 36) Hanovia medium pressure mercury lamp.

4-4 Photolysis of $Cu(acac)_2$ in the Presence of Different Sensitizers

Unless specified otherwise, all reactions were carried out in Apparatus I fitted with a Pyrex glass cover. A solution of $Cu(acac)_2$ (~100 mg) and sensitizer in 100 ml of solvent under nitrogen was irradiated with a 140-Watt Hanovia mercury lamp at running water temperature. The progress of the reaction was followed by examining the decrease in the visible absorption of $Cu(acac)_2$ at 630 nm. After photolysis copper was filtered and determined by colorimetric methods (153). The filtrate was distilled, the first fraction being collected in a receiver (cooled in an ice-water bath) containing a 2,4-DNPH solution. The yellow precipitate was filtered and recrystallized to afford the 2,4-DNPH of volatile carbonyl compounds. The second fraction containing the major part of the solvent was analyzed by hplc to give only one peak which had the same retention time as acetylacetone. The concentration of acetylacetone was calculated from its uv absorption at λ_{max} 273 nm. The residue was analyzed by vpc, tlc and gc-ms. Sensitizers and/or products were separated when possible, by preparative tlc or column chromatography on silica gel.

4-4-1 Benzophenone sensitization

a) in methanol

A solution of $Cu(acac)_2$ (150 mg, 0.57 mmol), benzophenone (112 mg, 0.64 mmol) in methanol (100 ml) was irradiated to give a black solid after ~3 h. Irradiation for 18 h gave metallic copper suspension. The filtered solution showed no absorption at 630 nm. Copper (98%) was separated by filtration using a sintered glass funnel. A cold trap containing 15 ml of 2,4-DNPH solution was used to trap volatile compounds during filtration. A yellow precipitate was filtered, washed and dried under vacuum to give the 2,4-dinitrophenylhydrazone of formaldehyde

(55 mg, 46%); the solid was recrystallized from methanol-H_2O; mp 166-168° (lit mp 166°) (154). The filtrate was evaporated in a flash evaporator to give a solid (107 mg, 96%); mp 48-50°; the ir spectrum superimposable with that of benzophenone. The distillate was analyzed by hplc to give one peak corresponding to acetylacetone. The uv spectrum of distillate (100-fold dilution) showed λ_{max} 273 nm, OD = 0.52. The yield of acetylacetone was estimated from the OD (0.76 mmol, 67%).

In a similar experiment, a solution of $Cu(acac)_2$, benzophenone in methanol was irradiated to give a black solid after ~2.5 h. The solid was quickly filtered and washed with the solvent; ir (nujol) 1580(s), 1550(s), 1530(s), 1220(m), 1190(w), 1020(m), 940(m), 785(m) cm^{-1}.

In another experiment, a similar solution of $Cu(acac)_2$ and benzophenone in methanol was irradiated for 3 h to give a black solid. The photolysate was divided in two parts. One part was left under nitrogen for 12 h to give a blue solution and metallic copper; uv (after filtration) showed that the $Cu(acac)_2$ absorption had decreased ~50% from the original absorption. The other part was left exposed to the air for 12 h to give a blue solution. Uv showed no decrease in the $Cu(acac)_2$ absorption.

In a related experiment, metallic copper (powder, Koch light lab, 0.32 g, 5 mmol) was treated with a solution of acetylacetone (1.0 g, 10 mmol) in methanol (50 ml) and left at room temperature with stirring for 24 h to give a blue precipitate. The solution was evaporated and the residue was treated with $CHCl_3$ (20 ml) and filtered. The blue filtrate was evaporated to give $Cu(acac)_2$ (0.92 g, 69.6%); mp 228-230° d (lit 230° d) (155); ir (KBr) 1580(s), 1550(s), 1530(s), 1420(m), 1357(m), 1278(m), 1192(w), 1020(m), 940(w), 785(s), 685(w) and 653(m) cm^{-1}.

b) <u>in ethanol</u>

A solution of $Cu(acac)_2$ (120 mg, 0.46 mmol), benzophenone (112 mg, 0.64 mmol) in ethanol (100 ml) was irradiated to give a black solid after ~1 h. After 3 h metallic copper suspension was observed and the absorption of filtered aliquot had disappeared. Usual work-up of the photolysate gave copper (~100%), acetylacetone (0.77 mmol, 84%), benzophenone (104 mg, 94%) and the 2,4-DNPH of acetaldehyde (29 mg, 28%); mp 146-148° (lit mp 147°) (154).

In a similar experiment, a solution of $Cu(acac)_2$ and benzophenone in ethanol was irradiated to give a black solid after 1 h. The solid was quickly filtered and washed with the solvent; ir (nujol) 1580(s), 1550(s), 1530(s), 1190(w), 1020(m), 940(m), and 785(m) cm^{-1}.

c) in isopropyl alcohol

A solution of Cu(acac)$_2$ (50 mg, 0.19 mmol), benzophenone (112 mg, 0.64 mmol) in isopropyl alcohol (100 ml) was photolyzed to give a black solid after 15 min. After 1 h copper suspension was formed and no absorption at 630 nm was observed. Copper (98%) was filtered out and determined by the usual method. The filtrate was distilled (3 ml) into a receiver containing a 2,4-DNPH solution to give a yellow solid, which was recrystallized from ethanol-H_2O to give the 2,4-DNPH of acetone (33 mg, 73%); mp 124-126.5° (lit mp 126°) (154). The remainder of the filtrate was evaporated to give benzophenone (98 mg, 88%). Hplc analysis of the distillate showed the presence of acetylacetone (0.29 mmol, 76%) as determined by its absorption at λ_{max} 273 nm.

d) in tetrahydrofuran (THF)

A solution of Cu(acac)$_2$ (200 mg, 0.77 mmol), benzophenone (164 mg, 0.94 mmol) in THF (100 ml) was irradiated to give a black solid after 3.5 h. After 7 h metallic copper was formed and the absorption at 630 nm disappeared. Copper (43 mg, 89%) was filtered. The filtrate was flash evaporated to give a yellow oil (214 mg).

e) in acetic acid

A solution of Cu(acac)$_2$ (250 mg, 0.96 mmol) and benzophenone (500 mg, 2.75 mmol) in acetic acid (80 ml) was irradiated under nitrogen with a 200-Watt lamp for 10 h to give metallic copper suspension. The filtrate, after removing copper was diluted with water (180 ml) and then extracted with ether (3 × 50 ml). The ether extracts were washed with 5% Na_2CO_3 solution, water and dried over $MgSO_4$. The solvent was evaporated to give a dark yellow oil (0.564 g). Column chromatography on silica gel using CH_2Cl_2 as eluent afforded benzophenone (0.4 g, 80%) and the following compounds: 1,1-diphenylacetone, <u>2-1</u> (33 mg, 8%) (53); nmr ($CDCl_3$) δ 2.07(s,3H), 5.0(s,1H), ~7.3(m, 10H); ms m/e (%) 210(M^+,4.0), 167(100), 43(12); 1,1-diphenyl-1-buten-3-one, <u>2-2</u> (18 mg, 4%) (156), nmr ($CDCl_3$) δ 1.90(s, 3H), 6.37(s,1H), ~7.3(m,10H); ms m/e (%) 222(M^+,58), 221(100), 207(53), 178(88), 105(99), 77(74), 43(92). Elution with 1% CH_3OH in CH_2Cl_2 afforded the diketo ether, <u>2-3</u> (41 mg, 11%), nmr ($CDCl_3$) δ 2.15(s,3H), 3.73(s,2H), 7.3(m,10H); ir (neat) 3500-3400(m,b), 1720(s), 1360(s), 1100(s,b), 760(m), 710(s) cm^{-1}; ms m/e (%) 239(96), 183(43), 167(46), 105(100), 77(30), 57(58), 43(49).

<u>Photolysis of Benzophenone and Acetylacetone</u>

A solution of benzophenone (2.0 g, 11 mmol) and acetylacetone (6.4 g, 64 mmol) in acetic acid (200 ml) was irradiated through a Pyrex filter under nitrogen with a 450-Watt mercury lamp for 10 h. The photolysate was diluted with water (400 ml) and extracted with ether

(3 × 50 ml). The ether extracts were washed with 5% sodium carbonate and water, dried over $MgSO_4$, and evaporated to give a yellow residue (2.62 g). Treatment with pentane afforded a solid which was recrystallized from ether-pentane to give cis-2,2-diphenyl-3-hydroxy-3-methyl-4-acetyloxetane, 2-4 (0.756 g, 24.4%); mp 109-112°; ir (nujol) 3500(s), 1715(s), 1170(m), 1070(m), 980(s), 765(s), 710(s) cm^{-1}; ir (dilute CCl_4 solution) 3550(s,sharp), 3500-3200(w,b), 1728, 1710 cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.37 (S,3H), 2.17(s,3H), 2.73(s,1H,D_2O exch), 4.92(s,1H), 7.5(m,10H); ^{13}C nmr ($CDCl_3$) 208.3(s), 142.7(s), 141.1(s), 129.0(d), 128.8(d), 128.2(d), 128.0(d), 126.6(d), 125.7(d), 95.7(s), 89.8(d), 81.4(s), 28.2(q), 25.7(q) ppm; ms m/e 282(M^+,0.1), 239(44), 183(68), 165(40), 105(100), 77(33); ms (CI) m/e 283(29.7,M^++H^+), 311(0.6,$M^++C_2H_5^+$), 325(0.1, $M^++C_3H_7^+$). Anal. calcd. for $C_{18}H_{18}O_3$: C 76.55%; H 6.49%. Found: C 76.48%; H 6.51%.

The filtrate (1.79 g) was chromatographed on silica gel. Elution with CH_2Cl_2 gave recovered benzophenone (36%) and a fraction of 2-1 (6%) contaminated with benzophenone as shown by vpc and nmr analysis. Elution with 1% CH_3OH in CH_2Cl_2 gave 2-3 (14%) as a yellow oil, as shown by ir and nmr.

4-4-2 Fluorenone sensitization

a) in methanol or isopropyl alcohol

A solution of Cu(acac)$_2$ (100 mg, 0.38 mmol) and fluorenone (200 mg, 1.10 mmol) in 100 ml of solvent was irradiated for 28 h. The visible spectra of the photolysate showed no decrease in the Cu(acac)$_2$ absorption at 630 nm. After work-up, Cu(acac)$_2$ and fluorenone were recovered.

4-4-3 1-Cyanonaphthalene sensitization

a) in methanol

Cu(acac)$_2$ (100 mg, 0.38 mmol) in methanol (100 ml) was irradiated in the presence of 1-cyanonaphthalene (100 mg, 0.65 mmol) for 48 h. The precipitate was filtered off, washed with methanol and dried under vacuum to give a blue solid (2-10, 15 mg); mp 205-209° d; ir (KBr) 2820(m), 1590(s), 1530(s), 1400(m), 1360(s), 1275(m), 1070(m), 1025(s), 775(s), 560(s) and 460(m) cm^{-1}; ms (%) 386(M^+,0.6), 355(1.0), 324(20.4), 261(100), 246(75), 231(56), 225(6.4) and 43(41). Anal. calcd. for $C_6H_{10}O_3Cu$: C 37.21; H 5.16. Found: C 36.81; H 5.04.

After work-up of the filtrate, 76 mg of Cu(acac)$_2$ were recovered. Analysis by vpc indicated that 1-cyanonaphthalene was recovered (89 mg).

Preparation of [Cu(acac)(OMe)]$_2$

In a separate experiment, [Cu(acac)(OMe)]$_2$, 2-10, was prepared by the method of Bertrand and Kaplan (69). $Cu(acac)_2$ (0.9 g, 3.5 mmol) was dissolved in hot methanol (150 ml) and the solution placed in a 250 ml three-necked round-bottom flask fitted with a nitrogen inlet tube, a reflux condenser and a dropping funnel containing a methanolic KOH solution (195 mg/50 ml). The KOH solution was added dropwise within 15 min and the mixture was refluxed under nitrogen for 4 h. Filtration of the hot solution afforded a blue-violet solid which was washed with cold methanol and dried under vacuum (530 mg); mp 204-209° d; ir and ms were identical to the product obtained above.

b) in ethanol or THF

Solutions of $Cu(acac)_2$ (80 mg) and 1-cyanonaphthalene (80 mg) were irradiated for 48 h. After the usual work-up the starting materials were quantitatively recovered.

4-4-4 Phenyl alkyl ketones

All the irradiations were carried out on Apparatus II using a 200-Watt Hg lamp.

a) acetophenone

A solution of $Cu(acac)_2$ (50 mg, 0.192 mmol) and acetophenone (480 mg, 4.8 mmol) in methanol (40 ml) was irradiated for 5 h to give metallic copper suspension.

The photolysate was analyzed by vpc (on SE-30, capillary, 15 mt, 80-220° at 15°/min) and showed a minor peak at 1.2 and a major peak at 1.8 min corresponding to acetylacetone and acetophenone as shown by coinjection with authentic samples.

b) <u>butyrophenone</u>

A solution of $Cu(acac)_2$ (100 mg, 0.38 mmol) and butyrophenone (700 mg, 4.7 mmol) in methanol (40 ml) was irradiated for 5 h to give metallic copper. The light blue photolysate was treated with water (100 ml) and extracted with ether (2 × 25 ml). The blue extracts were washed with water and dried over $MgSO_4$. The ether solution was analyzed by vpc (same conditions as above) and showed one minor peak at 2.2 min corresponding to acetophenone, <u>2-8</u>, (3%) and a major peak at 5.0 min corresponding to butyrophenone (97%). Peaks were identified by peak matching and yields were estimated from vpc peak areas.

c) <u>valerophenone</u>

A solution of $Cu(acac)_2$ (50 mg, 0.19 mmol) and valerophenone (700 mg, 4.3 mmol) in methanol (40 ml) was irradiated for 5 h to give metallic copper and a yellow solution. After the usual work-up and evaporation of the solvent a yellow liquid (0.504 g) was obtained; nmr ($CDCl_3$) δ 1.0(t,J~7 Hz), 1.6(m), 2.55(s), 2.95(t,J~7 Hz), 7.47(m), 7.83(m) ppm. Except for the singlet at 2.55, the spectrum was identical to that of valerophenone. The vpc analysis of the oil (same conditions as above) showed three peaks at 1.7, 3.7 and 4.1 min. Analysis by gc-ms gave the following results: the peak at 1.7 min, acetophenone (41%), m/e 120(M^+,46), 108(100), 77(89); at 3.7 min, 2-methyl-1-phenylcyclobutanol (8%), (61), m/e 162(M^+,3.0), 134(34), 133(39), 120(100), 105(88), 78(30); at 4.1 min, valerophenone (51%) (157), m/e 162(M^+,12), 120(82), 105(100), 77(84). Yields were estimated from vpc peak areas.

d) γ-methylvalerophenone

A solution of Cu(acac)$_2$ (50 mg, 0.19 mmol) and γ-methylvalerophenone (704 mg, 4.0 mmol) in methanol (40 ml) was irradiated for 5.0 h to give metallic copper. After the usual work-up and evaporation of the solvent a yellow viscous liquid (0.513 g) was obtained; nmr ($CDCl_3$) δ 0.93(d), ~1.62(m), 2.54(s), 2.92(t), 7.43(m), 7.87(m) ppm. Except for a singlet at 2.54 ppm, the spectrum was identical to that of γ-methylvalerophenone. The vpc analysis of the oil (same conditions as above) showed three peaks at 1.8, 4.0 and 4.7 min that were identified by gc-ms to be acetophenone (63%), 1.8 min, m/e 120(M^+,82), 105(100), 77(96); 2,2-dimethyl-1-phenylcyclobutanol (11%), 4.0 min (61), m/e 176(M^+,6.0), 120(100), 105(64), 78(25);

γ-methylvalerophenone (26%), 4.7 min (158), m/e 176(M^+,5), 120(91), 105(100), 77(73). Yields were estimated from vpc peak areas.

4-4-5 Other sensitizers

a) xanthone

A solution of $Cu(acac)_2$ (100 mg, 0.38 mmol) and xanthone (250 mg, 1.27 mmol) in methanol (100 ml) was irradiated for 8 h to give metallic copper suspension. A 50% decrease was observed in the 630 nm band. The usual work-up of the solution gave copper (48%) and acetylacetone (30%) determined as before. $Cu(acac)_2$ and xanthone were recovered in 40% and 96%, respectively.

b) biacetyl

A solution of $Cu(acac)_2$ (100 mg, 0.38 mmol) and biacetyl (5 g, 48 mmol) in ethanol (120 ml) was irradiated to give a black solid after 1 h. After 6.5 h metallic copper was formed and no absorption was observed at 630 nm. Copper was filtered and determined as usual in 81% yield. The filtrate was analyzed by vpc to show two major and five minor peaks. The major peaks were shown to be biacetyl and acetyl acetone by peak matching.

c) anthrone

A solution of $Cu(acac)_2$ (100 mg, 0.38 mmol) and anthrone (86 mg, 0.45 mmol) in ethanol (120 ml) was irradiated to give a black solid after 15 min. Irradiation for 3.5 h gave a metallic copper suspension and the solution showed no absorption at 630 nm. Filtration attempts were unsuccessful due to the colloidal nature of copper. The solution was flash evaporated to give a red-brown solid (99 mg). After treatment with ether, copper (92%) was filtered as usual. The filtrate was evaporated to give a yellow solid (74 mg). Treatment with acetone (10 ml) gave an unidentified white solid (~8 mg); mp 136-142°; ir (KBr) ~3500(m), 1470(m), 1190(w), 1035(m), 780(s), 740(m), 700(s), 670(m), 650(w), 640(s) cm^{-1}. Vpc analysis of the filtrate showed one major peak, matching in retention time with anthrone (92% recovery), and one unidentified minor peak. Acetylacetone (68%) was determined by uv from the distillate.

d) benzil

A solution of $Cu(acac)_2$ (50 mg, 0.19 mmol) and benzil (250 mg, 1.19 mmol) in methanol (40 ml) was irradiated in apparatus II with a 200-Watt Hg lamp to give a black precipitate after 30-40 min. Continued irradiation for 4 h gave metallic copper. The yellow photolysate was treated with water (100 ml) and extracted with ether (2 × 25 ml). The ether extracts were washed with water and the solvent evaporated to give a yellow oil (260 mg). Vpc analysis (on SE-30, 100-220° at 15°/min) showed three peaks at 1.3, 4.8 and 6.3 min which were examined by gc-ms; peak at 1.3, unknown (< 5%), m/e 136(50.2), 105(100), 77(40); peak at 4.8 min, unknown (~28%), m/e 186(0.2), 162(0.1), 151(0.8), 105(100), 77(26); peak at 6.3 min, benzil (~63%), m/e 210(M^+,5), 105(100), 77(57). Relative yields were estimated from vpc peak areas.

e) anthracene

A solution of $Cu(acac)_2$ (100 mg, 0.38 mmol) and anthracene (100 mg, 0.56 mmol) in methanol (100 ml) was photolyzed to give white crystals after 15 min. Irradiation for 28 h showed an ~60% decrease in absorption at 630 nm. Formation of copper was not observed. The solution was filtered to give anthracene dimer (76 mg, 76%); mp 274-276° (lit mp 275°) (68). The filtrate was flash evaporated to give a blue solid (120 mg). Analysis by tlc on silica gel (elution with CH_2Cl_2) showed two major spots (R_f ~0.95 and 0.15) and one minor spot (R_f ~0.5). Preparative tlc on silica gel (elution with CH_2Cl_2) gave $Cu(acac)_2$ (85 mg, 85%), anthracene (18 mg, 18%) and an unidentified solid (8 mg): ir (KBr), 2940(w), 1720(s), 1680(m), ~1600(m), 1450(m), 1290(m), 920(w), 740(s), 695(m) and 670(w) cm^{-1}.

f) phenothiazine

A solution of $Cu(acac)_2$ (100 mg, 0.38 mmol) and phenothiazine (120 mg, 0.6 mmol) in ethanol (120 ml) was irradiated for 48 h to give a dark brown solution. The absorption at 630 nm decreased about 60%. The solution was flash evaporated to give a brown solid (176 mg). After treatment with acetone (20 ml) a blue solid (56 mg) was separated; the ir spectrum was superimposable with that of Cu(acac)$_2$ (56%) (155). Analysis of the filtrate by vpc showed only one peak corresponding to phenothiazine by comparison with authentic sample.

g) 2-acetonaphthone

A solution of Cu(acac)$_2$ (50 mg, 0.19 mmol) and 2-acetonaphthone (25 mg, 0.15 mmol) in methanol (40 ml) was irradiated in apparatus II with a 200-Watt Hg lamp to give a black solid after ~1.5 h. Irradiation for 5 h gave metallic copper suspension and a colorless solution. Filtration attempts were unsuccessful due to the colloidal nature of copper. The solution was flash evaporated to give a red-brown solid (63 mg). After treatment with ether copper (73%) was filtered. The filtrate was evaporated to give a white solid (22 mg). Vpc analysis (on SE-30, 100-220°, 15°/min) showed two peaks at 1.8 min for acetylacetone and at 8.9 min for 2-acetonaphthone.

h) carbazole, phenanthrene, pyrene, perylene and p-methoxyacetophenone

A solution of Cu(acac)$_2$ (100 mg, 0.38 mmol) and the sensitizer[1] in ethanol (120 ml) was photolyzed for 24 h. No decrease was observed in the absorption of the 630 nm band. After work-up the unchanged starting materials were recovered.

---

[1] See Table 2-2 for sensitizer concentrations.

4-5 Photolysis of $Cu(acac)_2$ in the Presence of Various Ligands

4-5-1 Triphenylphosphine

A solution of $Cu(acac)_2$ (100 mg, 0.38 mmol), benzophenone (112 mg, 0.64 mmol) and triphenylphosphine (240 mg, 0.92 mmol) in ethanol (100 ml) was irradiated for 2 h to give a colorless solution. The absorption at 630 nm had disappeared. The solution was distilled and the distillate was worked-up as usual to give acetaldehyde (42%) and acetylacetone (80%). The residue was treated with ether and filtered to give a white solid (242 mg, 92%); mp 176-179°; ir (nujol) 1598(s), 1583(s), 1508(m), 745(s) and 700(m) cm^{-1}; nmr ($CDCl_3$) δ 1.76(s,6H), 5.08(s,1H) and 7.21(s,30H). The ir and nmr spectra were identical with those of $Cu(acac)(PPh_3)_2$ (52). Anal. calcd for $C_{41}H_{37}CuO_2P_2$: C 71.65; H 5.40. Found: C 71.76; H 5.56.

The filtrate was evaporated to give a white solid (171 mg). Preparative tlc on silica gel (elution with CH_2Cl_2) afforded benzophenone (109 mg, 97%) and PPh_3 (43 mg, 0.16 mmol).

4-5-2 2,5-Dithiahexane

A solution of $Cu(acac)_2$ (300 mg, 1.15 mmol), 2,5-dithiahexane (141 mg, 1.15 mmol) and benzophenone (400 mg, 2.7 mmol) in methanol (220 ml) was photolyzed under nitrogen with a 200-Watt Hg lamp to give a yellow solution after 20 min. A sample taken and exposed to the air became blue within ~30 sec. A fraction of the yellow photolysate (2 ml) was treated with a methanol solution of α,α'-bipyridyl (2 ml, 6 × 10^{-3} M) under nitrogen to give a red solution showing λ_{max} 427 nm (λ_{sh} 550 nm). On exposure to the air the solution gradually turned blue in ~10 min. To the remainder of the photolysate, triphenylphosphine (600 mg) in methanol (30 ml) was added under nitrogen. After 10 h the solution was evaporated to give a brown oil (949 mg). Treatment with ether (25 ml) and filtration afforded $Cu(acac)(PPh_3)_2$ (382 mg) (52); mp 165-170°; the ir and nmr spectra were identical with those of an authentic sample. Vpc analysis of the filtrate (on 10% SE-30, 80-240° at 15°/min) showed the presence of 2,5-dithiahexane (2.3 min), benzophenone (7.6 min) and triphenylphosphine (11.9 min) by comparison with authentic samples.

In a separate experiment, a methanol solution (5 ml) of $Cu(acac)_2$ (1.15 × 10^{-2} M), benzophenone (1.1 × 10^{-1} M) and 2,5-dithiahexane (2.3 × 10^{-2} M) was irradiated under nitrogen in a 1 cm uv cell with a 200-Watt Hg lamp (Pyrex jacket) for 3 h to give a yellow solution. The solution exhibited absorption maxima at λ 575 nm (OD = 1.64, ε = 140). Continued irradiation for two additional hours did not cause any change (no copper metal was formed).

4-5-3 α,α'-Bipyridyl

A solution of $Cu(acac)_2$ (300 mg, 1.15 mmol), benzophenone (400 mg, 2.2 mmol) and α,α'-bipyridyl (180 mg, 1.15 mmol) in methanol (200 ml) was irradiated (200-Watt Hg lamp) under nitrogen to give a red solution after 30 min. Uv spectra showed no absorption at 630 nm but a new absorption at ~550 nm. A sample taken and exposed to the air became blue within 30-60 sec. A fraction of the red solution (~100 ml) was treated with a methanolic solution of triphenylphosphine (10 mg) under nitrogen to give a colorless solution after ~5 h. The solvent was evaporated and the residue treated with ether (30 ml) to give, after filtration, $Cu(acac)(PPh_3)_2$, 2-7 (105 mg); mp 175-178°; ir spectrum identical to that of an authentic sample. The remainder of the red solution was irradiated for additional 18 h to give metallic copper. After the usual work-up, vpc analysis (on 10% SE-30, 100-200° at 10°/min) of the crude product showed the presence of α,α-bipyridyl (8.6 min) and benzophenone (12.6 min). The product was analyzed by gc-ms (on OV-101, 80-220° at 12°/min) to give the following mass spectra: for peak at 8.6 min, m/e 156(M^+,100), 78(20), 51(13) and for peak at 12.6 min, m/e 182 (M^+,75).

In a separate experiment, a methanol solution (5 ml) of $Cu(acac)_2$ (7.2×10^{-4} M), benzophenone (1.72 ×

10^{-3} M) and α,α'-bipyridyl (1.44×10^{-3} M) was irradiated under nitrogen in a 1 cm uv cell with a 200-Watt Hg lamp (Pyrex jacket) to give a red solution. At each 30 sec interval, uv spectra were recorded to show emergence of new maxima at 427 and 520 (shoulder) nm. After 8 min of irradiation, the optical density at λ_{max} 427 nm reached a stationary state of 1.845 (ε 2500). Further irradiation did not increase the O.D.

4-5-4 Ethylenediamine

A dark blue solution (λ_{max} 595 nm, ε = 694) of $Cu(acac)_2$ (100 mg, 0.38 mmol), benzophenone (138 mg, 0.76 mmol) and ethylenediamine (46 mg, 0.76 mmol) in methanol (40 ml) was irradiated under nitrogen to give a pale yellow solution in 1.5 h. The color immediately became the original deep blue within seconds after exposure to the air. A fraction of the yellow solution was treated with PPh_3 to give a colorless solution. The usual work-up afforded $Cu(acac)(PPh_3)_2$; mp 176-179°. The remainder of the yellow solution was irradiated for another one-half hour to give metallic copper.

4-5-5 Styrene

Irradiation of $Cu(acac)_2$ (500 mg, 1.92 mmol), benzophenone (1.0 g, 5.5 mmol) and styrene (1.0 g, 9.61 mmol) in methanol (200 ml) under nitrogen proceeded slowly. In 3 h the solution became pale blue but no black precipitate was formed. This solution immediately turned to a blue color on exposure to the air. Part of this solution was reacted with PPh_3 in methanol under nitrogen to give $Cu(acac)(PPh_3)_2$; mp 170-175°. The remainder of the solution was irradiated for five additional hours to give metallic copper. The photolysate was diluted with water (300 ml) and extracted with ether (3 × 50 ml) in the usual manner to give a crude oil (1.42 g); vpc analysis (on 10% SE-30, 120-240° at 10°/min) showed two peaks with retention times of 1.2 and 5.0 min, identified as styrene and benzophenone respectively, by coinjection with authentic samples.

4-5-6 Norbornene

On irradiation of a methanol solution (200 ml) of $Cu(acac)_2$ (500 mg, 1.92 mmol), benzophenone (1.0 g, 5.5 mmol) and norbornene (800 mg, 8.5 mmol) a red solution developed in 30 min and became more intense in 2 h. After 3 h of irradiation, metallic copper was formed as suspension and the solution became colorless. After filtration, the solution was diluted with water (400 ml) and extracted with ether (3 × 40 ml) to give a yellowish oil (1.892 g). Vpc analysis (on OV-101, 80-220° at 12°/min) showed five peaks with retention times of 1.8, 2.0, 13.0, 13.6 and 20.0 min. The gc-ms showed for the peak at 1.8 min, norbornene (21%), m/e 94(M^+,13), 65(100); at 2.0 min, acetylacetone; at 13.0 min, benzophenone (82%); at 13.6 min, benzhydrol (15%), m/e 184(M^+,45), 165(14), 105(100), 77(51); at 20.0 min, oxetane 2-18 (3%), m/e 276(M^+, 24), 205(12), 183(100). %yields are based on benzophenone.

4-5-7 Bis-(2-methoxyethyl)ether

A solution of Cu(acac)$_2$ (250 mg, 0.95 mmol), benzophenone (500 mg, 2.75 mmol) and bis-(2-methoxyethyl)ether (650 mg, 4.75 mmol) in methanol was irradiated under nitrogen to give metallic copper after 15 min. In 25 min the solution became colorless and a shiny copper mirror was formed. The photolysate was worked up as usual to give a pale yellow liquid (892 mg). Vpc analysis (on 10% SE-30, 100-220° at 10°/min) showed three peaks at 2.1, 2.7 and 7.4 min, assigned to acetylacetone, diglyme and benzophenone respectively by coinjection with authentic samples.

4-5-8 1,10-Phenanthroline

A methanol solution (5 ml) of Cu(acac)$_2$ (1.44×10^{-4} M), benzophenone (1.72×10^{-3} M) and 1,10-phenanthroline (2.88×10^{-4} M) was irradiated under nitrogen in a 1 cm uv cell with a 200-Watt Hg lamp (Pyrex jacket) to give a red solution. At each 4-min interval a uv spectrum was recorded until a stationary state was reached. After 25 min, the solution exhibited absorption maxima at

430 nm (O.D. 1.10, ε 7600) and 570 nm (O.D. 0.38, ε 2600). Further irradiation did not increase the O.D.

4-5-9 Carbon monoxide

A solution containing Cu(acac)$_2$ (1.2×10^{-2} M) and benzophenone (6×10^{-2} M) in methanol-methylene chloride (1:1, 5 ml) was irradiated under carbon monoxide for 5.5 h to afford a colorless solution. The ir spectrum of the solution showed weak absorption at ~2100 cm^{-1}. The solution rapidly changed to a blue color on exposure to the air. Continued irradiation (2 h) of the colorless solution caused the deposition of metallic copper.

4-6 Photolysis of Cu(acac)$_2$ in the Presence of Acetylenes

Phenylacetylene (bp 142-144°, Aldrich), 1-hexyne (bp 71-72°, K & K), 1,5-hexadiyne (bp 86°, K & K), 3,5-dimethyl-1-hexyn-3-ol (bp 149-151°, AIRCO) were all distilled before use. Diphenylacetylene (mp 59-61°, Aldrich) was used without purification.

t-Butylacetylene was synthesized using a modification of the Bartlett-Rosen procedure (159,160).

To 12.0 g (0.12 mol) of cold (0°C) of pinacolone (bp 104-106°, MCB) was added during 2 h, 26 g (0.12 mmol) of powdered PCl$_5$ (Fischer). The mixture was stirred for 3 h at 0° and then poured into 75 g of ice. The product was then extracted with ether (3 × 50 ml). After washing with H_2O the ether extract was dried and carefully concentrated under reduced pressure on a rotary evaporator until the crude product just began to sublime, to give a yellow semisolid (16.25 g, ~88%). Analysis by vpc (on 10% SE-30, 70° isoth) showed two peaks with retention times of 2.8 and 9.8 min. By gc-ms, a peak at 2.8 min was shown to be 3,3-dimethyl-2-chloro-1-butene; m/e 118(M^+,36), and the peak at 9.8 min pinacolone dichloride; m/e 154(M^+,1.0); nmr ($CDCl_3$) δ 1.19(s,9H), 1.22(s,9H), 2.13(s,3H) and 5.1(m,2H) ppm. The nmr integration showed the crude product contained ~66% of the dichloride and ~34% of the chloro olefin in addition to some diethyl ether. The crude mixture, in 20 ml of DMSO (Fischer), was slowly added to a solution of potassium t-butoxide (24.5, 0.219 mol, Alfa) in DMSO (50 ml) at a rate sufficient to maintain the temperature below 40°. After the addition was complete, the reflux condenser was replaced by a distilling head and nitrogen passed through the reaction mixture. The reaction flask was heated on an oil bath, its temperature gradually increasing to 90-95°. Material boiling up to 35° was collected to give a colorless liquid (~5 ml); nmr (neat) δ 1.18(s,9H) and 2.03(s,1H) ppm; nmr integration showed the product contained about 35% of ether. Spinning band distillation afforded pure t-butylacetylene (bp 34-35°); ms m/e 82(M^+,4), 81(23), 67(100) and 41(63).

4-6-1 Phenylacetylene

A solution of $Cu(acac)_2$ (500 mg, 1.91 mmol), benzophenone (1.0 g, 5.5 mmol) and phenylacetylene (500 mg, 4.9 mmol) in methanol (200 ml) was irradiated (with a 200-Watt Hg lamp) under nitrogen for 2 h to give a yellow solid. The solution was filtered to give the yellow copper(I)phenylacetylide (112 mg, 36%); mp 230° d (lit mp 230-235°) (78); ir (nujol) 1930(w), 1485(m), 750(s) and 690(s) cm^{-1}. The pale blue filtrate was diluted with water (200 ml) and extracted with ether (3 × 50 ml). The ether extract was washed with water (3 × 50 ml), dried and evaporated to give a pale yellow liquid (1.243 g). Analysis by vpc (on 10% SE-30, 100-240° at 10°/min) showed acetylacetone (rt 1.2 min), phenylacetylene (rt 1.7 min) and benzophenone (rt 7.3 min) matching with authentic samples.

The cuprous phenylacetylide (180 mg, 1.1 mmol) was added to a solution of iodobenzene (224 mg, 1.1 mmol) in dry pyridine (25 ml), under nitrogen with stirring. The mixture was heated on an oil bath at 120° for 8 h. The solution was cooled and diluted with water (100 ml). After filtration the mixture was extracted with ether (3 × 25 ml). The ether extracts were washed with dilute HCl, 5% $NaHCO_3$ solution and water and then dried and evaporated to give a dark yellow liquid (271 mg). Analysis by vpc showed four peaks with retention times of 2.0, 4.0, 8.5 and 13.0 min. By peak matching with authentic samples, peaks at 2.0, 4.0 and 13.0 min were assigned to phenylacetylene (38%), iodobenzene and diphenylacetylene (62%), respectively. Analysis by gc-ms showed for the peak at 8.5 min, 1-iodo-phenylacetylene (<3%), m/e 228(M^+,100), 101(23). Products were not isolated and yields were estimated from vpc areas.

The cuprous acetylide (50 mg, 3.05 mmol) was also treated with triphenylphosphine (80 mg, 3.05 mmol) in acetonitrile (10 ml) and the mixture left under nitrogen at room temperature for 12 h. The solvent was evaporated under vacuum and the residue treated with hot toluene (10 ml) and filtered while hot. Petroleum ether (30-60°) was added to the filtrate while heating until cloudy and cooled at 0°C for 6 h. Filtration afforded pale yellow needles of phenylethynyl(triphenylphosphine)copper(I) (71 mg, 55%); mp 201-203° (lit mp 202-204° d) (75); ir (nujol) 2030(m), 1435(s), 750(s) and 700(s) cm^{-1}. Anal. calcd. for $C_{26}H_{20}CuP$: C 73.17; H 4.69. Found: C 72.92; H 4.76.

In a separate experiment a solution of $Cu(acac)_2$ (250 mg, 0.95 mmol) and benzophenone (500 mg, 2.74 mmol) in methanol (100 ml) was irradiated under nitrogen for 15 min to give a black solid. Phenylacetylene (930 mg, 9.1 mmol) was added and the reaction mixture left under nitrogen for 2 h. Some metallic copper was formed and the solution turned to pale blue. No yellow solid was formed.

In a large scale experiment using a "hamburger" type cell (described in Ref. 161) a solution of Cu(acac)$_2$ (2.5 g, 9.57 mmol), benzophenone (5.0 g, 27.4 mmol) and phenylacetylene (2.5 g, 25 mmol) in methanol (1000 ml) was irradiated with a 140-Watt Hg lamp for 12 h to give a yellow precipitate of copper(I)phenylacetylide (1.12 g, 72%).

4-6-2 <u>1-Hexyne</u>

A solution of Cu(acac)$_2$ (500 mg, 1.91 mmol), benzophenone (1.0 g, 5.5 mmol) and 1-hexyne (315 mg, 3.84 mmol) in methanol (200 ml) was irradiated under nitrogen for 4 h to give a yellow-green solid. Filtration afforded the yellow-green cuprous n-butylacetylide (248 mg, 89.9%); mp 145-185° d (lit mp 182° d) (77); ir (nujol) 1927(m) cm^{-1}. The pale blue filtrate was diluted with water and extracted with ether (3 × 50 ml). The ether extracts were washed with water (2 × 100 ml), dried and evaporated to give a colorless oil (1.182 g). Analysis by vpc showed three peaks corresponding to acetylacetone (rt 1.7 min, ~74%), 1-hexyne (rt 2.0 min) and benzophenone (rt ~7.9 min), by comparison with authentic samples.

Cuprous n-butylacetylide (185 mg, 1.3 mmol) was added to a solution of iodobenzene (224 mg, 1.15 mmol) in dry pyridine (25 ml) and was refluxed under nitrogen for 9 h and worked up as above to give a yellow-brown liquid (187 mg). Analysis by vpc showed two peaks with retention times of 4 and 5.4 min. Gc-ms analysis (on 10% SE-30, 80-200°, 20% min) showed the first peak to be iodobenzene; the second peak was 1-phenylhexyne (16%, det. by nmr), m/e 158(M^+18), 115(100) and 77(13).

4-6-3 t-Butylacetylene

A solution of $Cu(acac)_2$ (500 mg, 1.91 mmol), benzophenone (1.0 g , 5.5 mmol) and t-butylacetylene (400 mg, 10.9 mmol) in methanol (200 ml) was irradiated under nitrogen for 1.5 h to give a yellow solution. The photolysate was diluted with H_2O (200 ml) and extracted with ether (3 × 50 ml). After washing with water (2 × 70 ml), the ether extract was dried and evaporated to give an orange semi-solid (1.104 g). The product was chromatographed on silica gel and elution with methylene chloride gave benzophenone (0.984 g). Elution with ether gave cuprous t-butylacetylide (0.102 g, 37%)(78); mp 82° (d) (lit mp 80-140°) (79); ir (CCl_4) 2000 (vw) cm^{-1}; nmr (CCl_4) δ 1.33(s).

4-6-4 1,5-Hexadiyne

A solution of $Cu(acac)_2$ (500 mg, 1.91 mmol), benzophenone (1.0 g, 5.5 mmol) and 1,5-hexadiyne (0.8 g, 10.3 mmol) in methanol (200 ml) was irradiated under nitrogen for 1 h. The photolysate was filtered to give the cuprous acetylide, 2-11, as a brown-yellow solid (134 mg, 69.8%); mp 140-155° (d); ir (nujol) 2120(w,broad), 1280(s), 1020(w) cm^{-1}; nmr (pyr) δ 4.07(s); (caution: explosive on drying!). The filtrate was diluted with water (200 ml) and extracted with ether (3 × 50 ml). The ether extracts were washed with water, dried over $MgSO_4$ and evaporated to give a colorless liquid (1.19 g). Vpc analysis showed two peaks with retention times of 2.1 and 7.2 min, identified by comparison with authentic samples as 1,5-hexadiyne and benzophenone respectively.

The cuprous acetylide, 2-11 (100 mg, 0.5 mmol), and iodobenzene (202 mg, 9.92 mmol) in pyridine (15 ml) were refluxed under nitrogen for 72 h and worked up as above to give a brownish liquid (190 mg). Iodobenzene was evaporated under reduced pressure and the residue (79 mg) recrystallized twice from ethanol to give 1,6-diphenyl-1,5-hexadiyne (80) as a pale yellow solid (51 mg, 44%); mp 45-48° (lit mp 48°); nmr ($CDCl_3$) 2.70(s,4H), 7.27(m, 10H); ms 230(M^+, 15), 115(100).

4-6-5 3,5-Dimethyl-1-hexyn-3-ol

A solution of $Cu(acac)_2$ (500 mg, 1.91 mmol), benzophenone (1.0 g, 5.5 mmol) and 3,5-dimethyl-1-hexyn-3-ol (500 mg, 3.96 mmol) in methanol (200 ml) was irradiated under nitrogen for 4 h. The yellow-brown solution was diluted with water (200 ml) and extracted with ether (4 × 50 ml). The ether layer was brown-yellow whereas the aqueous layer was pale blue. The ether extract was washed with water, dried over $MgSO_4$ and evaporated to give a red-brown semi-solid (2.03 g). Treatment with hot petroleum ether (30-60°) and filtration afforded a brownish solid (185 mg); ir (nujol) was identical to that of $Cu(acac)_2$. The filtrate was evaporated to give a brown semi-solid (1.24 g); vpc analysis showed two major peaks with retention times of 2.1 and 7.5 min, assigned to 3,5-dimethyl-1-hexyn-3-ol and benzophenone by coinjection with authentic samples. The nmr spectrum ($CDCl_3$) showed characteristic peaks of the alkynol (δ 1.03d, 1.56d, 1.47m, 2.00m, 2.34s and 2.44s) and benzophenone (δ ~7.3 m).

In a separate experiment a solution of $Cu(acac)_2$ (250 mg, 0.96 mmol), benzophenone (500 mg, 2.75 mmol) and 3,5-dimethyl-1-hexyn-3-ol (350 mg, 2.77 mmol) in methanol (80 ml) was irradiated under nitrogen for 1 h. To the red-brown photolysate a solution of PPh_3 (500 mg, 1.92 mmol) in methanol (10 ml) was added and the solution left under nitrogen for 1 h. The solvent was evaporated under vacuum to give a brown semi-solid (0.976 g). The solid was treated with ether (20 ml) and filtered to give $Cu(acac)(PPh_3)_2$ as a beige solid (190 mg, 30%);

The vpc analysis of the filtrate (on 10% SE-30, 100-240° at 20°/min) showed two major peaks corresponding to the alkyn-ol (1.9 min) and benzophenone (7.2 min).

In a related experiment, a solution of Cu(acac)$_2$ (100 mg, 0.38 mmol) and benzophenone (200 mg, 1.1 mmol) in methanol (30 ml) was irradiated under nitrogen for 30 min to give a black suspension. 3,5-Dimethyl-1-hexyn-3-ol (171 mg, 1.35 mmol) was added and the mixture left under nitrogen for 48 h to give a red-brown solution. The solvent was evaporated to give a brown semisolid (385 mg); nmr ($CDCl_3$) showed only peaks corresponding to the alkyn-ol and benzophenone.

4-6-6 Diphenylacetylene

A solution of Cu(acac)$_2$ (500 mg, 1.91 mmol), benzophenone (2.5 g, 13.7 mmol) and diphenylacetylene (700 mg, 3.93 mmol) in methanol (200 ml) was irradiated under nitrogen to give a white precipitate after 20 min. The photolysate was filtered through a sintered glass funnel to afford white needles of Cu(acac)PhC≡CPh), 2-13 (194mg, 29%); mp (under N_2) 115° d; ir (nujol) 1970(m), 1593(s), 1540(s), 1280(m), 1035(m), 793(m), 767(s) and 705(s) cm^{-1}; ms m/e 340 (M^+,1.0), 179(20), 178(100), 152(16); ms (by chemical ionization) m/e 356(1.0), 180(14), 179(100), 101 (7.0). The compund turned brown after 30 min of exposure to the air. It also quickly decomposed when dissolved in CH_2Cl_2, CH_3OH or acetone, to give a brown solution. The nmr of a decomposed solution (in distilled $CDCl_3$) showed the methyl signals for acetylacetone at 2.02 and 2.30 ppm and phenyl proton signal for the acetylene at 7.43 in a ratio of 6 : 10. The pale blue filtrate was diluted with water (200 ml) and extracted with ether (3x50 ml). The ether extracts were washed with water, dried over $MgSO_4$ and evaporated to give a white semisolid (2.84 g). Vpc analysis showed two peaks with retention times of 7.1 and 8.2 min corresponding to benzophenone and diphenylacetylene respectively.

In a similar experiment, a same methanol solution was irradiated under similar conditions to give a white precipitate in 25 min. Prolonged irradiation (30 min to 1 h) caused the formation of metallic copper and a colorless solution. Vpc analysis of the photolysate showed the peaks for acetylacetone (1.9 min), benzophenone (7.3 min) and diphenylacetylene (8.5 min).

The complex 2-13 (50 mg, 0.15 mmol) was treated with a solution of triphenylphosphine (100 mg, 0.38 mmol) in ether (10 ml) and the mixture stirred under nitrogen for 48 h. The solution was filtered to give a beige solid of $Cu(acac)(PPh_3)_2$ (26 mg, 25%), mp 171-176°.

4-7 Photolysis of $Cu(acac)_2$ in the Presence of Olefins

The photoreactions were carried out in apparatus III using a 450-Watt Hg lamp (Pyrex filter) unless specified otherwise. The yields were estimated from vpc peak areas of compounds derived from olefins unless specified otherwise.

4-7-1 Norbornene

a) in acetic acid

A solution of $Cu(acac)_2$ (0.5 g, 1.92 mmol), benzophenone (1.0 g, 5.55 mmol) and norbornene (0.6 g, 6.5 mmol) in glacial acetic acid (200 ml) was irradiated under nitrogen for 2.5 h to give a yellow solution. Irradiation was continued for 16 h until metallic copper was formed. The photolysate was diluted with water (400 ml) and extracted with ether (3 × 100 ml). The ether extracts were washed with 5% Na_2CO_3 solution, and water and then dried over $MgSO_4$. The solvent was evaporated to give a brown oil (1.469 g) which showed on vpc analysis (on 10% SE-30, 100-240° at 10°/min) one major peak at 11.8 min and seven minor peaks. Gc-ms showed the following spectral pattern: the peak at 3.8 min, 2-acetylnorbornane 2-15 (4% from vpc peak areas), m/e 138(M^+,4.2), 95(62), 80(70), 71(100), 67(53), 43(94); the peak at 5.2 min, 2-exo-norbornylacetone, 2-16 (11%), m/e 152(M^+,1.2), 95(16), 66_35), 43(100); the peak at 7.9 min (2.6%), m/e 152(M^+, 5.0), 95(21), 79(31), 67(100), 41(33); the peak at

9.4 min, 3-(exo-2-norbornyl)acetylacetone, 2-17 (30%); the peak at 11.8 min, benzophenone; the peak at 12.8 min, 2-1 (19%) m/e 210(M^+,2.0), 167(100), 152(19), 105(21), 77(24), 51(20), 43(36); the peak at 15.2 min, 2-2 (9%), m/e 222(M^+,62), 207(60), 178(100), 105(99), 77(74), 51(71), 43(93); peak at 25.9 min, 2-3 (20%), m/e 282(M^+, 1.0), 239(36), 183(23), 165(30), 105(100), 77(66), 57(58), 43(49).

The crude mixture (0.5 g) was chromatographed on alumina (25 g). Elution with benzene gave benzophenone (112 mg, 32% recovery), a fraction containing 2-17 (~10%) and 2-16 (~6%) (81). Continued elution with CH_2Cl_2 gave a pale yellow liquid (82 mg, 24%) showing a single peak on vpc. This liquid was distilled (81°/1.5 mm) and identified as 2-17; ir (neat) 2960(s), 2880(m), 1700(s), 1360(m) cm^{-1}; 400 MHz ^1H nmr ($CDCl_3$) δ 3.46(d, J=11.0 Hz,1H), 2.32(m,J=11.0,8.2 and 5.4 Hz by decoupling experiments,1H), 2.17(s,3H), 2.13(s,3H), 1.82(m,1H), 1.51(m,4H), 1.28(m,2H), 1.14(m,2H); ^{13}C nmr (ppm) 203.8(s, C=0), 203.5(s,c=0), 76.0(d,C_3 in acacH), 41.4(d,C_2), 39.3(d,C_1), 36.4(d,C_4), 35.8(t,C_7), 35.2(t,C_3), 29.7 and 29.4(t,C_5 and C_6), 28.9 and 28.2(t,CH_3 in acacH); hrms m/e (%) 194.1306(M^+,11.4; calcd. for $C_{12}H_{18}O_2$: 194.1307), 152.1155(49.4; calcd. for $C_{10}H_{16}O$: 152.1202), 134.1106(47.9; calcd. for $C_{10}H_{14}$: 134.1096), 101.0603(20;

calcd. for $C_5H_9O_2$: 101.0603), 94.0778(97.8; calcd. for C_7H_{10}: 94.0783), 43(100); uv (CH_3OH) λ_{max} 306 nm (sh, ε 430), 282 nm (ε 530); uv (CH_3OH/0.5 M NaOH) λ_{max} 295 nm (ε 950). On irradiation of the multiplet at δ 2.32, the doublet at δ 3.46 became a singlet. On irradiation of the doublet at δ 3.46 the multiplet at δ 2.32 was modified to a double doublet (J = 8.2 and 5.4 Hz). Anal. calcd. for $C_{12}H_{18}O_2$: C 74.23; H 9.28. Found: C 73.98; H 9.30.

The diketone, 2-17 (200 mg, 1.03 mmol) in methanol (5 ml) was treated with aqueous NaOH solution (25 mg/2 ml) and the mixture refluxed for 15 min. The solution was concentrated and extracted with ether (2 × 5 ml). The ether extracts were washed with H_2O (20 ml), dried over $MgSO_4$ and evaporated to give 2-16 (156 mg, 98%) after vacuum distillation (90-92°/10 mm); vpc analysis (on 10% SE-30, 150-240° at 10°/min) showed one single peak (rt = 4.7 min); ir (neat) 2960(s), 2880(m), 1715(s), 1355(m) cm^{-1}; ^1H nmr ($CDCl_3$) δ 2.34(m,J=3.4 Hz,2H), 2.11(s,3H), 1.90(m,2H), 0.9-1.6(m,9H); ^{13}C nmr ($CDCl_3$) 208.4(s,C=O), 50.7(t,CH_2CO), 40.9(d,C_2), 37.7(t,C_7), 37.1(d,C_1), 36.4(d,C_4), 35.0(t,C_3), 29.7 and 29.6(t,C_5 and C_6), 28.3(q,CH_3); hrms m/e (%) 152.1199(M^+,8.1; calcd. for $C_{10}H_{16}O$: 152.1202), 109.1018(16.2; calcd. for C_8H_{13}: 109.1018), 95.0860(31.9; calcd. for C_7H_{11}:

95.0861), 67.0558(61; calcd. for C_5H_7: 67.0548), 43.0217(100; calcd. for C_2H_3O: 43.0184). Anal. calcd. for $C_{10}H_{16}O$: C 78.90; H 10.59. Found: C 78.82; H 10.54.

Ketone 2-16 (50 mg, 0.33 mmol) was treated with a semicarbazide hydrochloride solution (162) and refluxed for 12 h to give the semicarbazone as white needles. After recrystallization from ethanol; mp 192-195° (lit mp 194-195°) (81).

In a separate experiment, an ethanol solution of the diketone 2-17 (200 mg in 5ml) was treated with conc. HCl (0.5 ml) and refluxed for 18 h. The solvent was evaporated and the mixture extracted with ether. The ether extracts were washed with water, 5% Na_2CO_3 solution and dried over $MgSO_4$. The ether was evaporated to give a brown viscous liquid; vpc analysis (on 10% SE-30, 150-240° at 20°/min) showed two major peaks, 2:1 ratio, which were identified as acetone 2-16 (rt 1.7 min), and the starting diketone 2-17 (rt 2.4 min).

In a related experiment, a solution of $Cu(OAc)_2$ (1.0 g, 5.0 mmol), benzophenone (2.0 g, 11 mmol), norbornene (1.0 g, 11 mmol) and acetylacetone (6.35 g, 64 mmol) in glacial acetic acid (200 ml) was irradiated for 28 h as above to give a yellow solution and metallic copper. The photolysate was worked up as above to give a brown oil (1.28 g); vpc analysis (peak matching) and gc-ms showed the following peaks: the peak at 0.7 min, norbornene (3 %), m/e 94(M^+,19); the peak at 1.5 min, acetylacetone; the peak at 7.6 min, diketone 2-17 (91%); at 10.5 min, benzophenone; the peak at 11.6 min, 2-1, the peak at 14.7 min, 2-2, the peak at 17.6 min, 2-3; the peak at 20.0 min, oxetane 2-18 (6%), m/e 276 (M^+,24). Yields are based on norbornene. The ratio of 2-1, 2-2 and 2-3 is 8 : 6 : 2.

b) in acetonitrile

A solution of Cu(acac)$_2$ (0.5 g, 1.92 mmol), benzophenone (1.0 g, 5.55 mmol) and norbornene (0.6 g, 6.4 mmol) in acetonitrile (200 ml) was irradiated for 36 h to give a light blue solution and small amounts of metallic copper. The photolysate was concentrated under reduced pressure and the residue was diluted with water (100 ml) and extracted with ether (3 × 40 ml). The ether extracts were washed with water (3 × 50 ml) and dried over MgSO$_4$. The solvent was evaporated to give a yellow oil (1.23 g); vpc analysis (on 10% SE-30, 100-240° at 10°/min) showed one minor peak and two major peaks with retention times of 9.7, 12.0 and 19.3 min; gc-ms and peak matching identified the peak at 9.7 min as 2-17 (27%), the peak at 12.0 min as benzophenone, and the peak at 19.3 min as oxetane 2-18 (25%).

In a related experiment a solution of Cu(acac)$_2$ (500 mg, 1.92 mmol), benzophenone (1.0 g, 5.5 mmol), norbornene (0.6 g, 6.4 mmol) and acetylacetone (1.3 g, 12.8 mmol) in acetonitrile (200 ml) was irradiated for 16 h to give a pale blue solution and metallic copper. The photolysate was worked up as above to give a yellow oil (1.144 g); gc-ms (on 10% SE-30, 70-220° at 20°/min) showed the peak at 0.6 min for norbornene (77%); the peak at 0.8 min for acetylacetone; the peak at 5.4 min for 2-17 (15%); the peak at 6.8 min for benzophenone; the peak at 7.3 min for 2-1; the peak at 7.7 min for benzhydrol, m/e 184 (M^+,9.0), 183(66), 105(100), 77(49); the peak at 8.2 min for 2-2; the peak at 9.2 min for 2-3 and the peak at 10.1 min for oxetane 2-18 (8%). Yields are based on norbornene. The ratio of 2-1, 2-2 and 2-3 is 39 : 12 : 50.

An authentic sample of 3-exo-(2-norbornyl)acetylacetone was prepared by the following method (84): Mn(OAc)$_2$ · 4H$_2$0 (4.9 g, 0.02 mmol) was dissolved in glacial acetic acid (50 ml) by heating up to 80° in an oil bath. To the solution, KMnO$_4$ (0.8 g, 0.005 mmol) was added in portions within 20 min. The brown solution was left for an additional 20 min while N$_2$ was bubbled estimated from vpc peak areas and products were not isolated.

In a related experiment a solution of Cu(acac)$_2$ (500 mg, 1.92 mmol), benzophenone (1.0 g, 5.5 mmol), norbornene (0.6 g, 6.4 mmol) and acetylacetone (1.3 g, 12.8 mmol) in acetonitrile (200 ml) was irradiated for 16 h to give a pale blue solution and metallic copper. The photolysate was worked-up as above to give a yellow oil (1.144 g); gc-ms (on 10% SE-30, 70-220° at 20°/min) showed for peak at 0.6 min, norbornene; for peak at 0.8 min, acetylacetone; for peak at 5.4 min, 2-17 (14%); for peak at 6.8 min, benzophenone; for peak at 7.3 min, 2-1 (16%); for peak at 7.7 min, benzhydrol (<5%), m/e 184(M^+,9.0), 183(66), 105(100), 77(49); for peak at 8.2 min, 2-2 (6%); for peak at 9.2 min, 2-3 (32%); for peak at 10.1 min, 2-18 (18%). The yields were estimated from vpc peak areas and products were not isolated.

An authentic sample of 3-exo-(2-norbornyl)acetylacetone was prepared by the following method (84): Mn(OAc)$_2$·4H$_2$O (4.9 g, 0.02 mmol) was dissolved in glacial acetic acid (50 ml) by heating up to 80° in an oil bath. To the solution, KMnO$_4$ (0.8 g, 0.005 mole) was added in portions within 20 min. The brown solution was left for an addition 20 min while nitrogen was bubbled through. A solution of norbornene (2.35 g, 0.025 mol) in acetylacetone (5 g, 0.05 mol) was added. After 20 min the brown color disappeared to give a beige solid and a yellow solution. After cooling the solid was filtered and the filtrate diluted with water (200 ml) and extracted with ether (4 × 50 ml). After washing with 5% Na_2CO_3 solution and water the solvent was evaporated to give a brown viscous liquid (3.71 g). Vacuum distillation (90-92°, 1.5 mm) afforded a yellow liquid (1.25 g); vpc analysis (on 10% SE-30, 150-200° at 10°/min) showed one major peak (rt 4.7 min) and two minor peaks (<5%) (at 6.0 and 8.0 min). Preparative vpc on a 10 ft 10% SE-30 column (160-220°, 10°/min) afford 2-17 (24%) as a colorless viscous liquid.

4-7-2 Neo-hexene

a) in acetic acid

A solution of $Cu(acac)_2$ (0.5 g, 1.92 mmol), benzophenone (1.0 g, 5.55 mmol) and neo-hexene (1.31 g, 15.5 mmol) in glacial acetic acid (200 ml) was irradiated under nitrogen for 3.5 h to give a yellow solution. Irradiation was continued for 12 h until metallic copper was formed. The photolysate was worked-up as above to give a dark yellow oil (1.47 g). Vpc analysis (on 10% SE-30, 150-240° at 10°/min) showed six peaks with retention times of 3.4, 4.1, 4.5, 4.9, 6.4 and 7.2 min.

Column chromatography (on silica gel, 45 g) of the mixture gave, on elution with CH_2Cl_2, benzophenone (0.87 g, 87% recovery); elution with 1% $CH_3OH:CH_2Cl_2$ gave a mixture showing two major and two minor peaks on vpc. By preparative HPLC (on Whatman PAC-Magnum 9 column, 2% isopropanol:hexane as the solvent) three fractions were collected. The first fraction afforded 3-acetyl-6,6-dimethyl-2-heptanone, 2-19 (72 mg, 35%) as a colorless liquid showing a single peak on vpc; ir (neat) 2960(s), 2910(m), 2880(m), 1730(m,sh), 1703(s), 1600(m,b), 1370(s), 1250(m), 1150(m,b), 960(w,b) cm^{-1}; ^1H nmr ($CDCl_3$) δ 16.47(s), 3.54(t,J=6.5 Hz), 2.30(m), 2.17(s), 2.12(s), 1.20(m), 0.96(s), 0.90(s) ppm; ^{13}C nmr ($CDCl_3$) ppm, 205.1(s,CO keto), 191.3(s,CO enol), 111.0(s,C enol), 70.2(d,CH keto), 45.2(t,C_3), 42.1(t,C_2), 30.8(s), 29.6(s), 24.2(q,CH_3), 23.1(q,CH_3); ms m/e 184(M^+,3.2), 127(20), 113(29.7), 100(25), 71(31), 43(100); uv(MeOH) 275 nm, ε= 7200; uv(MeOH/NaOH) 287 nm, ε= 15200. Anal. calcd. for $C_{11}H_{20}O_2$: C 71.74; H 10.87. Found: C 71.62; H 10.79.

The second fraction afforded 2,5,6,6-tetramethyl-3-acetyl-dihydropyran, 2-20 (21 mg, 11%) as a colorless liquid having a single peak on vpc; ir (neat) 2980(s), 2940(m), 1670(s), 1580(s,b), 1375(s), 1278(s), 1250(m), 1180(m), 1150(s), 1127(s), 1010(m), 945(s) cm^{-1}; ^1H ($CDCl_3$) 2.20(s,3H), 2.17(s,3H), 2.14(m,2H), 1.30(s,3H), 1.07(s, 3H), 0.95(d,J=7 Hz,3H); ^{13}C nmr ($CDCl_3$) ppm 199.5(s,CO), 164.1(s,C_2), 109.3(s,C_3), 79.6(s,C_6), 35.9(d,C_5), 30.1, 29.7, 27.7, 22.1, 20.2, 17.0(q,CH_3); ms m/e 182(M^+,15.0), 130(10), 113(22), 70(63), 55(31), 43(100); uv (CH_3OH) λ_{max} 263 nm, ε= 13500. Anal. Calcd. for $C_{11}H_{18}O_2$: C 72.53, H 9.89. Found: C 72.42; H 10.02.

The third fraction (83 mg) showed two peaks on vpc (on SE-30, 100° isothermal) with retention times of 4.9 and 5.1 min; ir (neat) 2980(s), 1720(m,b), 1675(s), ~1600(vs,b), 1390(s,b), 1240(s), 940(s), 630(m) cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 16.41(bs), 4.23(t,J~10 Hz), 2.75(m), 2.17(bs), 1.27(m), ~0.93(m), 0.90(s); gc-ms (same conditions as vpc) showed for peak at 4.9 min, m/e 182(M^+, 64), 139(100), 97(45), 70(25), 43(79) and for peak at 5.1 min, m/e 182(M^+,59.5), 167(30), 125(100), 113(35), 70(56), 43(41).

b) in acetonitrile

A solution of $Cu(acac)_2$ (0.5 g, 1.92 mmol), benzophenone (1.0 g, 5.55 mmol), neo-hexene (1.3 g, 15 mmol) and acetylacetone (0.6 g, 6.4 mmol) in acetonitrile (200 ml) was irradiated for 24 h to give a pale blue solution and small amounts of metallic copper. The solvent was evaporated to give yellow oil (1.12 g); vpc (on 10% SE-30, 60-220° at 15°/min) showed one major peak at 7.4 min and five minor peaks at 4.0, 4.8, 9.1, 9.9 and 10.1 min. Gc-ms and peak matching identified the peak at 4.0 min as 2-19 (51%), the peak at 4.8 min as 2-20 (6%), the peak at 7.4 min, benzophenone, the peak at 9.1 min, 2-1, the peak at 9.9 min, 2-3, and the peak at 10.1 min as the oxetane (18%), m/e 276(M^+,12), 183 (100), 105(54), 77(19), 57(84). Yields are based on neohexene. The ratio of 2-1 and 2-3 is 60 : 40.

4-7-3 1-Hexene

a) in acetic acid

A solution of Cu(acac)$_2$ (500 mg, 1.92 mmol), benzophenone (1.0 g, 5.5 mmol), 1-hexene (1.5 g, 17.8 mmol) and acetylacetone (0.96 g, 9.6 mmol) in glacial acetic acid (200 ml) was irradiated under nitrogen for 3 h to give metallic copper. The photolysate was diluted with water (400 ml) and extracted with ether (3 × 50 ml). After washing with 5% Na_2CO_3 and water, the solvent was evaporated to give a yellow oil (1.72 g). Gc-ms (on SE-30 capillary, 100-220° at 10°/min) and peak matching identified the peaks at 1.5 min as acetylacetone, at 3.03 min as 3-acetyl-5-nonen-2-one, 2-23, m/e 182(M^+,4.0), 139(100), 97(18), 67(21), 43(49); at 3.13 min as 3-acetyl-2-nonanone, 2-24, m/e 184(M^+,2.4), 142(25), 113(42), 100(54), 85(39), 71(100), 43(49); at 4.16 min as 3-acetyl-5-(n-butyl)-2-methyldihydrofuran, 2-25, m/e 182(M^+,59), 167(29), 125(50), 97(61), 43(100); at 8.1 min as benzophenone, at 9.1 min as 2-1, at 10.9 min as 2-2, m/e 222(M^+,63), 221(100), 207(44), 178(46); at 11.4 min as <u>2-3</u>, m/e 282(M^+,0.2), 239(68), 183(38), 167(82), 105(100), 77(44), 43(42). This oil was chromatographed on silica gel (80 g). Elution with CH_2Cl_2 gave several fractions. Fraction A (640 mg) contained recovered benzophenone (64%) as shown by vpc analysis. Fraction B (79 mg) contained <u>2-1</u> (~7%) contaminated with benzophenone as shown by vpc. Fraction C (346 mg) gave a viscous liquid showing four peaks on vpc (at 1.7, 3.12, 3.24 and 4.28 min). Separation by preparative gas chromatography (on 25% SE-30, 150-240° at 15°/min) gave three fractions. Fraction 1 (22 mg) contained acetylacetone as shown by nmr and vpc. Fraction 2 (144 mg) contained a mixture of <u>2-23</u> (4.2%) and <u>2-24</u> (16.1%); vpc (on SE-30 capillary, 100-220° at 10°/min) showed two peaks at 3.01 min and 3.12 min; ir (neat) 2990(m), 2895(m), 1729(s), 1728(s), 1705(m), 1680(s), 1610(m), 1354(m), 969(m) cm^{-1}; ^1H nmr ($CDCl_3$) δ 16.62(bs), 5.43(m), 3.70(t,J~7.5 Hz), 3.63(t,J~7.5 Hz), 2.5(m), 2.15(s), 1.87(m), 1.27(m), 0.88(t) ppm; ^{13}C nmr ($CDCl_3$) 205.01(s), 204.5(s), 134.3(d), 126.0(d), 69.5(d), 69.2(d), 32.0, 29.8, 29.6, 28.9, 28.1, 23.1, 14.6, 14.4 ppm; gc-ms showed for peak at 3.01 min, m/e 182(M^+,4.1), 139(100), 97(22), 67(167), 43(45); for peak at 3.12 min, m/e 184(M^+,1.1), 142(20), 113(30), 100(47), 85(31), 71(100), 43(36). Fraction 3 (89 mg) contained <u>2-25</u> (12.6%) showing one single peak on vpc (same conditions as above, rt 4.12 min); ms m/e 182(M^+,61), 167(36), 125(59), 97(64), 43(100); ir (neat) 2985(s), 2970(m), 1670(s), 1602(s), 1390(s), 1240(s), 1017(m) cm^{-1}; ^1H nmr ($CDCl_3$) δ 4.62(m,1H), 2.6-3.1(m,2H), 2.18(s,6H), 1.43(m,6H), 0.92(t,3H) ppm; ^{13}C nmr (CCl_4) 195.1(s), 168.4(s), 112.5(s), 83.3(d), 36.5, 36.3, 29.8, 27.7, 23.0, 15.6, 14.5 ppm; uv (CH_3OH) λ_{max} 260 nm, ε= 12,500. Anal, calcd. for $C_{11}H_{18}O_2$: C 72.53; H 9.89. Found: C 72.46, H 9.81.

Elution with 1% CH_3OH/CH_2Cl_2 gave a fraction (62 mg) containing a mixture of 2-2 and 2-3 as shown by vpc peak matching (same conditions as above, at 10.7 and 11.1 min).

b) in acetonitrile

A solution of $Cu(acac)_2$ (0.5 g, 1.92 mmol), benzophenone (0.8 g, 4.3 mmol) and 1-hexene (1.2 g, 14 mmol) in acetonitrile (200 ml) was irradiated for 14 h to give a yellow-green solution and traces of metallic copper. The photolysate was concentrated on a flash evaporator to give a blue solid. The solid ($Cu(acac)_2$, 392 mg) was filtered off and the filtrate (~30 ml) was treated with water (100 ml) and extracted with ether (2 × 50 ml). The ether extracts were evaporated to give a yellowish oil (1.048 g); gc-ms (on capillary SE-30, 80-220° at 10°/min) showed the peak at 1.4 min for acetylacetone, the peak at 3.2 min for 2-24 (57%), m/e 184(M^+,1.3), 139(36), 97(100), 67(10), 43(47); the peak at 8.2 min for benzophenone, the peak at 12.3 min, oxetane (43%), m/e 276 (M^+,15%), 236(44), 193(100), 178(37), 115(74). Yields are based on 1-hexene.

4-7-4 Cyclohexene

a) in acetic acid

A solution of $Cu(acac)_2$ (0.5 g, 1.9 mmol), benzophenone (1.0 g, 5.5 mmol) and cyclohexene (0.5 g, 6 mmol) in glacial acetic acid (240 ml) was irradiated under N_2 for 4 h to give metallic copper. The photolysate was diluted with water (250 ml) and extracted with ether (3 × 50 ml) to give a yellow oil (1.148 g) which by gc-ms (on SP-1000, 50-200° at 20°/min) showed the peak at 2.0 min for cyclohexene, the peak at 5.9 min for Δ'-cyclohexenyl-3-acetate, 2-26 (58%), m/e 140(M^+,13), 98(57), 80(38), 79(100), 43(39), the peak at 8.5 min for 3,3'-bicyclohexenyl (7.5%), m/e 162(M^+,2.4), 96(63), 81(100), 80(58), 79(46), the peak at 11.0 min for benzophenone, and the peak at 12.4 min for 2-1. Peaks were identified by coinjection with authentic samples. Yields were estimated from vpc and are based on starting cyclohexene.

An authentic sample of cyclohexene-3-acetate, 2-26, was prepared (95) by heating a solution of cyclohexene (0.82 g, 0.01 mol) and mercuric acetate (6.37 g, 0.02 mol), in glacial acetic acid (40 ml) for 6 h to afford the product (0.8 g, 60%); ir (neat) 2945(m), 1733(s), 1245(s) cm^{-1}; ms 140(M^+,8), 98(65), 80(44), 79(100), 43(35); ^1H nmr (CCl_4) 1.74(m,4H), 1.99(m,5H), 5.16(m,1H), 5.52-6.0(m, 1H) ppm; ^{13}C (CCl_4) 169.28(s), 132.06(d), 126.99(d), 67.86(d), 28.86(t), 25.44(t), 21.43(q), 19.52(t) ppm.

b) in acetonitrile

A solution of Cu(acac)$_2$ (200 mg, 0.77 mmol), benzophenone (350 mg, 1.92 mmol) and cyclohexene (500 mg, 6.1 mmol) in acetonitrile (120 ml) was irradiated under nitrogen with a 200 Watt Hg lamp for 2 h to give metallic copper. After the usual work-up a colorless oil (761 mg) was obtained; gc-ms (on SE-30, 80-220° at 15°/min) showed the peak at 1.16 min for cyclohexene, at 1.26 for acetylacetone, at 5.2 min for 3,3'-bicyclohexenyl (12%), at 7.7 min for benzophenone, at 10.3 min for an oxetane (163) (25%), m/e 264(M^+,24), 183(100), 105(55).

4-8 Photolysis of Cu(acac)$_2$ in the Presence of Polyenes

The photoreactions were carried out in App. III. For vpc analyses, aliquots were taken (1 ml), diluted with water (2 ml) and extracted with ether before being injected into the GC.

4-8-1 Cis,cis-1,5-cyclooctadiene (1,5-COD)

A solution of Cu(acac)$_2$ (1.0 g, 3.83 mmol), benzophenone (1.0 g, 5.5 mmol) and 1,5-COD (3.5 g, 32.5 mmol) in methanol (200 ml) was irradiated under nitrogen with a

200-Watt Hg lamp to give a colorless solution in 16 h. A sample taken turned blue on exposure to the air. The photolysate was diluted with water (400 ml) and extracted with ether (3 × 80 ml). The ether extracts were washed with water, dried over $MgSO_4$ and evaporated to afford a yellowish oil (5.02 g); vpc analysis (on 10% SE-30, 70-240° at 8°/min showed four major peaks at 1.5, 3.7, 4.5 and 13.9 min and a minor peak at 18.2 min. Gc-ms showed for the peak at 1.5 min, acetylacetone, for the peak at 3.7 min, 1,3-cyclooctadiene (124), m/e 108(M^+,81), 93(85), 79(100), 67(78), 39(62); for the peak at 4.5 min, 1,5-COD (124), m/e 108(M^+, 6.5), 80(52), 67(98), 54(100), 39(55); for the peak at 13.9 min, benzophenone; for the peak at 18.2 min, m/e 290(M^+,1.5), 183 (100).

The oil (1.0 g) was column chromatographed on silica gel to afford, on elution with pet.-ether (30-60°) a fraction (502 mg) containing a mixture of 1,3-cyclooctadiene and 1,5-cyclooctadiene in a 46:54 ratio, as shown by vpc analysis (peaks at 3.8 and 4.5 min respectively; nmr ($CDCl_3$) δ 1.50(m), 2.25(m), 2.38(m), 5.58(m), 5.77(m) ppm (97,98); elution with pet. ether:ether (7:1) afforded benzophenone (1.42 g, 77% recovery) mp 49-51°; and acetylacetone (42 mg, 30%).

In a similar experiment a solution of $Cu(acac)_2$ (1.0 g, 3.83 mmol), benzophenone (1.0 g, 5.5 mmol) and

1,5-COD (3.53 g, 32.6 mmol) in methanol (200 ml) was irradiated as above for 16 h to give a colorless solution and small amounts of metallic copper. One-half of the photolysate was removed and worked-up as above to give a yellowish oil (1.89 g); vpc (same conditions as above) showed a peak at 1.7 min for acetylacetone, two peaks at 3.8 and 4.4 min for 1,3 and 1,5-COD respectively in a 34:66 ratio, and the peak for benzophenone at 14.1 min. The other half of the photolysate was left under nitrogen for 36 h to give a blue solution and more metallic copper in suspension. The usual work-up gave a yellowish oil (1.64 g); vpc analysis showed the same pattern as above with the peaks for 1,3 and 1,5-COD in a 35:65 ratio as determined by peak area calculations.

In a separate experiment, a solution of Cu(acac)$_2$ (1.0 g, 3.83 mmol) and 1,5-COD (3.5 g, 32.5 mmol) in methanol (200 ml) was irradiated for 18 h as above. Uv and vpc analysis showed no change in the Cu(acac)$_2$ or diene concentration.

In another experiment, a solution of benzophenone (0.46 g, 2.5 mmol) and 1,5-COD (0.54 g, 5.0 mmol) in methanol (50 ml) was irradiated for 9.5 h as above. The photolysate was evaporated to give a yellow oil (0.832 g). Gc-ms (on 10% SE-30, 70-220° at 10°/min) gave the peak at 7.8 min for benzophenone, at 9.9 min for benzhydrol (22%)

and at 21.2 min, oxetane 2-28 (28%) (99), m/e 290(M^+,1.1), 183(100), 105(52).

4-8-2 Norbornadiene

a) in methanol, under N_2

A solution of $Cu(acac)_2$ (500 mg, 1.92 mmoles), benzophenone (1.0 g, 5.5 mmol) and norbornadiene (2.0 g, 21.7 mmol) in methanol (200 ml) was irradiated under nitrogen with a 200-Watt Hg lamp for 18 h. The solution was light blue and some metallic copper was formed. A sample taken reverted to a more intense blue color on exposure to the air. The photolysate was diluted with water (400 ml) and extracted with ether (4 × 50 ml). Ether extracts were washed with H_2O, dried over $MgSO_4$ and evaporated to give a yellowish oil (1.81 g). Vpc analysis (on 10% SE-30, 80° isoth. 5 min, to 240° at 20°/min) showed six peaks at 1.6, 2.4, 4.1, 9.8, 16.8 min. The peak matching and gc-ms showed the peak at 1.6 min as norbornadiene (22%), m/e 92(M^+,83), 91(100), 66(71), 65(32), 39(15); at 2.4 min as quadricyclene (59%), m/e 92(M^+,65), 91(100), 66(96), 65(90), 51(55), 40(56), 39(72); at 4.1, unknown, m/e 124(M^+,36), 92(95), 91(100), 79(98), 66(96), 28(51); at 9.8 min, as benzophenone; at 16.8 min as oxetane (15%) (105), m/e 274(M^+,5.7), 167(81), 165(57), 105(31), 91(100), 81(74), 77(51); at 18.2 min as oxetane (5%) (105), m/e 274(10), 167(66), 165(54), 115(26), 91(100), 77(16).

Preparative vpc of the crude product (300 mg) (on 10% Apiezon L, 120° isoth. for 15 min, to 250° at 10°/min) afforded norbornadiene (colorless liquid, 26 mg); nmr ($CDCl_3$) δ 1.99(m,2H), 3.57(m,2H), 6.74(m,4H) ppm, and quadricyclene (yellowish liquid, 24 mg); nmr ($CDCl_3$) δ 1.43(m,6H), 2.02(m,2H) ppm (101); ir (neat) 3070(s), 2940(s), 2860(s), 1330(m), 1260(m), 1240(s), 950(m), 910(s), 890(s), 800(s), 765(s) cm^{-1}. A third fraction was collected (56 mg) containing benzophenone and oxetane, as shown by vpc.

In a separate experiment a solution of $Cu(acac)_2$ (0.5 g, 1.9 mmol), benzophenone (1.0 g, 5.5 mmol) and norbornadiene (2.0 g, 22 mmol) in methanol under nitrogen was irradiated for 7 h to give a yellow solution. The photolysate was left under nitrogen in the dark for 48 h after which the solution was light blue and metallic copper had formed. The progress of the reaction during and after irradiation was monitored by vpc (on 10% SE-30, 80-220° at 10°/min) and the relative yields of norbornadiene and quadricyclene determined (see P. 61).

In a related experiment a solution of benzophenone (1.0 g, 5.5 mmol) and norbornadiene (2.0 g, 22 mmol) in methanol (200 ml) under nitrogen was irradiated with a 200-Watt Hg lamp for 7 h, and the reaction monitored by vpc analysis as above (see P. 62).

4-8-3 Trans,Trans,Trans-1,5,9-Cyclododecatriene

a) in benzene under hydrogen

A solution of Cu(acac)$_2$ (0.5 g, 1.92 mmol), benzophenone (1.0 g, 5.5 mmol) and t,t,t-CDT (0.62 g, 3.85 mmol) in benzene (200 ml) was irradiated under hydrogen with a 450 Watt Hg lamp for 8 h to give a cloudy yellow solution. Prolonged irradiation did not deposite copper. A sample taken turned blue in a few seconds when exposed to the air. Vpc of the photolysate (on SE-30, 80-230° at 15°/min) showed peaks at 1.2, 4.4, 4.7, 4.85 and 7.2 min. Peak matching and gc-ms (same conditions as above) identified the peak at 1.2 min as acetylacetone; at 4.4 min as t,t,t-CDT (43%), m/e 162(M^+,39), 134(70), 133(100), 119(56), 93(76); at 4.7 min as c,t,t-CDT (45%), m/e 162(M^+,21), 134(75), 133 (100), 93(78), 79(79); at 4.85 min, tentatively assigned as c,c,t-CDT (12%), m/e 162(M^+,9), 133(72), 93(80), 91 (65), 79(100); at 7.3 min as benzophenone. The photolysate was distilled on a steam bath to give a blue-yellow semisolid. Treatment with ether (15 ml) gave a blue solid (0.43 g) identified as Cu(acac)$_2$. The filtrate was evaporated to give a yellow oil (1.02 g); nmr ($CDCl_3$) 1.97(m), 2.0(m), 2.07(m), 4.93(m), 5.4(m), 7.23(m) ppm. The progress of the reaction was also monitored by vpc analysis (see P. 58). After irradiation the photolysate was left under hydrogen for 24 h with no change in the vpc pattern.

analysis showed the same pattern as above with identical relative yields.

In a related experiment a solution of benzophenone (0.5 g, 2.25 mmol) and t,t,t-CDT (0.32 g, 1.92 mmol) in benzene (100 ml) under hydrogen was irradiated with a 450-Watt Hg lamp for 8 h. Vpc analysis of the photolysate (same conditions as above) showed peaks at 5.1 min for t,t,t-CDT (89.3%), at 5.35 min for c,t,t-CDT (10.7%) and at 7.9 min for benzophenone.

b) <u>in acetonitrile under hydrogen</u>

A solution of $Cu(acac)_2$ (0.5 g, 1.92 mmol), benzophenone (1.0 g, 5.5 mmol) and t,t,t-CDT (0.62 g, 3.84 mmol) in acetonitrile (200 ml) was irradiated under hydrogen with a 450-Watt Hg lamp for 8 h to give a blue-green solution. Vpc analysis of the photolysate (on 10% SE-30, 50-220° at 15°/min) showed peaks at 4.6 min for t,t,t-CDT (95%), at 4.75 min for c,t,t-CDT (4 %) and at 7.4 min for benzophenone.

c) <u>in methanol under nitrogen</u>

A solution of $Cu(acac)_2$ (0.5 g, 1.92 mmol), benzophenone (1.0 g, 5.5 mmol) and t,t,t-CDT (0.62 g, 3.84 mmol) in methanol (200 ml) was irradiated under nitrogen with a 200-Watt Hg lamp to give metallic copper after 1 h. Vpc analysis of the photolysate after work-up (same conditions as above) showed peaks at 1.2 min for acetylacetone, at 4.55 min for t,t,t-CDT and 7.4 min for benzophenone.

4-8-4 Cis,Trans,Trans-1,5,9-Cyclododecatriene

a) in benzene under hydrogen

A solution of Cu(acac)$_2$ (0.5 g, 1.92 mmol), benzophenone (1.0 g, 5.5 mmol) and c,t,t-CDT (0.62 g, 3.84 mmol) in benzene (200 ml) was irradiated under hydrogen with a 450-Watt Hg lamp for 10 h to give a yellow solution. Vpc analysis of the photolysate (on SE-30, 50-220° at 15°/min) showed the peaks at 1.0 min for acetylacetone, at 4.65 min for t,t,t-CDT (~56%), at 4.9 min for c,t,t-CDT, at 5.1 min for c,c,t-CDT (~8%) and at 7.7 min for benzophenone. The progress of the reaction was monitored by vpc analysis and relative yields (from peak areas) were determined (see P. 59). The photolysate was kept in the dark under hydrogen for 24 h but showed the same vpc pattern.

4-8-5 Benzophenone Sensitized Photolysis of Cu(acac)$_2$ in benzene under hydrogen

A solution of Cu(acac)$_2$ (0.5 g, 1.92 mmol) and benzo phenone (1.0 g, 5.5 mmol) in benzene (200 ml) was irradiated under hydrogen with a 450 Watt Hg lamp to give after 15-20 min a cloudy yellow solution which turned blue in seconds when exposed to the air. Prolonged irradiation for

6 h did not show the formation of any precipitate nor metallic copper. Vpc analysis of the photolysate (on SE-30, capillary column, 15 mt, 50-220° at 15°/min) showed only the peak for benzophenone at 7.9 min.

4-9 Quantum Yield Determinations

Quantum yield determinations were carried out in a "merry-go-'round" apparatus as described before (164). The apparatus consists of a turntable which revolves around the light source (Hanovia 679A36, 450-Watt medium pressure mercury lamp) contained in a Pyrex cooling well held in the center.

Actinometer and sample cells of ca. 5 ml capacity (1.2 cm diameter × 10 cm length) were made from Pyrex test tubes (Kimax). They were joined to a B-14 male ground glass joint equipped with a gas inlet and outlet with a mercury seal for degassing.

The absorbed light intensity (in Einstein/h) was determined using a benzophenone-benzhydrol actinometer (165). Solutions 0.05 M in benzophenone and 0.1 M in benzhydrol in benzene, were degassed and irradiated for fixed periods of time. The residual benzophenone was then determined spectrophotometrically at ~340 nm using a 0.1 cm uv cell to avoid dilution. A quantum yield of 0.74 has been reported for this process (106).

Generally, stock solutions of Cu(acac)$_2$, triphenylphosphine and sensitizers were freshly prepared. Aliquots of each solution were pipetted into a volumetric flask (10 ml) and diluted with solvent to prepare solutions for irradiation of the required concentration. These solutions (4-5 ml) were placed in the phototubes, deaerated with purified nitrogen for 5 min and irradiated for a prescribed length of time to cause 10-20% conversion of the reactants.

For quantum yields of Cu(acac)$_2$ disappearance, Cu(acac)$_2$ was analyzed spectrophotometrically by determining the absorbance of the undilute solutions at 630 nm before and after irradiation.

For quantum yields of benzophenone disappearance, the amount of benzophenone reacted was determined by hplc analysis (on a Partisil PXS 10/25 Whatman, 2% iso-propanol in hexane as solvent) using anisole as an internal standard. Before and after irradiation, to 1 ml of solution, 1 ml of standard solution of anisole (0.922 M) was added and injected three times into the hplc.

4-10 Flash Photolysis Experiments

These experiments were performed by Miss Carol Beddard at the National Research Council laboratories, Chemistry Division, using the facilities provided by Dr. J.C. Scaiano.

Materials: The solvents, methanol (Aldrich, Gold Label), benzene (Fisher, Spectro.), and acetonitrile (Photex, Spectro.) were used as received.

Sample preparation: The solutions of sensitizers (*ca*. 10^{-2}-10^{-3} M) and Cu(acac)$_2$ (10^{-3}-10^{-4} M) were placed in suprasil cells with a 3 mm optical path and deaerated using oxygen-free nitrogen.

Laser photolysis[1]: The samples were excited by using the pulses from a Molectron UV-24 nitrogen laser which produces 8-10 ns pulses of up to 10 mJ at 337.1 nm. Transient decays were monitored by using a pulsed 200-Watt xenon lamp as a light source, a high intensity B & L monochromator and a RCA-4840 photomultiplier tube at the detection end. Signals from the detector system were processed through a R7912 Tektronix transient digitizer which was interphased with a PDP 11/55 computer that controlled the experiments and processed the data.

4-11 Reduction Potential Measurements

The half-wave reduction potentials (E1/2) were determined in acetonitrile by cyclic voltammetry, using a three electrode cell, with a P.A.R. Electrochemistry System, Model 170 (Princeton Applied Research Corp., Princeton, New Jersey). The working electrode was a platinum microdisc and the counter electrode was a platinum wire. A silver wire electrode was used as a reference electrode and 0.1 M tetraethyl ammonium chloride (TEACl) as a supporting eletrode.

---

[1] A more detailed description of the laser flash photolysis facility has been described (57,166).

4-12 Benzophenone Sensitized Photolysis of Cu(hfa)$_2$.

a) in methanol

A solution of Cu(hfa)$_2$ (0.5 g, 1.05 mmol), benzophenone (0.8 g, 4.4 mmol) in methanol (120 ml) was irradiated with a 200 Watt Hg lamp under nitrogen for 1 h to give metallic copper and a colorless solution. The photolysate was diluted with water (300 ml) and extracted with ether (3x50 ml). The ether extracts were washed with water and dried over MgSO$_4$. The solution was concentrated on a flash evaporator at 10°. Vpc analysis (on 10% SE-30, 80-240° at 20°/min) showed only one peak at 7.3 min corresponding to benzophenone, Tlc analysis (on silica gel, elution with CH$_2$Cl$_2$) showed two spots for benzophenone (R_f = 0.76) and hexafluoroacetylacetone (R_f = 0.35).

b) in the presence of triphenylphosphine

A solution of Cu(hfa)$_2$ (0.67 g, 1.14 mmol), benzophenone (0.42 g, 2.28 mmol) and triphenylphosphine (0.60 g, 2.28 mmol) in methanol (200 ml) was irradiated with a 200 Watt Hg lamp under nitrogen to give a yellow solution which was stable on prolonged irradiation (4 h). The absorption of Cu(hfa)$_2$ at 750 nm had disappeared. The solvent was evaporated to give a yellow semi-solid (1.62 g) which was dissolved in warm ethanol (20 ml) and left at O° C for 12 h. Filtration afforded yellow needles of Cu(hfa)(PPh$_3$)$_2$ (0.59 g, 65%); mp 156-158° (lit. mp 157-

-159°) (52, 110); Anal. calcd. for $C_{41}H_{31}O_2P_2F_6Cu$: C 61.93%, H 3.90%; Found: C 61.78%, H 3.93%.

REFERENCES

1. D.W. Barnum, J. Inorg. Nucl. Chem., 21, 221 (1961).
2. J.P. Fackler, Progr. Inorg. Chem., 7, 361 (1966).
3. R.H. Holm and F.A. Cotton, J. Am. Chem. Soc., 88, 2951 (1966).
4. A.M. Fatta and R.L. Lintvedt, Inorg. Chem., 10, 478 (1971).
5. J.P. Collman, R.A. Moss, H. Maetz and C.C. Heindel, J. Am. Chem. Soc., 83, 531 (1961).
6. D.W. Thompson, J. Chem. Ed., 48, 79 (1971).
7. S. Okeya, N. Yanase, Y. Nakamura and S. Kawaguchi, Chem. Lett., 669 (1978).
8. R.K. Lintvedt, in "Concepts of Inorganic Photochemistry". Edited by A.W. Adamson and P.D. Fleischauer. John Wiley & Sons, New York, 1975. Chapter 7.
9. C.K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes", Addison-Wesley, Reading, Mass. 1962.
10. K. DeArmond and L.S. Förster, Spectrochim. Acta, 19, 1393, 1403, 1687 (1963).
11. V. Balzani and V. Carassitti, "Photochemistry of Coordination Compounds", Academic, New York, 1970.
12. M.S. Wrighton, Chem. Rev., 74, 401 (1974).
13. G.L. Geoffroy and M.S. Wrighton, "Organometallic Photochemistry", Academic, New York, 1979.
14. Ref. 8 and references therein.
15. C. Kutal, D.B. Yang and G. Ferraudi, Inorg. Chem., 19, 2907 (1980).
16. G. Ferraudi, D.B. Yang and C. Kutal, J.C.S. Chem. Comm., 1050 (1979).
17. D.B. Yang and C. Kutal, J.C.S. Chem. Comm., 363 (1978).

18. S.S. Minor and G.W. Everett, Jr., Inorg. Chim. Acta, 20, L51 (1976).

19. Ref. 8, Chapter 9; H.D. Gafney, Ph.D. Thesis, Wayne State University, 1970.

20. H.D. Gafney, R.L. Lintvedt and I.S. Jaivorwsky, Inorg. Chem., 9, 1728 (1970).

21. N. Filipescu and H. Way, Inorg. Chem., 8, 1863 (1969).

22. H.D. Gafney and R.L. Lintvedt, J. Am. Chem. Soc., 92, 6996 (1970).

23. H.D. Gafney and R.L. Lintvedt, J. Am. Chem. Soc., 93, 1623 (1971).

24. G. Ferraudi, P.A. Grutsch and C. Kutal, J.C.S. Chem. Comm., 15 (1979).

25. P.A. Grutsch and C. Kutal, J. Am. Chem. Soc., 99, 7397 (1977).

26. J.Y. Morimoto and B.A. DeGraff, J. Phys. Chem., 79, 326 (1975).

27. J.Y. Morimoto and B.A. DeGraff, J. Phys. Chem., 76, 1387 (1972).

28. P. Natarajan, K. Chandrasekaran and M. Santappa, Polym. Lett. Ed., 14, 455 (1976).

29. J.P. Fackler, Jr., F.A. Cotton and D.W. Barnum, Inorg. Chem., 2, 97 (1963); ibid., 2, 102 (1963).

30. P. Courtot, R. Pichon and J. LeSaint, Bull. Soc. Chim. France, 9-10, II-457 (1980).

31. D.C. Nonhebel, Tetrahedron, 26, 4443 (1970).

32. P. Courtot, J. LeSaint and R. Pichon, Bull. Soc. Chim. France, 2538 (1975).

33. V. Balzani, F. Bolletta and L. Moggi, Spectr. Letters, 11, 525 (1978).

34. V. Balzani, L. Moggi, M.F. Manfrin, F. Bolletta and G.L. Lawrence, Coord. Chem. Revs., 15, 321 (1975).

35. C.T. Lim, W. Böttcher, M. Chou, C. Creutz and N. Sutin, J. Am. Chem. Soc., 98, 6536 (1976) and references therein.

36. H. Juris, M.T. Gandolfi, M.F. Manfrin and V. Balzani, J. Am. Chem. Soc., 98, 1047 (1976).

37. T.J. Meyer, Israel J. Chem., 15, 200 (1977).

38. A.R. Gutierrez, T.J. Meyer and D.G. Whitten, Mol. Photochem., 7, 349 (1976).

39. J.A. Bell and H. Linschitz, J. Am. Chem. Soc., 85, 528 (1963).

40. G.S. Hammond and R.P. Foss, J. Phys. Chem., 68, 3739 (1964).

41. F. Wilkinson and A. Farmilo, J.C.S. Faraday Trans II, 604 (1976).

42. F. Wilkinson, Pure and Appl. Chem., 41, 661 (1975).

43. A.J. Fry, R.S.H. Liu and G.S. Hammond, J. Am. Chem. Soc., 88, 4783 (1966).

44. Dr. Y.L. Chow, personal communication.

45. V.I. Saloutin, K.I. Pashkevich and I. Ya. Postovskii, Bull. Acad. Sci. USSR, D. Chem. Sci., 26 (4), Part 2, 882 (1977).

46. D.P. Graddon, Coord. Chem. Revs., 4, 1 (1969).

47. J.T. Adams and C.R. Hauser, J. Am. Chem. Soc., 66. 1220 (1944).

48. J. Ferguson, J. Chem. Phys., 34, 1609 (1961).

49. S. Barnatt, R.G. Charles and L.W. Littan, J. Phys. Chem., 62, 763 (1958).

50. K. Sato and O. Kammori, Bull. Chem. Soc. Japan, 42, 2778 (1969).

51. R. Nast, R. Mohr and C. Schultze, Chem. Ber., 96, 2127 (1963).

52. W.A. Anderson, A.J. Carty, G.J. Palenik and G. Schreiber, Can. J. Chem., 49, 761 (1971).

53. E.M. Schultz and S. Mickey, Org. Synth., Coll. Vol. III, 343 (1955).

54. N. Filipescu, E. Avram and K.D. Welk, J. Org. Chem., 42, 507 (1977) and references therein.

55. W.G. Bentrude and K.R. Darnall, J.C.S. Chem. Comm., 810 (1968).

56. V. Zanker and E. Ehrhardt, Bull. Chem. Soc. Japan, 39, 1694 (1966).

57. J.C. Scaiano, J. Am. Chem. Soc., 102, 7747 (1980).

58. D.L. Bunbury and C.T. Wang, Can. J. Chem., 46, 1473 (1968).

59. P.J. Wagner, Acc. Chem. Res., 4, 168 (1971).

60. P.J. Wagner, P.A. Kelso and R.G. Zepp, J. Am. Chem. Soc., 94, 7480 (1972).

61. P.J. Wagner, P.A. Kelso, A.E. Kemippainen, J.M. McGrath, H.N. Schott and R.G. Zepp, J. Am. Chem. Soc., 94, 7506 (1972).

62. R.D. Small and J.C. Scaiano, Chem. Phys. Lett., 50, 431 (1977).

63. M.V. Encinas, P.J. Wagner and J.C. Scaiano, J. Am. Chem. Soc., 102, 1357 (1980).

64. S.L. Murov, "Handbook of Photochemistry", Marcel Dekker, Inc., New York, N.Y., 1973.

65. D.O. Cowan and R.L. Drisko, "Elements of Organic Photochemistry", Pullman Press, New York, N.Y., 1976.

66. N.J. Turro, "Modern Molecular Photochemistry", The Benjamin/Cummings Publishing Co., Menlo Park, California, 1978.

67. G.A. Davis, P.A. Carapelluci, K. Szoc and J.D. Gresser, J. Am. Chem. Soc., 91, 2264 (1969).

68. E.J. Bowen and D.W. Turner, Trans. Faraday Soc., 51, 475 (1955).

69. J.A. Bertrand and R.I. Kaplan, Inorg. Chem., 11, 1657 (1965).

70. J.A. Bertrand and D. Caine, J. Am. Chem. Soc., 86, 2298 (1964).

71. R.W. Adams, C.G. Barraclough, R.L. Martin and G. Winter, Aust. J. Chem., 20, 2351 (1967).

72. T. Saegusa, T. Tsuda and K. Isayama, J. Macromol. Sci.-Chem., A4, 1463 (1970).

73. H.F. Holtzclaw, Jr., R.L. Lintvedt, H.F. Banngarten, R.G. Parker, M.M. Bursey and R.K. Rogerson, J. Am. Chem. Soc., 91, 3774 (1969).

74. K.E. Lawson, Spectrochim. Acta, 17, 248 (1961).

75. G.E. Coates and C. Parkin, J. Inorg. Nucl. Chem., 22, 59 (1961).

76. I.A. Garbusova, V.T. Alexanjan, L.A. Leites, I.R. Golding and A.M. Sladkov, J. Organomet. Chem., 54, 341 (1973).

77. C.E. Castro, E.J. Gaugham and D.C. Owsley, J. Org. Chem., 31, 4071 (1966).

78. H.O. House and M.J. Umen, J. Org. Chem., 38, 3893 (1973).

79. A.E. Favorskii and L. Morev, J. Russ. Phys.-Chem. Soc., 50, 571 (1920).

80. F. Bohlmann and E. Bresinsky, Ber., 100, 1209 (1967).

81. W. Reusch, J. Org. Chem., 27, 1882 (1962).

82. L.M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd Ed., Pergamon Press, Oxofrd, 1969, Chapter 4.

83. Ref. 47.

84. M.G. Vinogradov, T.M. Fedorova and G.I. Nikishin, Russ. J. Org. Chem., 12, 1183 (1976).

85. J.H. Edwards, F.J. McQuillin and M. Wood, J.C.S. Chem. Comm., 438 (1978).

86. F.J. McQuillin and M. Wood, J.C.S. Perkin I, 1762 (1976).

87. E.I. Heiba and R.M. Dessan, J. Org. Chem., 39, 3457 (1974).

88. D.R. Arnold, R.L. Hinman and A.H. Glick, Tetrahedron Lett., 1425 (1964).

89. W. Simon and T. Clerc, "Structural Analysis of Organic Compounds by Spectroscopic Methods", Macdonald, London, 1971, P. 18.

90. J.B. Stothers, "Carbon-13 NMR Spectroscopy", Academic, New York, 1972, Chapter 8.

91. Ref. 90, P. 283.

92. Ref. 90, P. 395.

93. Ref. 90, P. 274.

94. J.S. Bradshaw, J. Org. Chem., 31, 237 (1966).

95. L.F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, John Wiley & Sons, Inc., New York, 1967, P. 646.

96. W. Treibs and H. Bast, Ann., 561, 165 (1947).

97. Varian Spectra Catalog, Vol. 2, Varian Associates, Palo Alto, California, Spectrum #511.

98. Ref. 97, Vol. 1, Spectrum #209.

99. D.R. Arnold, in "Advances in Photochemistry", Vol. 6, Interscience Publishers, 1968, P. 301.

100. H. Nozaki, Y. Nisikawa, M. Kawanisi and R. Noyori, Tetrahedron, 23, 2173 (1967).

101. Org. Synth., 51, 133 (1971).

102. T. Kubota, K. Shima and H. Sakurai, Chem. Lett., 343 (1972).

103. A.J.G. Barwise, A.A. Gorman, R.L. Leyland, P.G. Smith and M.A.J. Rodgers, J. Am. Chem. Soc., 100, 1814 (1978).

104. A.A. Gorman, R.L. Leyland, M.A.J. Rodgers and P.G. Smith, Tetrahedron Lett., 5085 (1973).

105. A.A. Gorman and R.L. Leyland, Tetrahedron Lett., 5345 (1972).

106. G.S. Hammond and P.A. Leermaker, J. Phys. Chem., 66, 1148 (1962).

107. M. Topp, Chem. Phys. Lett., 32, 144 (1975).

108. D. Rehm and A. Weller, Ber. Bunsenges, 73, 834 (1969).

109. F. Cotton and G. Wilkinson, "Advances Inorganic Chemistry", 3rd Ed., Wiley, New York, 1972, P. 918.

110. D. Gibson, B.F.G. Johnson and J. Lewis, J. Chem. Soc. A, 367 (1970).

111. Ref. 109, P. 907.

112. E.N. Baker and P.M. Garrick, J.C.S. Dalton, 416 (1978).

112a. K.F. Purcell and J.C. Kotz, "Inorganic Chemistry", W.B. Saunders Co., 1977, Chapter 16.

113. T.H. Lowry and K.S. Richardson, "Mechanism and Theory in Organic Chemistry", 2nd Ed., Harper and Row Publishers, New York, 1981, P. 280.

114. R.G. Pearson and R.L. Dillon, J. Am. Chem. Soc., 75, 2439 (1953).

115. G.E. Coates, M.L.H. Green and K. Wadl, "Organo-Metallic Compounds", Vol. II, Chapter 8, 1968.

116. S. Otsuka and A. Nakamura, Adv. Organomet. Chem. 14, 245 (1976).

117. F.L. Carter and E.W. Hughes, Acta Cryst., 10, 801 (1957).

118. B.C. Ward and J.L. Templeton, J. Am. Chem. Soc., 102, 1532 (1980).

119. R.G. Salomon, in "Inorganic and Organometallic Photochemistry", Ed. M.S. Wrighton, Ad. in Chem. Ser., 1978, P. 174, and references therein.

120. R.G. Salomon, K. Folting, N. Streil and J.K. Kochi, J. Am. Chem. Soc., 96, 1145 (1974).

121. R.G. Salomon and J.K. Kochi, J. Am. Chem. Soc., 96, 1137 (1974).

122. J. Th. M. Evers and A. Mackor, Tetrahedron Lett., 26, 2317, 2321 (1978).

123. R. Srinivasan, J. Am. Chem. Soc., 86, 3318 (1964)

124. G. Whitesides, G.L. Goe and A.C. Cope, J. Am. Chem. Soc., 91, 2608 (1969).

125. P.A. Grutsch and C. Kutal, J Am. Chem. Soc., 101, 4228 (1979).

126. R.F. Sterling and C. Kutal, Inorg. Chem., 19, 1502 (1980).

127. K. Maruyama, K. Terada, Y. Naruta and Y. Yamamoto, Chem. Lett., 1259 (1980).

128. R.G. Salomon and N. El Sanadi, J. Am. Chem. Soc., 97, 6214 (1975).

129. Ref. 103.

130. A.J. Cessna, S.E. Sugamori, R.W. Yip, M.P. Lau, R.S. Snyder and Y.L. Chow, J. Am. Chem. Soc., 99, 4044 (1977).

131. G.A. Russell and J. Lokensgard, J. Am. Chem. Soc., 89, 5059 (1967).

132. H. Schäfer and A. Alazrak, Angew. Chem. Internat. Edit., 7, 474 (1968).

133. D.J. Edge, B.C. Gilbert, R.O.C. Norman and P.R. West, J. Chem. Soc. (B), 189 (1971).

134. H. Nozaki, M. Kwita, T. Mori and R. Noyori, Tetrahedron, 24, 1821 (1968).

135. Ref. 66, Chapter 10, and references therein.

136. J.A. Barltrop and J.D. Coyle, "Excited States in Organic Chemistry", John Wiley & Sons, London, 1975, and references therein.

137. J.C. Scaiano, J. Photochem., 2, 81 (1973/74).

138. G.H. Jones, D.W. Edwards and D. Parr, J.C.S. Chem. Comm., 969 (1976).

139. Ref. 136, Chapters 2, 3 and 4.

140. P.K. Das, Tetrahedron Lett., 1307 (1981).

141. S.A. Alkaitis, G. Beck and M. Grätzel, J. Am. Chem. Soc., 97, 5723 (1975).

142. D. Rehm and A. Weller, Israel J. Chem., 8, 259 (1970).

143. A. Weller, in "Exciplex", M.S. Gordon and W.R. Ware (Ed.), Academic Press, New York, 1975, Chapter 2.

144. A. Weller, Pure Appl. Chem., 16, 116 (1968).

145. J.B. Guttenplan and S.G. Cohen, J. Am. Chem. Soc., 94, 4040 (1972); Tetrahedron Lett., 2163 (1972).

146. J.C. Scaiano and G.G. Wubbels, J. Am. Chem. Soc., 103, 641 (1981).

147. R.F. Bartholomew, R.S. Davidson, P.F. Lambeth, J.F. Mekeller and P.H. Turner, J.C.S. Perkin, II, 517 (1972).

148. M.V. Encinas and J.C. Scaiano, J. Am. Chem. Soc., 101, 7740 (1979).

149. Inorg. Synthesis, 5, 105 (1957).

150. H. Richard, Ph.D. Dissertation, Simon Fraser University, 1979, P. 135-6.

151. G. Buono-Core, K. Iwai, Y.L. Chow, T. Koyanagi, A. Kaji and J. Hayami, Can. J. Chem., 57, 8 (1979).

152. S.C. Chen, Ph.D. Dissertation, Simon Fraser University, 1970, P. 122.

153. N.H. Furman, "Standard Methods of Chemical Analysis", Vol. I, 6th Ed., D. Van Nostrand Co., New Jersey, 1962, P. 408.

154. R.L. Shriner, R.C. Fuson and D.Y. Curtin, "The Systematic Identication of Organic Compounds", 5th Ed., John Wiley & Sons, New York, 1965.

155. E.W. Berg and J.T. Truemper, J. Phys. Chem., 64, 487 (1960).

156. D.R. Paulson, A.L. Hartwig and G.F. Moran, J. Chem. Ed., 50, 216 (1973).

157. Ms of an authentic sample showed m/e (%) 162(15), 134(29), 133(32), 120(100), 105(73), 77(29).

158. Ms of an authentic sample showed m/e (%) 176(8), 120(85), 105(100), 77(69).

159. P.J. Kocienski, J. Org. Chem., 39, 3285 (1974).

160. P.D. Bartlett and J.L. Rosen, J.Am. Chem. Soc., 64, 543 (1942).

161. J.S. Tam, Ph.D. Dissertation, Simon Fraser University, 1970, P. 145.

162. Solution was prepared by dissolving 50 mg of semicarbazide hydrochloride and 75 mg of sodium acetate in 1 ml of water and 1 ml of ethanol.

163. J.S. Bradshaw, J. Org. Chem., 31, 237 (1966).

164. M.G. Moses, R.S.H. Liu and B.M. Monroe, J. Mol. Photochem., 1, 245 (1969).

165. Ref. 64, P. 125.

166. M. Encinas and J.C. Scaiano, J. Am. Chem. Soc., 101, 2146 (1979).

167. J.C. Scaiano, personal communication.