CHAPTER - II

INFLUENCE OF TRANSITION METAL IONS ON PHOTOCYCLIZATIONS

CONTENTS

		Page
	Abstract	107
SECTION -I :	INTRODUCTION	108 - 135
	Titanium	109
	Iron	111
	Chromium, Manganese and Cobalt	114
	Zinc, Nickel, Vanadium and Rhodium	114
	Mercury, Silver and Gold	115
	Cerium and Uranium	116
	Copper	117
	Conclusion	127
	References	128
SECTION -II :	PRESENT WORK	136 - 171
	Photochemistry of Citronellyl Iodide	138
	Photochemistry of Geranyl Iodide	149
	Photochemistry of Neryl Iodide	152
	Photochemistry of 1-Iodo-5-hexene	156
	Use of an optically active base	158
	Conclusion	159
	Experimental	160
	References	170

ABSTRACT

This chapter consists of two sections. Section I discusses the various uses of transition metal ions in photochemistry. Section II describes our attempts to enhance photocyclizations with the use of transition metal ions. Transition metal ions which complex with olefins, particularly cuprous chloride, have been found to enhance photocyclization significatly. The metal ion appears to function as a template. Attempts to induce assymetry in these cyclizations were however unsuccessful.

SECTION - I

INTRODUCTION : TRANSITION METAL IONS IN PHOTOCHEMISTRY

Transition metals, which may be defined as those possessing partly filled 'd' or 'f' shells in their commonly occurring oxidation states[1], have, over the past few years played an ever increasing roll in the photochemistry of organic substrates[2]. Numerous reactions of organic molecules are accelerated by light in the presence of catalytic amounts of transition metal ions. Recently studied examples of such metal-catalyzed photoassisted processes include hydrogenation[3], polymerization[30], double bond migration[4], fragmentation[70] and *cis*-*trans* isomerizations[5]. The metal(M) is thought to modify the reactivity of the organic substrate(S) via formation of an complex (M-S) which subsequently undergoes conversion to the product(P) followed by its release in the system. Light may assist in one, two or all three steps of the sequence.

$$M + S \xrightleftharpoons{\text{Step 1}} M - S \xrightleftharpoons{\text{Step 2}} M - P \xrightleftharpoons{\text{Step 3}} M + P$$

This section discusses some of the more important aspects of the developments over the past one decade in this area. The discussion is restricted to the influence of non-coordinated(distiguishing from solvated)transition metal ions. Grouping of metals wherever done are merely for the sake of convenience and not due to any similarity in reactivity or properties. The contribution of the copper ion being enormous it is discussed last.

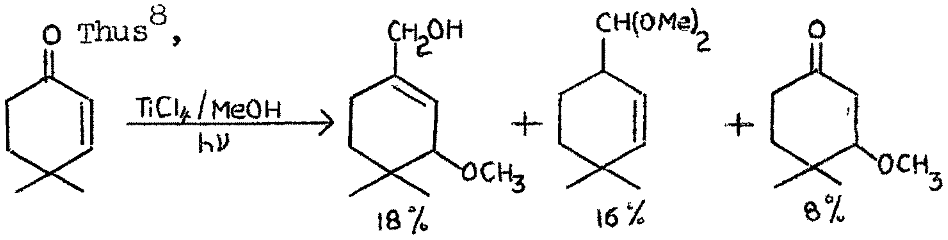
(i) Titanium

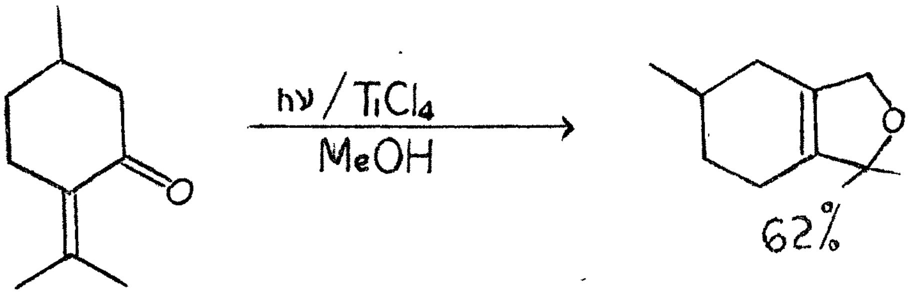
Photolysis of $TiCl_4$ in alcohol solvents gives the Ti(IV) species and the alkoxy radical which subsequently furnishes the aldehyde or ketone[6]. In methanol solvent $TiCl_4$ also exerts a striking influence on the photochemistry of α,β-unsaturated ketones and esters[7] and related substrates like cyclopropyl ketones,β-diketones, Schiffs bases and nitriles[8]. Two types of reactions were observed[7];(A) cyclization to form dihydrofuran and (B) formation of a dimethylacetal. The reactions of pulegone(1) and dypnone(2) belong to type(A) affording the corresponding cyclic ether (3) and (4) respectively.

An extra(solvent derived) carbon atom fragment has been incorporated into the products(3) and (4). The reaction of mesityl oxide(5) and 3-methyl-2-cyclohexenone(6) belong to the type(B) affording(7) and (8) respectively.

The primary process in these reactions appears to be the photooxidation of the solvent[9]. In all these cases the α-carbon atom of the primary alcohol undergoes a bond formation generally with the C=X or C≡N carbon atom of the substrates.

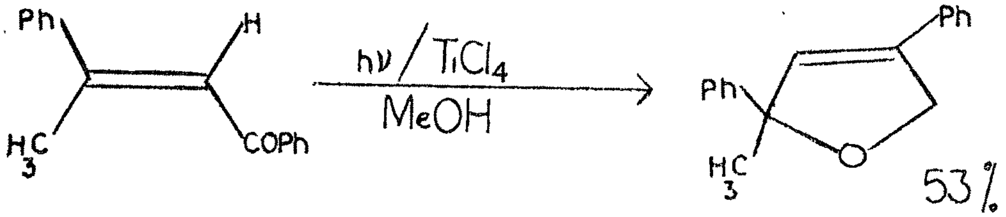
Thus[8],




hν / TiCl$_4$
MeOH
62%

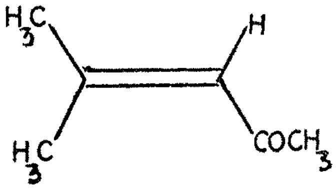
1.

3.

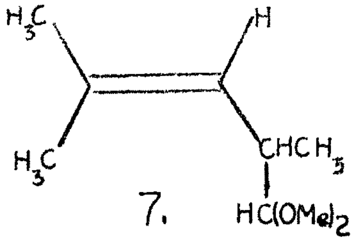

Ph
H
H$_3$C
COPh
hν / TiCl$_4$
MeOH
Ph
Ph
H$_3$C
53%

2.

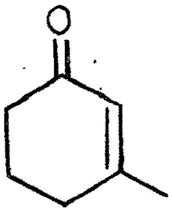
4.


H$_3$C
H
H$_3$C
COCH$_3$

5.


H$_3$C
H
H$_3$C
CHCH$_3$
HC(OMe)$_2$

7.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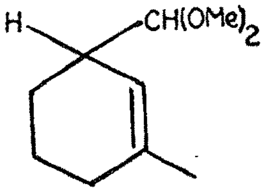
6.


H
CH(OMe)$_2$

8.

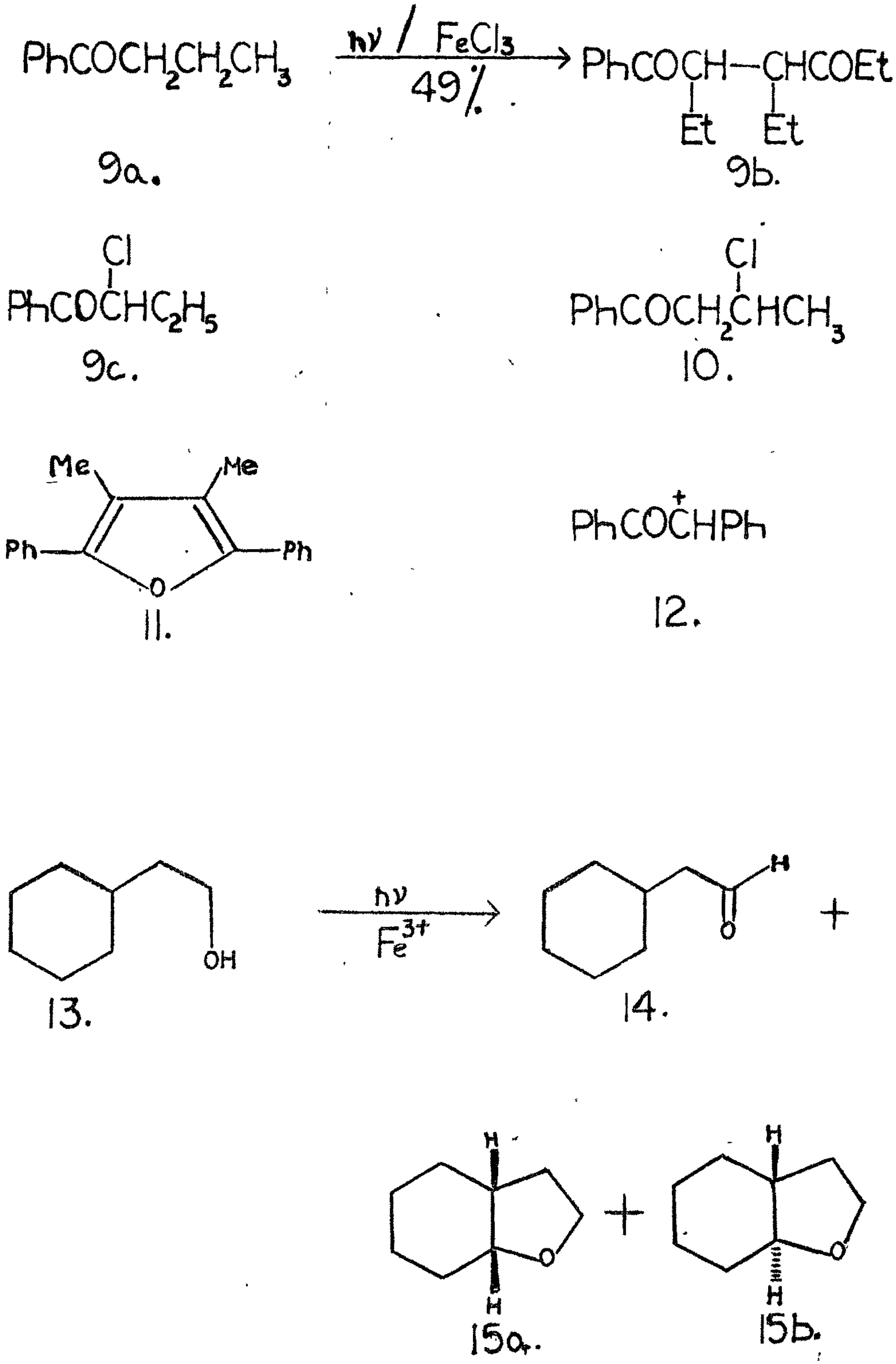
In addition Ti(IV) halides also play the role of photoinitiators in many polymerizations[10,11] presumably via the intermediacy of a radical cation[11]. The photocatalyzed degradation of polychlorinated biphenyls by TiO_2 has been suggested as a possible pathway for the environmental degradation of these compounds in water systems[12]. Heterogenous photooxidations of several organic substrates are catalyzed by TiO_2[13]. In substituted aromatic substrates both ring and side chain oxidation may occur depending upon the reaction conditions[14].

(ii) Iron

Iron(III) carboxylates and alkoxides decompose on irradiation to give the Fe(II) species and the corresponding organic radical which may decarboxylate as in the former case[15] or lead to the corresponding carbonyl compound as in the latter[16]. The photopolymerization of several vinyl monomers in solutions containing saccharides and Fe(III) salts have also been reported[17]. $FeCl_3$ catalyzes a novel photooxidative coupling of an enolizable ketone eg: butyrophenone(9a)[18,19]. A solution of (9a) on irradiation in presence of $FeCl_3$ gives 3,4-benzoyl hexane(9b),α-chlorobutyrophenone(9c), β-chlorobutyrophenone(<u>10</u>) a diphenylfuran derivative(<u>11</u>)

and acetophenone. The formation of $(\overset{9b}{8})$ and $(\overset{c}{9})$ indicates that the initial step involves oxidation of the ketone by $FeCl_3$ thereby leading to the α-keto radical. This reaction has also been extended to benzyl phenyl ketones[20]. A cationic intermediate(12) has been proposed. The photoreaction of iron(III) hydrate in the presence of cyclohexanol leads to a distribution of isomeric diols[21a]. Photolysis of an acetonitrile solution of 2-cyclohexyl ethanol(13) in the presence of anhydrous $Fe(ClO_4)_3$ gives cyclohexylacetaldehyde(14) and cis- and trans-perhydrobenzofuran i.e.(15a) and (15b) respectively with (15b) as major(Scheme-1)[21b].

The photooxidation of ethylene glycol in the presence of hexaquo iron(III) perchlorate has also been studied[22]. The major products are acetaldehyde and formaldehyde arising separately from two distinct mechanisms. A variety of primary and secondary alcohols have been oxidized by irradiation in an ethanolic $FeCl_3$ solution to the corresponding ketone or aldehydes[23]. Tertiary alcohols give the corresponding diols. By the same token aryl ethers have also been oxidized by irradiation in presence of $FeCl_3$ to alcohols, aldehydes(or ketones) and N-alkylacetamides[24].

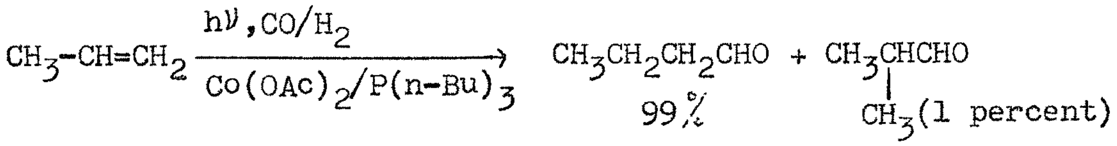

PhCOCH$_2$CH$_2$CH$_3$
hν / FeCl$_3$
49%
PhCOCH—CHCOEt
Et
Et
9a.
9b.
Cl
PhCOCHC$_2$H$_5$
9c.
Cl
PhCOCH$_2$CHCH$_3$
10.
Me
Me
Ph
Ph
O
11.
PhCO$\overset{+}{C}$HPh
12.
OH
13.
hν
Fe^{3+}
H
O
14.
+
H
H
O
15a.
+
H
H
O
15b.

SCHEME-1.

(iii) Chromium Manganese and Cobalt

Cobalt(III) and Manganese(III) catalyze the photopolymerization of styrene, methyl methacrylate[25] and acrylamide[26] while Cr(IV) catalyzes the photooxidation of pinacols[27] and phenols[28].

An interesting and in terms of synthetic utility the most important application is the photochemical hydroformylation of olefins with cobalt catalysts[29]. In the presence of carbon monoxide, hydrogen and $P(n\text{-}Bu)_3$ a methanolic solution of cobalt acetate is photochemically reduced to a low-valent cobalt carbonyl which is an active catalyst for the hydroformylation of olefins.

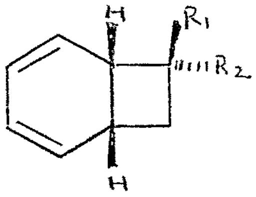


$$CH_3\text{-}CH{=}CH_2 \xrightarrow[Co(OAc)_2/P(n\text{-}Bu)_3]{h\nu,\ CO/H_2} \underset{99\%}{CH_3CH_2CH_2CHO} + \underset{\underset{CH_3\ (1\ \text{percent})}{|}}{CH_3CHCHO}$$

16 17

(iv) Zinc, Nickel, Vanadium and Rhodium

Ni(II), V(V) and Zn(II) species function as photoinitiators of various polymerizations[10,30]. The zinc chloride complex has been used in the 1,2-photoaddition of acrylonitrile to benzene[31]. Irradiation of an acrylonitrile-benzene-$ZnCl_2$ complex $[(AN)_2B_2 - ZnCl_2]$ and its analogues in place of a simple mixture of the olefin and benzenoid remarkably increases the 1:1 1,2-adduct formation(18).



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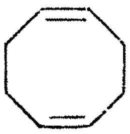

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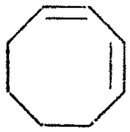

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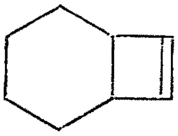

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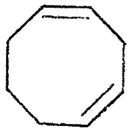


22.

Photolysis of cis-1,5-cyclooctadiene(19) in the presence of Rh_2Cl_2 in ether gives a mixture of 1,3-cyclooctadiene (20) and bicyclo [4.2.0] octene-7(21) along with a little 1,4-cyclooctadiene(22).

(v) Mercury, Silver and Gold

Silver(I) salts enhance the rate of many photopolymerizations[32,75b] and photooxidations[33,77]. Silver trifluoroacetate on irradiation in benzene undergoes decarboxylation to give the trifluoromethyl radical[34]. This is a convenient route to this species.

Au(III) compounds also have application as photoinitiators[35,36]. Photolysis of aliphatic α-amino acids in the presence of inorganic mercury results in the formation of methyl mercury[37].

$$\mathrm{RCH(NH_2)COOH} \xrightarrow[\mathrm{HgCl_2}]{h\nu} \mathrm{MeHgCl}$$

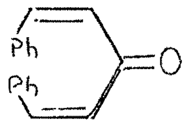
It is suggested that aliphatic α-aminoacids are a possible source for the photochemical formation of the highly neurotoxic methyl mercury in nature.

(vi) Cerium and Uranium

Irradiation of Ce(IV) ions in solutions of alcohols (RCH_2OH) or in methanolic solutions containing carboxylic acids (RCOOH) generates the alkyl radical ($R^{\cdot}$)[38]. These radicals can be trapped by molecular oxygen to give the corresponding alkyl peroxylradicals thus providing a convenient route to this species[39].

The uranyl(VI) ion catalyzes a wide range of photoreactions which include double bond isomerizations[40], oxidation of alcohols[41] and decarboxylations[42]. The photochemistry of uranyl(VI) ions in the presence of alcohols has been reviewed[43]. The quenching photo-excited [UO_2^{2+}] proceeds by a number of mechanisms depending on the substrate[44].

Direct photodimerization of(23) gives(24) while in the presence of (UO_2^{2+}) the product obtained is(25)[45].



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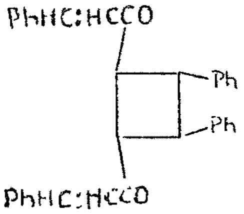

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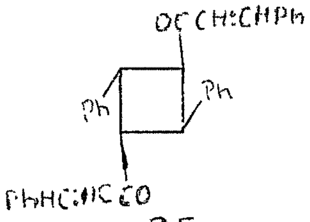


25.

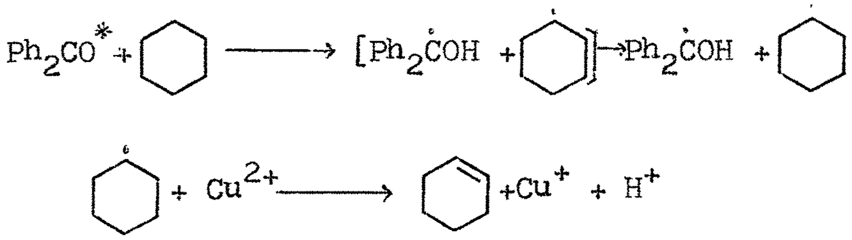
The stereospecificity is attributed to the bulk of the uranyl group to which one molecule of (23) coordinates.

Similar to the Ti(IV) ion, U(VI) also affects the photochemistry of α,β-unsaturated carbonyl and related compounds[8]. In contrast to Ti(IV) however, bond formations occur on a C=C carbon atom of the substrate.

(vii) Copper

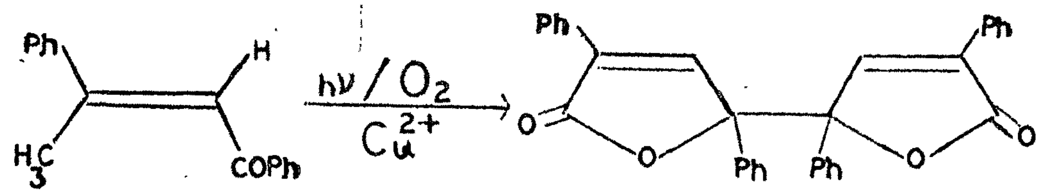
The contribution of the copper ion to the area of transition metal ion catalyzed organic photochemistry being enormous the Cu(I) and Cu(II) ions are discussed separately. Several reviews have appeared on this subject[46].

(a) The Copper(II) Ion:- It has been used to promote photochemical cyclizations[47], dimerizations[48] and allylic halide isomerizations[49]. The powerful oxidizing capacity of the photosensitized Cu(II) species has been made use of to introduce unsaturation in a variety of hydrocarbons in the presence of benzophenone[50]. Irradiation results in the efficient production of the alkyl radical by the photoexcited benzophenone which is then oxidized by the excited Cu(II) to olefin(Scheme-2).



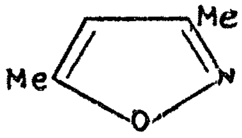
Scheme - 2

α,β-Unsaturated ketones may also be photooxidized in the presence of Cu(II). When a methanolic solution of dypnone(2) containing catalytic amounts of $CuSO_4$ was irradiated for 6 hrs in the presence of air (26) was the chief product obtained[51]. In the absence of Cu(II) cis-trans isomerization was the sole reaction pattern.



2.

26.



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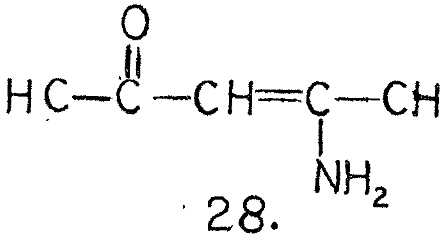
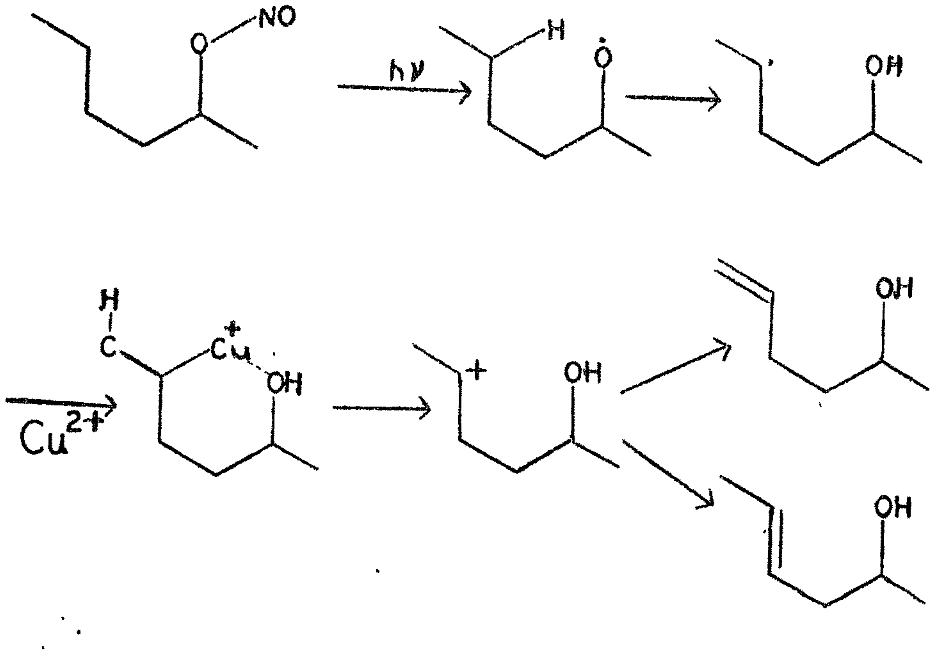


$$\mathrm{HC{-}\overset{O}{\overset{\|}{C}}{-}CH{=}\underset{NH_2}{\underset{|}{C}}{-}CH}$$

28.



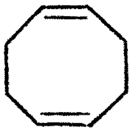
SCHEME-3

Cu(II) also promotes photo-induced ring cleavage of 3,5-dimethyl isooxazole(27) to give the aminoenone(28)[52]. Irradiation of pyridine oxides in the presence of Cu(II) gives an increased yield of formyl pyrroles[53]. An interesting offshoot has been a modification of the famed Barton reaction[54]. Cu(II) has been used to intercept the δ -alkyl radical generated by the photolysis of alkyl nitrites[55]. An oxidative elimination occurs resulting in the formation of a double bond at a remote carbon atom(Scheme-3). Cu(II) also functions as a light stabilizer for polyamides[56].

(b) The copper(I) ion:- The copper(I) ion which is known to form π-complexes with olefins[57] has a profound effect on the photochemistry of various substrates with unsaturated sites. An unusual catalytic effect due to such a complex on the photochemistry of cis,cis-1,5-cyclooctadiene(29) was first reported by Srinivasan[58] to give as one of the products tricyclo[3.3.0.0.] octane (30). Though a radical intermediate(31) has been proposed[59] the mechanism is probably an intramolecular one where the primary photochemical step involves the absorption of light by the uncomplexed(29) and the Cu(I) exerts its influence in the subsequent stabilization of the initially formed excited state(Scheme-4)[60]. The formation of (30) is probably via an initial isomerization to cis, trans-1,5-cyclooctadiene(32)[61].

The first clear cut example of a new type of dimerization, the light-induced cycloaddition of olefins in the presence of Cu(I) was reported by Trecker and co-workers[62a]. Norbornene(33) on irradiation in a solution containing Cu(I) halide affords exo,trans,exo-dodecahydro-1,4:5,8-dimethanobiphenyl(34). A transient complex(35) was suggested where the Cu(I) serves as a template for dimerization[62b]. In the presence of CuCl, norbornadiene(36) effectively isomerizes to quadricyclene(37) via a 1:1 norbornadiene-CuCl complex(Scheme-5)[63]. This CuCl catalyzed valence bond isomerization is an attractive process for the chemical storage of light energy as the catalytic reconversion of (37) to (36) would release ~260 cal/g of energy[64,65]. The mechanism of sensitization by Cu(I) of (36) can be controlled by the judicious addition of ligands like Ph_3P to the system[66].

Though cuprous halides have been used widely to promote a variety of photochemical reactions it has more recently been demonstrated that copper(I) triflate is superior as a catalyst[67]. Several simple non-conjugated unstrained olefins have been photodimerized with this



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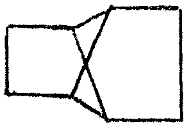

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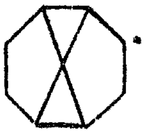

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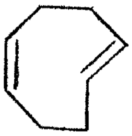

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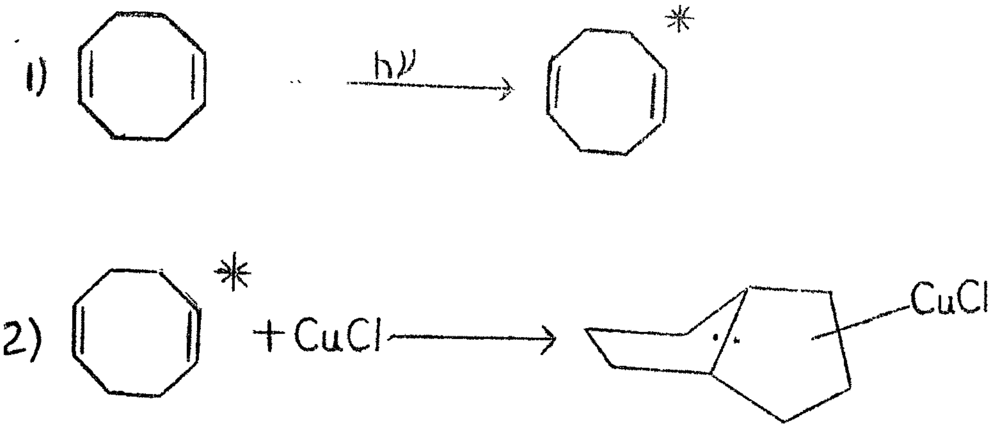

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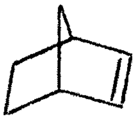

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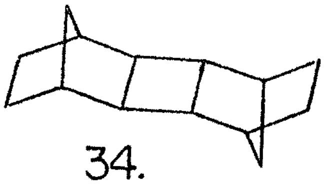

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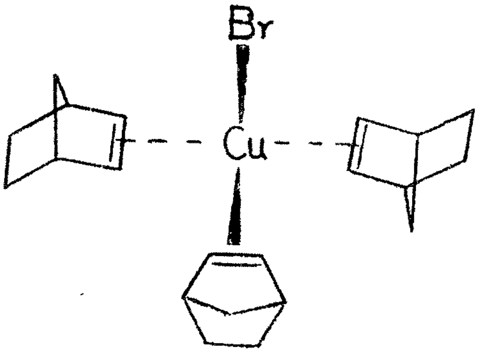

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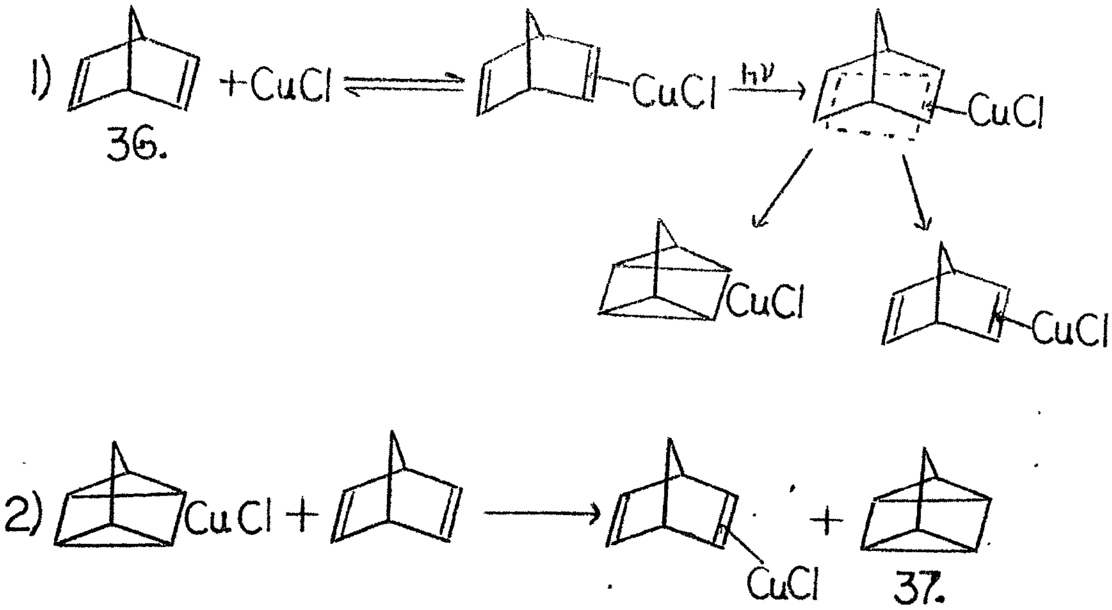
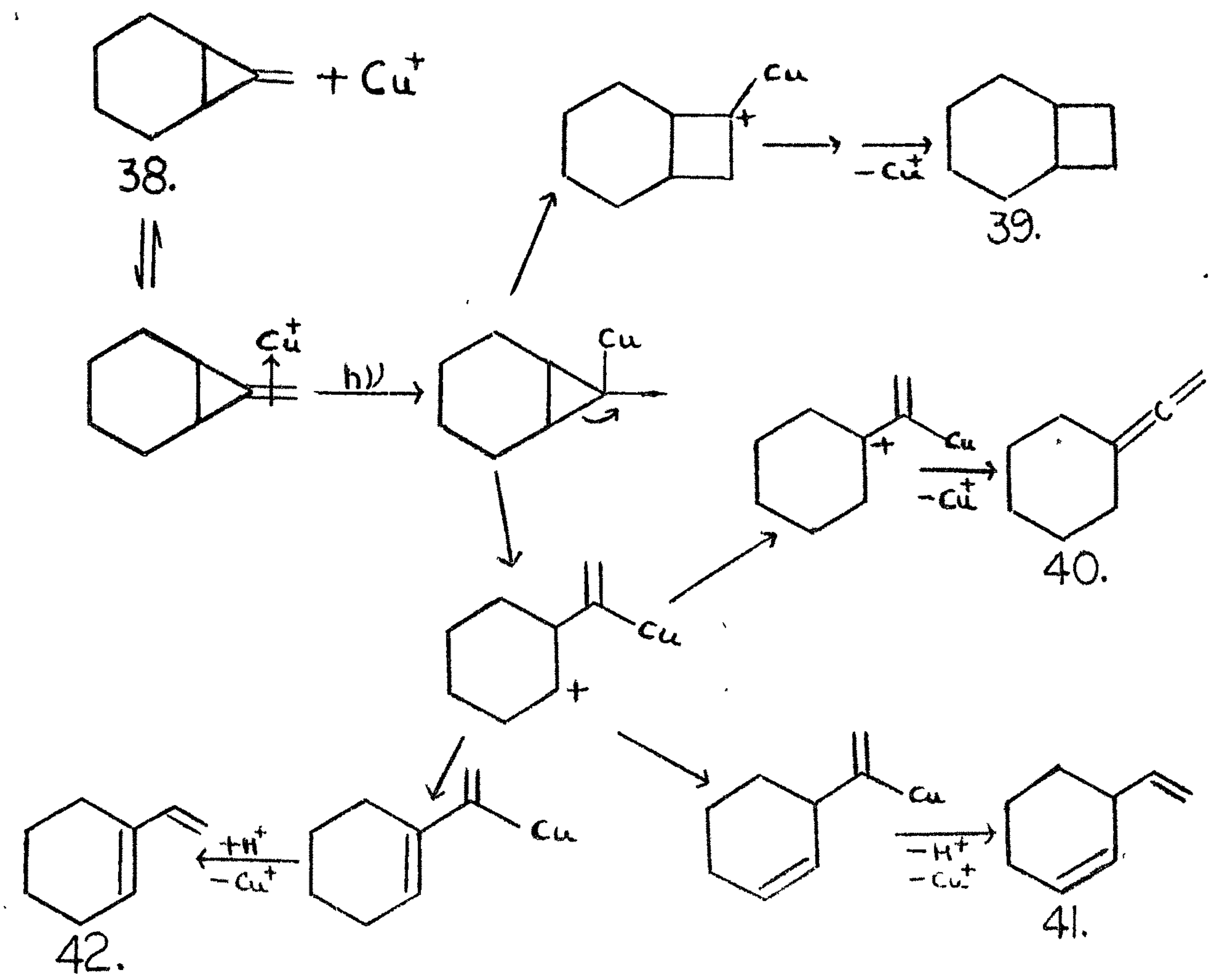


SCHEME—5

catalyst giving usually the thermodynamically less stable *trans*-fused[2+2] cyclodimers[68]. CuOTf also promotes the photocyclization of functionally substituted olefins[69]. The photochemistry of 7-methylene norcarane(38) in the presence of Cu(I) is charactierized by a host of novel molecular transformations involving carbon skeletal reorganization; a new class of copper catalyzed photochemistry involving preliminary photocupration(Scheme-6)[70]. Cu(I) also induces a photochemical stepwise metathesis of olefins giving a synthetic route to cyclopent-2-en-1-ones(45) via a photobicyclization of 3-hydroxyhepta-1,6-dienes(43)[71](Scheme-7). Similarly, β- and γ-alkenyl allyl alcohols may also be bicyclized in this manner[72]. This approach has been utilized in the synthesis of several complex tricyclic-ring systems[73]. Thus for example(47) can be obtained from(46). The key step in the synthesis of α- and β-panasinsene(48) involves a CuOTf catalyzed intramolecular [2+2] photocycloaddition of (49)[74].

Other photoreactions catalyzed by Cu(I) include polymerization of ethers[75], ring contraction of cycloalkenes[76], addition across double bonds[77] and oxidative dimerizations. The latter approach has been used to prepare high energy molecules which have potential for storage and controlled recovery of light[78].



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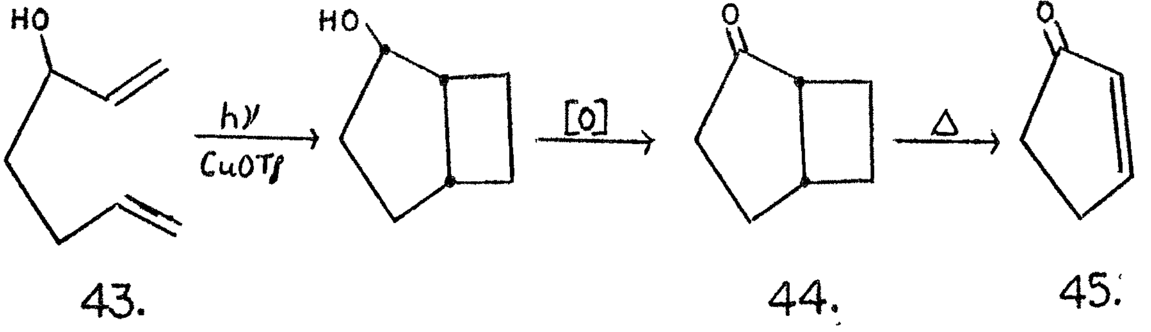

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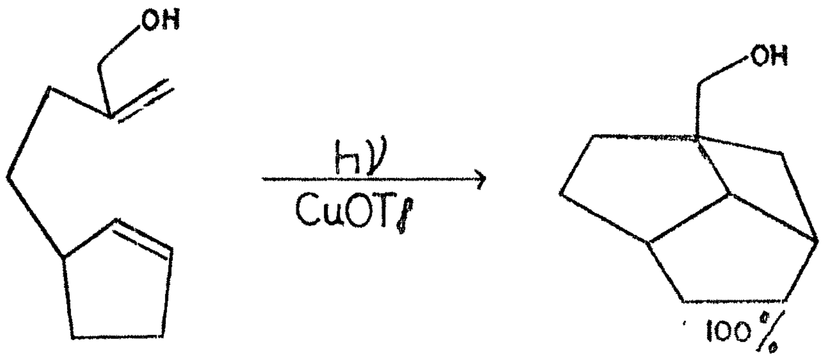

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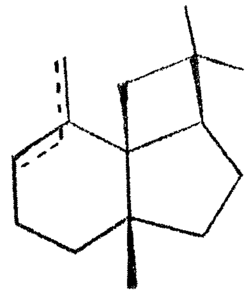

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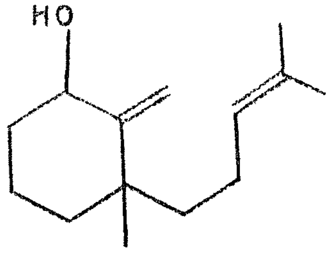

49.

In conclusion

That the transition metal ions have an important role to play in the photochemistry of a wide array of organic substrates is a well established and documented fact. Interest in this area ranges from mechanistic considerations to synthetic utility. Utilitarian aspects include, inter-alia, dimerizations, cyclizations, isomerizations and polymerizations. An interesting and probably at some future date viable development has been the use of transition metal ions to prepare, photochemically, high energy molecules as a mechanism for storage and controlled release of light energy.

The work described in the following section discusses our investigations into the use of some transition metal ions, those known to form π-complexes with olefins, in the photocyclization of some aliphatic iodide systems.

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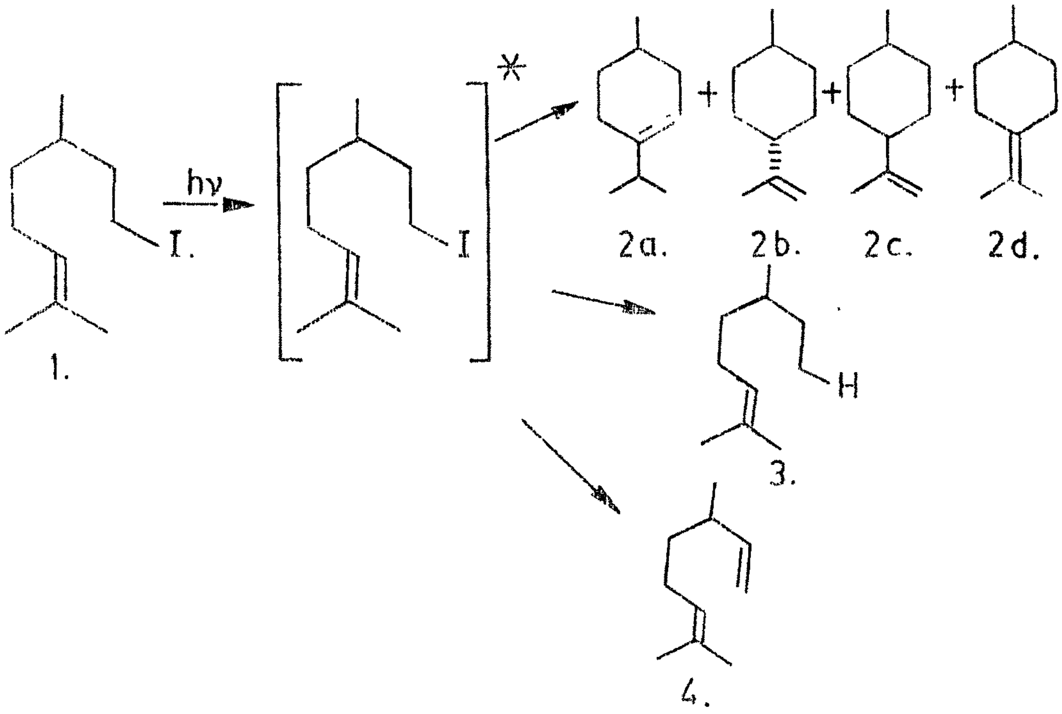
SECTION - II

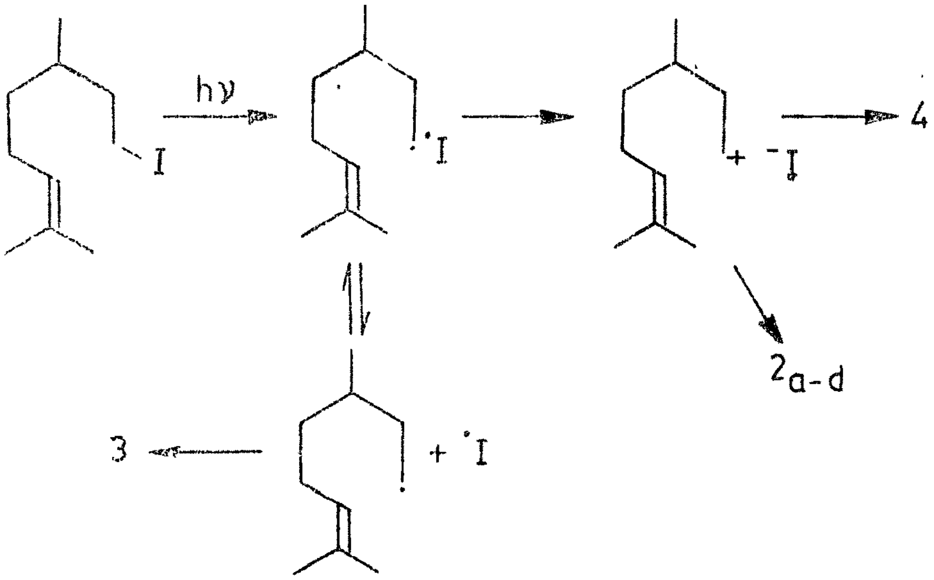
PRESENT WORK

The photochemistry of organic iodides has been the subject of extensive study[1] and the cyclization of systems with suitably located olefinic linkages established to be synthetically viable[2,3]. In order to increase the synthetic utility it would be desirable to maximise the percentage of cyclization in the product mixture. Some success has been achieved by varying the reaction conditions and an optimum yield of cyclization requires THF as solvent and a reaction temperature of 50° [3b,c]. Under these conditions citronellyl iodide(1) yields, inter alia, 54 percent of the cyclization products(2a-d). Of the other products the major are the ones corresponding to (i) reduction at the C-I bond(3) and (ii) elimination of HI(4). (Scheme-1).

Photoexcitation of an organic iodide results in the cleavage of the C-I bond(quantum efficiency ~1) to give a radical pair[4]. Mechanistic studies have shown that the radical pair, to a large extent, undergoes an electron transfer in the solvent cage giving rise to a 'hot', unencumbered cation[5,6]. While the reduction product(3) is derived exclusively from the alkyl radical, the hot carbocation goes over to the elimination(4) and cyclic(2a-d) products (Scheme-2).



SCHEME-1



SCHEME-2

A. Influence of transition metal ions on the photochemistry of Citronellyl Iodide(1)

In an effort to further improve the percentage of cyclization the effect of transition metal ions on the photochemistry of (1) was investigated. It was visualized that metal ions known to complex with olefins may function as a template via a loose complexation with the olefinic moiety and an electrostatic bond with the iodine substituent, thereby arresting the molecule in a conformation conducive to cyclization. The rationale underlying this approach was based on the Franck-Condon principle[7]. In accordance with this principle that nuclear movements are very slow in comparison with electronic motion it was felt that the conformation of the molecule would retain itself over the very short period required for photoexcitation. If this holds true then the excited state also has the favourable conformation, resulting in an enhancement of cyclization-a rapid process from the 'hot' carbocation (see ChapterI, Section II).

The salts chosen for this particular study were the halides of Cu(I), Pd(II), Ag(I),Pt(II) and Hg(II) all known to form reasonably stable complexes with olefins[8].

For photolysis, a 1 percent solution of(1)in THF containing a molar equivalent of Et_3N was used. Preliminary experiments using saturated solutions of the metal halides gave promising results(Table I). For these experiments the citronellyl iodide solution was stirred with excess metal halide(~1.0 g) for 15 min and filtered. The clear filtrate was then irradiated with a 400 watts med. pressure Hg vapour lamp at 50° for 2 hrs. At the end of this period conversion was 93-97 percent(GLC, 10 percent CW,170°).

Table I: A comparison of the total cyclic products obtained in the presence of some metal halides during photolysis of Citronellyl Iodide.

No.	Salt*	Total cyclization products (%)
1	No salt[3c]	54
2	CuCl	64
3	CuI	60
4	$PdCl_2$	55.2
5	AgCl	58.1
6	$PtCl_2$	54.6
7	$HgCl_2$	41.0

*Saturated solution

Table-I gives a comparison of the % of total cyclized products (2a-d) obtained under the influence of various transition metal halides vis-a-vis that obtained in the absence of any salt. It is obvious that the metal ions do exert some influence on the photochemistry though to varying degrees. Further it appears, prima facie, that the influence of Cu(I) ion is most profound.

Considering the differing solubilities of the metal halides a more quantified evaluation of the effect would require a uniform concentration of the metal ions throughout. For this purpose AgCl(which has the least solubility was taken as the standard. Its solubility was found to correspond to 2.5×10^{-4} moles(35 mg) in a solution of 2.7 g of (1) in 270 ml THF containing a molar equivalent of Et_3N. This corresponds to an 8.9×10^{-4} M conc. of AgCl in THF.

Irradiation of the above solution containing an 8.9×10^{-4} M conc. of the different metal halides gave a remarkable improvement in the yield of the total cyclization products(Table-2). It can be seen that

TABLE 2

Photolysis of Citronellyl Iodide* in the presence of an 8.9×10^{-4} M conc. of Metal Chloride

No.	Salt	Amt. of Salt (mg) $\equiv 2.5 \times 10^{-4}$ moles	Product composition (%, GLC)**							Product+ yield (%)	Total cyclized products (%)
			3	4	unknown	2a	2b	2c	2d		
1	No Solt	-	9.0	27.0	8.0	2.0	36.0	7.0	10.0	74	54
2	CuCl	24.0	9.6	17.1	-	-	51.4	13.7	8.2	70	73.3
3	$PdCl_2$	42.5	10.0	27.3	-	-	38.0	13.0	12.0	68	63.0
4	AgCl	35.0	11.0	30.6	-	-	40.0	12.0	6.4	70	58.4
5	$PtCl_2$	64.0	13.7	31.25	-	-	37.11	9.8	8.2	68	55.11
6	$HgCl_2$	65.2	19.2	18.3	-	-	41.3	12.5	9.7	77	63.5

* 2.7g Citronellyl iodide in 270 ml THF contg. amolar eq. of Et_3N

** Column :- 360 cm × 0.6 cm Al column, packed with 10 % CW; temp.- 100°
(the 10% DEGS-CuCl column gave better resolution)

+ Total distilled product. (% computed of basis of elimination of HI) though there is a noticeable improvement in cyclization in all the cases, CuCl gives the best results.(See Fig.1a-e).

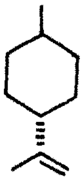
From Table-2 it is evident that an enhancement of cyclization(2a-d) by the metal ion is at the expense of the elimination product(4), While the proportion of reduction product(3) remains fairly constant. This would seem to indicate that the metal ion has no noticeable effect on the electron transfer process in the radical pair(Scheme-2). That the metal ion does not behave as an electron acceptor is also suggested from an examination of the standard reduction potential data for the metal ions under consideration(Table-3)[9].

Table - 3:- Standard Reduction Potential for the metal ions.

Reaction	Std.Red.Pot. (Volts)
$Cu^+ + e^- \rightarrow Cu$	0.522
$Pd^{2+} + 2e^- \rightarrow Pd$	0.83
$Ag^+ + e^- \rightarrow Ag$	0.7996
$Pt^{2+} + 2e^- \rightarrow Pt$	~ 1.2
$Hg^{2+} + 2e^- \rightarrow Hg$	0.851

GLC's of the products of photolysis of Citronellyl Iodide in THF in the presence of an $8{\cdot}9\times10^{-4}$ M conc. Metal halide (MX_n) Fig. 1a to 1e

Peak identify

Peak No.	Compound
1	
2	
3	
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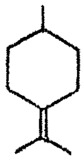
5	

Column Conditions

Column length - 12'
Stationary phase - 10% DEGS-CuCl
Temperature - 100°
Carrier gas - Hydrogen
Flow rate - 60 ml/min

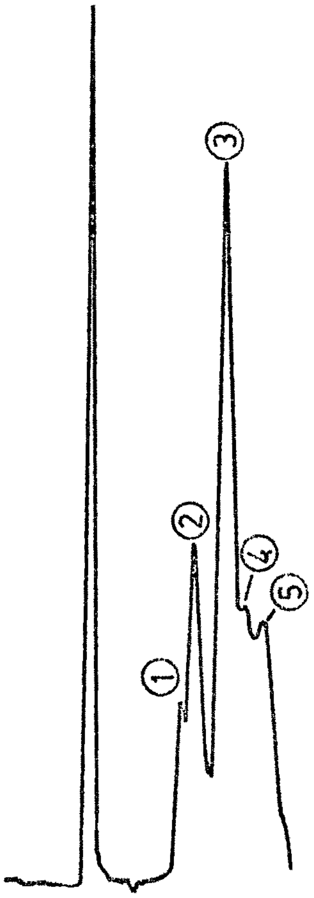


Fig. 1a : MX_n = CuCl

Column Conditions

Column length - 12'
Stationary phase - 10 % DEGS CuCl
Temperature - 100°
Carrier gas - Hydrogen
Flow rate - 60 ml/min.

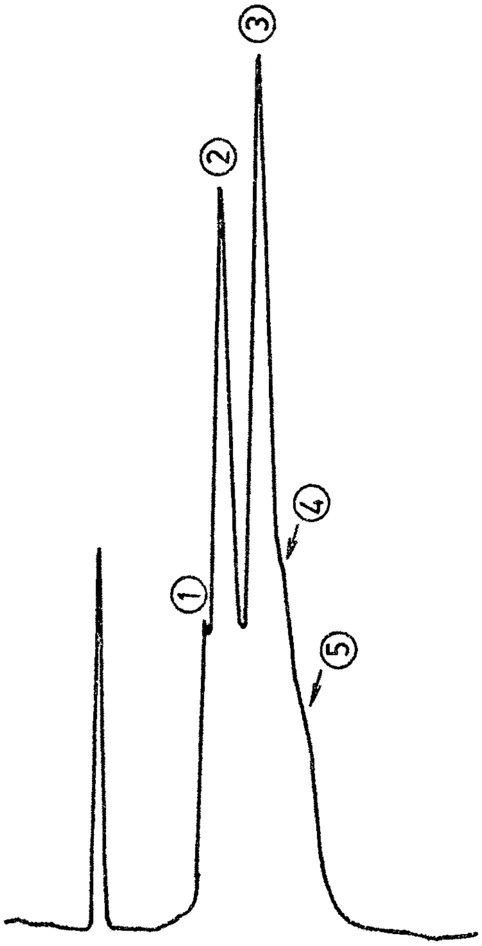


Fig. 1b: $MX_n = AgCl$

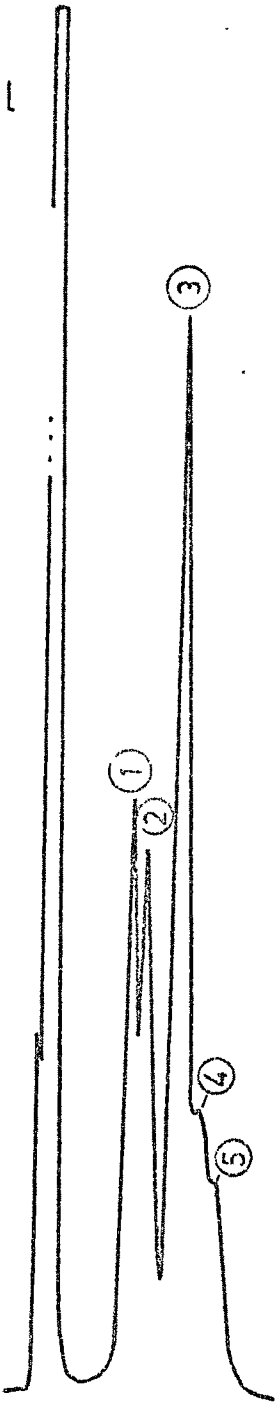


Fig. 1c : $MX_n = HgCl_2$

Column Condition

Column length - 12'
Stationary phase -10 % DEGS-CaCl
Temperature - 100°
Carrier gas -Hydrogen
Flow rate - 60 ml/min.

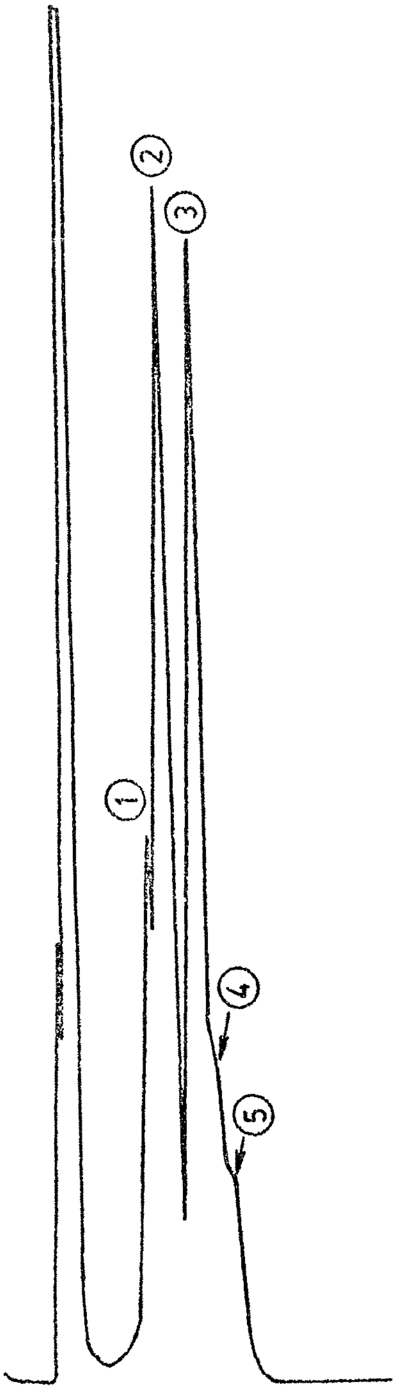


Fig. 1d : $MX_n = PtCl_2$

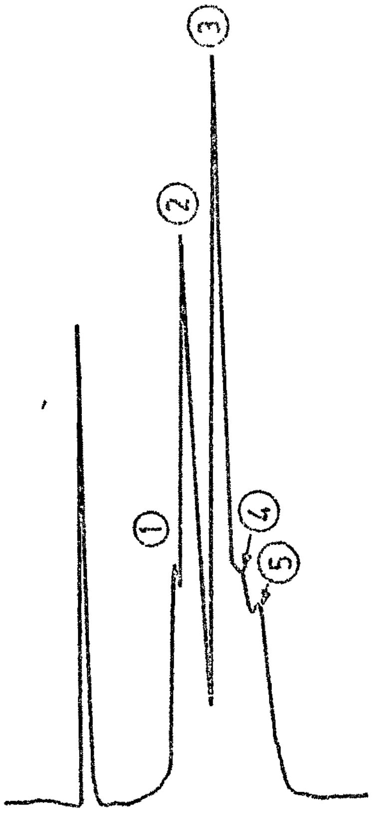


Fig. 1e : $MX_n = PdCl_2$

It can be seen that while the reduction potential of the Cu(I) ion is the lowest, nevertheless its effect on cyclization is the most pfrofound. Also in agreement with this is the high proportion of citronellyl iodide to metal halide(~41:1) used.

All these considerations suggest that the metal ion functions chiefly as a 'template'. The observed increase in the percentage of the reduction spin orbit coupling produced by the 'heavy' metal atom. The increase corresponds to the increase in atomic weight from Cu to Hg.

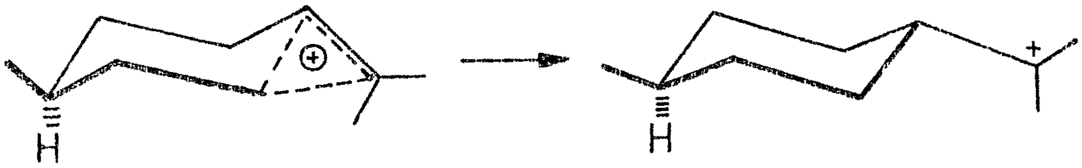
In view of the fact that a decrease in the concentration of metal halide gives a larger proportion of the cyclic products(Tables 1 and 2) the effect of varying Cu(I) ion concentration was examined(Table-4).

Table 4:- Effect of Cu(I) concentration on cyclization

No.	Conc. of CuCl in 270 ml THF (M)	wt. of CuCl (mg)	Total cyclized products (%)
1	5.6×10^{-4}	15	63
2	8.9×10^{-4}	24	73.3
3	1.3×10^{-3}	35	67

From tables-1,2 and 4 it follows that of the metal halides studied, CuCl is the most effective in enhancement of the photocyclization of citronellyl iodide(1) under the experimental conditions when present in an optimum concentration of 8.9 x 10^{-4} M(in THF).

Discussion:- The major product obtained in the cyclization viz:- p-menth-8-ene(2b) has the *trans*-stereochemistry. The preferred conformation was deduced to be(5) leading to(6)[3c]. By the same token the effect of Cu(I) would be to hold the ground state molecule(1) in this conformation. Molecular models suggest a preference for this conformation since the approach of the Cu(I) ion would be from the β-face with respect to the molecular plane(7). The possibility of a preliminary photocupration as suggested in the case of 7-methylnorcarane[10] cannot however be ruled out, in which case the intermediate would be (8)



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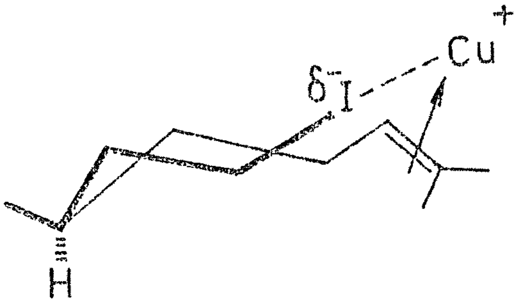

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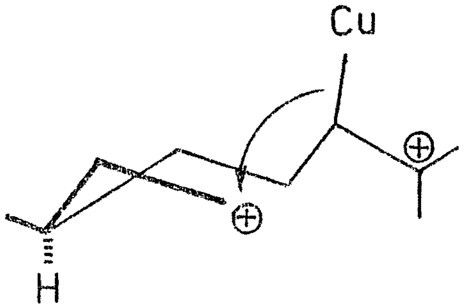


8.

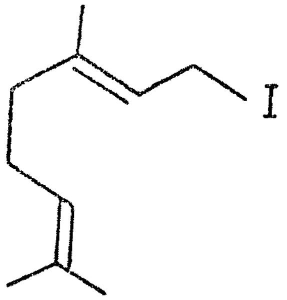
B. Cu(I) catalyzed photochemistry of Geranyl and Neryl Iodides

Having thus realized that some transition metal ions, particularly the Cu(I) ion, may be used to enhance the photocyclization of citronellyl iodide it was of interest to extend this approach to other similar systems in order to ascertain the generality of this method.

In view of the importance of the geranyl cation in monoterpene biogenesis the photochemistry of geranyl(9) and neryl(10) iodides have already been studied[3c,d]. The photolysis of both (9) and (10) under conditions similar to those used for citronelly iodide[3c] gave apart from the cyclization products(11) and (12) the elimination products (13), (14) and (15). The reduction product(16) was not detected in the product mixture. As might well be expected ~~in~~ the *Z*-isomer(10) gave a larger proportion of cyclization in comparison with the *E*-isomer(9).

(a) Effect of Cu(I) on the photochemistry of Geranyl Iodide(9)

The influence of Cu(I) ion on the photocyclization of geranyl iodide(9) was first ivestigated. For this purpose a 1 percent solution of(9) with a molar equivalent of



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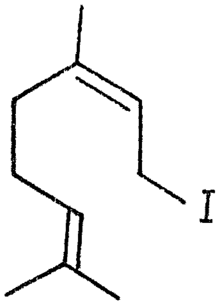

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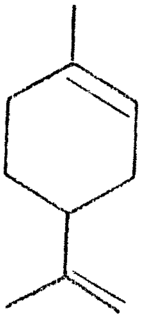

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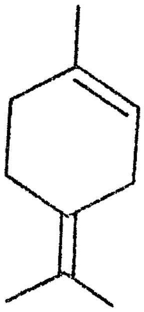

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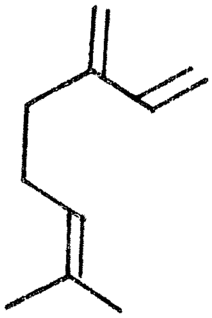

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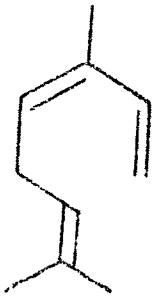

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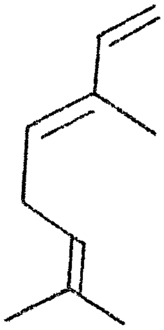

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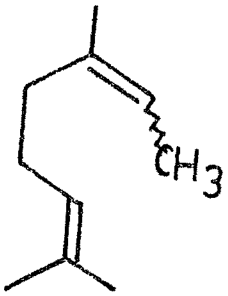


16.

triethyl amine in THF containing an 8.9 x10^{-4} M.conc. of CuCl was irradiated for 2 hrs and the products obtained identified by mixed injection with authentic samples on GLC. Table-5 shows a comparison of the product distribution obtained in the presence and absence of CuCl under otherwise identical experimental conditions. An almost 3.5 fold increase in the cyclization to elimination ratio may be noted when CuCl is used. Terpinolene(12) is the predominant cyclic product obtained while of the elimination products *trans*-ocimene(15) increases at the expense of myrcene(13)(Fig.2a).

Table 5: Effect of Cu(I) on the photolysis of Geranyl Iodide.

Peak No.	Compd^{+}	Composition (%)	
		without CuCl	with CuCl
U	Unidentified	25.6	14.4
1	13	48.53	28.8
2	Unidentified	1.6	3.6
3	11	5.3	10.3
4	14	4.7	2.7
5	15	5.3	27.3
6	12	0.88	12.3

See Fig.

\+ identification was by mixed GLC with authentic samples on 10 percent CW, 10 percent DEGS and 10 percent DEGS-CuCl columns(80°)

(b) Effect of Cu(I) on the photochemistry of Neryl Iodide(10)

(10) was photolysed in the presence of CuCl as described for (9) and the product obtained was compared to that obtained in the absence of CuCl(Table-6). Here again a marked improvement in cyclization was observed with a >2 fold increase in the cyclization to elimination ratio. The relative product distribution was the same as that of observed for (9)(Fig. 2b.).

Table 6:- Effect of Cu(I) on the photolysis of Neryl Iodide

Peak No.	Compound	Composition (%)	
		without CuCl	with CuCl
U	Unidentified	29.3	22.3
1	13	29.8	10.6
2	Unidentified	1.0	3.2
3	11	22.6	26.4
4	14	3.3	—
5	15	4.1	15.6
6	12	10.4	22.0
$\frac{\text{Cyclization}}{\text{Elimination}}$		0.875	1.347

See Fig

See table-5, Footnote

GLC's of the products of photolysis of Neryl and Geranyl Iodides in THF presence of an 8.9 × 10^{-4} M conc. of CuCl.

GLC Conditions

Column length - 12'
Stationary phase - 10 % cw
Temperature - 80°
Carrier gas - Hydrogen
Flow rate - 60 ml/min

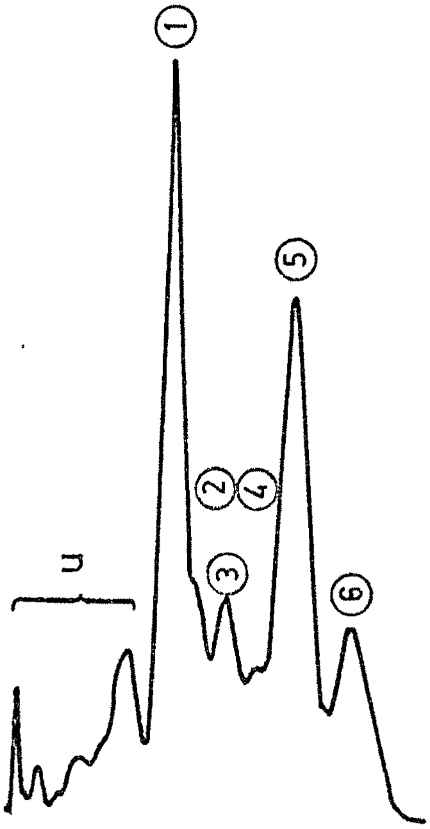


Fig. 2a : Geranyl Iodide

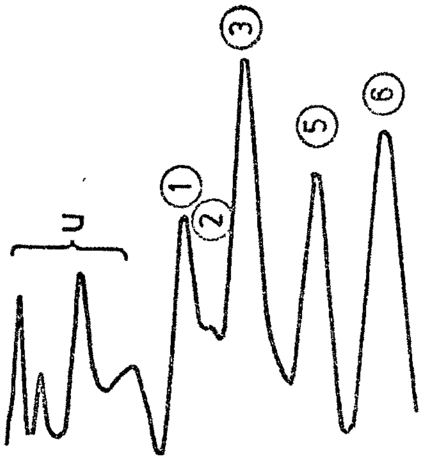


Fig. 2b : Neryl Iodide

(c) Discussion

We have demonstrated therefore that catalytic amounts of CuCl bring about a significant enhancement in phtocyclization of the allylic iodide systems (9) and (10). Though the mechanism appears to be chiefly via a 'template' effect of the Cu(I) ion, as pointed out earlier, a preliminary photocupration pathway cannot be ignored(eg.8)[10].

A 1 percent solution of myrcene(13) in THF containing a **molar** equivalent of triethylamine and an 8.9 x 10^{-4} M.conc. of CuCl was irradiated for 2 hrs. The product mixture obtained consisted of 48 percent unreacted(13) and of the products only 4.6 percent was limonene(11) while terpinolene (12) was not detectable (GLC). As the interaction of Cu(I) with the π-system of myrcene does not give, in significant amounts, the desired cyclic products it is unlikely that (11) and (12) are obtained via a photocupration pathway from the iodide.

A contrasting feature of the Cu(I)-catalyzed photocyclization of these systems in comparison with the non-catalyzed photoreaction is the predominance of the thermodynamically more stable isomer ie(12) over(11)(see tables 5 and 6). It is possible therefore that in these reactions much of the terpinolene arises due to a Cu(I) catalyzed double bond isomerization of initially formed(11). To ascertain this a 1 percent soln. of (11) in THF containing a molar equivalent of Et_3N and an 8.9 x 10^{-4} M.conc. of CuCl was irradiated for 2 hrs. No change in the starting (11) was observed.

Thus both these experiments demonstrate that the enhancement of cyclization by the Cu(I) ion is purely due to a template effect. The cyclized products(11) and (12) arise directly from either (9) or (10) and are not due to catalysis of any secondary reaction of a primary photoproduct.

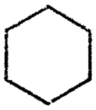
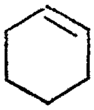
C. Cu(I) catalyzed photochemistry of 1-Iodo-5-hexene

The photochemistry of 1-iodo-5-hexene(16) has already been discussed, its point of interest being that it offers a distinction between the radical and cationic pathways of cyclization(see Chapter I, Section II).

16.

In order to study the relative effect of Cu(I) on these pathways a 1 percent solution of (16) with molar equivalent of Et_3N in THF containing an 8.9×10^{-4} M.conc. of CuCl was irradiated. The work-up and product identification procedure was the same as that described earlier (Chapter I, Experimental). Table 7 gives a comparison of the product distribution obtained in the presence and absence of CuCl.

Table 7:- Effect of Cu(I) on the photochemistry of 1-Iodo-5-hexene.

Compound	Composition (%)	
	without CuCl	With CuCl
	20.08	29.2
	32.96	32.7
	29.3	15.9
Unidentified	9.2	22.9

It can be seen that while the cyclohexane and 1-methyl cyclopentene proportions remain fairly constant there is a significant reduction in the amount of cyclohexene with a corresponding increase in the unidentified material when CuCl is used. With regard to our initial objective these results throw no light and can at best be termed **inconclusive**.

D. Use of an optically active base

In all the above photolyses a molar equivalent of Et_3N was used as HI scavenger. It was felt that in the Cu(I)-catalyzed photocyclizations the use of an optically active base instead of Et_3N could result in an asymmetric centre(eg.(11) from (9) or (10)). Asymmetric induction, it was visualized, would probably result through a CuCl-base coordination complex. Neryl iodide(10) was chosen for this study and its Cu(I)-catalyzed photochemistry in the presence of two optically active bases viz:- *l*-menthyl amine and N-dimethyl-*l*-menthyl amine was investigated for a possible asymmetric induction in the cyclized product limonene(11). In both the cases however the results were inconclusive as the proportion of (11) in the product mixture was too low (<5 percent) to permit isolation. Several higher boiling components formed a major part of this product mixture.

E. Conclusion

Thus transition metal ions, particularly those that form reasonably stable complexes with olefins, may be used in catalytic amount to enhance the photocyclization of aliphatic iodides with suitably situated ethyleneic linkages. Of the metal ions studied Cu(I) gave the best results functioning as a 'template' which holds the ground state molecule in a conformation conducive to cyclization in the excited state. Attempts to induce asymmetry in the cyclization process were however not very successful.

EXPERIMENTAL

All bp's are uncorrected. All solvent extracts were finally washed with brine before drying(Na_2SO_4). For general remarks, see Chapter I, Section II(Experimental).

Solvents:-

Solvents used for photoirradiation were purified as under.

Tetrahydrofuran - by refluxing and distilling over LAH[12].

Triethylamine - by refluxing with KOH pellets and distilling over Na[13].

CuCl and CuI were freshly prepared everytime[14].

NaI was dried by azeotropic distillation with xylene until no more water separated.

General procedure for photoirradiation

Photoirradiations were carried out at 50° with Applied Photophysics medium pressure mercury lamp, 400 LQ(400 watts) suspended in a double-walled, water-cooled, clear-fused quartz well without filter under a blanket of dry, oxygen free nitrogen gas. A 1 percent solution of the substrate in dry, peroxide free THF containing a molar equivalent of triethylamine was stirred vigorously with the requisite amount of metal halide(see tables 1,2,4) for 15 min. prior to irradiation. The reaction was monitored by tlc(10 percent benzene in pet. ether). When the photostationary state was reached(~2 hrs) the solvent was carefully stripped off through an efficient Vigreaux column. The product so obtained was passed through a short column of SiO_2-gel/IIB[15] and eluted with pet.ether. The hydrocarbon mixture obtained by removing the pet.ether was distilled *in vacuo* and the individual compounds identified by mixed glc. with authentic samples on at least three stationary phases(10 percent CW, 10 percent SE-30, 10 percent DEGS).

I) Preparation and photoirradiation of Citronellyl Iodide

a) Citronellyl tosylate:- To a cooled solution of (0-1°) of citronellol(3.27 g, 0.021 mole) in dry pyridine(16 ml) was added p-toluene sulphonyl chloride(5.98 g, 0.03 mole) in portions under intermittent shaking of the reaction mixture which was then kept at ~4° for 24 hrs. The reaction mixture was then poured into crushed ice, extd. with Et_2O(50 ml x 3) and the combined extract washed with 10 percent HCl(5 ml x 3), followed by water. Removal of solvent at room temp.(~30°) under reduced pressure afforded the crude citronellyl tosylate(5.57 g, 85.8 percent yield).

PMR: $\underline{CH_3}CH$(3H, d, 0.87 ppm, J=6 Hz); $(\underline{CH_3})_2C=C$(6H,3H singlets at 1.58 and 1.67 ppm); CH_3Ar(3H, s, 2.46 ppm); $\underline{CH_2}OSO_2$(2H,t, 4.03 ppm, J=6 Hz); $\underline{HC}=C$(1H, ill resolved t, 5.01 ppm); H-Ar(4H; 2H, d, 7.3 ppm, J=8Hz; 2H, d, 7.75 ppm, J=8 Hz).

b) Citronellyl Iodide

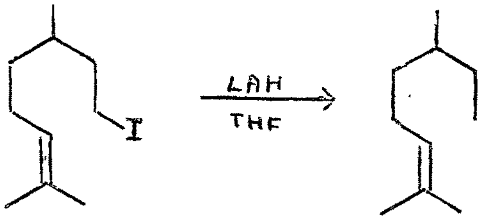
To citronelly tosylate(5.5 g, 0.0177 mole) was added 9 g(0.059 mole) of dry NaI dissolved in dry acetone and the reaction mixture stirred at room temp.(~30°) for 13 hrs. The bulk of the solvent was stripped off and the residue treated with water(30 ml) and the product taken up in ether(50 ml x3). The combined ether extract washed with 10 percent $Na_2S_2O_3$(10 ml x 2) and H_2O. The solvent was distilled off and the residue distilled to furnish pure citronellyl iodide as a pale yellow oil(4.29 g); b.p. 116-118°/10 mm.

PMR: $\underline{CH_3}CH$(3H, d, 0.9 ppm, J = 6 Hz); $(\underline{CH_3})_2C{=}C$(6H; 3H singlets at 1.60 and 1.67 ppm); $-CH_2I$(2H, m, bet.3.05 - 3.3 ppm); $\underline{HC}{=}C(CH_3)_2$ (1H, t, 5.05 ppm, J= 7 Hz).

c) Photoirradiation of Citronelly Iodide

In a 250 ml, three-necked RBF fitted with a mechanical stirrer was added 2.7 g (0.01 mole)citronellyl iodide and 1.0 g(0.01 mol) of Et_3N dissolved in 50 ml THF. To it was added the required amount of the metal halide(see tables -1,2,4) and the mixture stirred vigorously for five minutes during which period it develops a slight colouration. 150 ml more of THF was added and the stirring continued for a further period of 15 min. The solution was removed and the flask washed with 60 ml THF to bring the total volume of the solution to 270 ml. This was then irradiated for 2 hrs as described under General Procedure. Distillation of the crude product(b.p.116-127°(bath)/100 mm) gives a colourless liquid (0.9 to 1.0 g) and a residue(0.7 to 0.8 g). Identification of products was by mix. glc with authentic samples on three stationary phases(10 percent CW, 10 percent DEGS and 10 percent DEGS-CuCl ; temp.,100°).

d) Preparation of 2,6-dimethyloct-2-ene(3)



0.7 g(0.0026 mole) Citronellyl iodide in dry THF(~3 ml) was added to a suspension of LAH(0.08 g) in dry THF(3 ml) and the mixture refluxed for 5 hrs. When the reduction was complete(TLC, 10 percent benzene in pet. ether). The excess LAH was destroyed with ice-cold 5 percent NaOH, the solution filtered and the residue washed with water till neutral. Extraction with ether(5 ml x 3) followed by washing the combined extract with water till the washings are neutral, drying (Na_2SO_4) and careful removal of solvent furnishes the crude 2,6-dimethyloct-2-ene. Distillation(b.p.109-111°(bath)/94 mm) affords the reasonably pure(95 percent by GLC) material (0.3 g).

IR(Film): 1650, 830 cm^{-1}

PMR: $\underline{CH_3}CH$, $\underline{CH_3}CH_2$(6H, m, overlapping d and t at 0.9 ppm); $(\underline{CH_3})_2C{=}C$ (3H singlets at 1.59 and 1.67 ppm); $\underline{CH}{=}C(CH_3)_2$ (1H, ill resolved t, 5.05 ppm).

II) Preparation and photoirradiation of Geranyl Iodide

a) Geranyl Chloride: A stirred mixture of geraniol(3.08 g, 0.02 mole) and s-collidine(2.6 g, 0.022 mole) under N_2 was treated with LiCl(1.8 g, 0.0428 mole) dissolved in dry DMF. It was cooled to 0° and freshly distilled methane sulphonylchloride(2.508 g, 0.022 mole) was added dropwise while maintaining the temperature. Stirring was continued at 0° for 1.5 hrs and then kept at -2 to -1° for 3 hrs. The reaction mixture was poured over ice water and extd. with ether:pet ether(1:1)(30 ml x 3). The combined extract was washed with sat. cupric nitrate soln. until no further intensification of the blue copper soln. occurred (10 ml x 5) indicating complete removal of s-collidine. The organic layer dried (Na_2SO_4) and concd. at room temperature to afford the crude product which was distilled (b.p.59-60°/2.4 mm) to give pure geranyl chloride(2.95 g, 85 percent yield.).

PMR: three $\underline{CH_3}$-C=C(9H; 3H singlets at 1.6, 1.68 and 1.73 ppm); CH_2-Cl(2H, d, 4.0 ppm, J=8 Hz); $\underline{HC}$ =(1H, ill resolved m, 5.04 ppm); =$\underline{CH}CH_2Cl$(1H, t, 5.41 ppm, J= 8 Hz).

b) Geranyl iodide: To geranyl chloride(1.5 g, 0.0087 mole) was added 6.0 g (0.04 mole) dry NaI dissolved in acetone (dry) and the reaction mixture kept in an ice bath(0-2°) for 2.5 hrs under total exclusion of light. A rapid work-up involving removal of solvent in vacuo at room temp., addition of water(20 ml) to the residue, ether extraction(30 ml x 2) followed by washing the combined extract with aq. $Na_2S_2O_3$(5 percent, 10 ml x 2), brine, drying (Na_2SO_4) and removal of the ether at room temp. gives the geranyl iodide(1.7 g, 75 percent yield). In view of its extreme instability it had to be immediately taken up for the next step.

PMR:- three $\underline{CH_3}$-C=(9H, 3H, s, 1.6 and 6H, s, 1.67 ppm); $\underline{CH_2}$-I (2H, d, 3.87 ppm,J=9 Hz); $\underline{HC}$=C(1H,ill resolved m, at 5.05 ppm); =$\underline{CH}$ CH_2I(1H, t, 5.53 ppm, J=9 Hz).

c) Photoirradiation of Geranyl iodide in the presence of an 8.9×10^{-4}M conc.(in THF) of CuCl.

In a 250 ml, three-necked RBF fitted with a mechanical stirrer was added 2.27 g(0.009 mole) geranyl iodide and 0.90 g Et_3N(0.009 mole) in 50 ml THF. To this solution 0.020 g CuCl(freshly prepared) was added and stirred vigorously for 5 min. 150 ml more of THF was added and the stirring continued for a further period of 15 min. The solution was then removed and the flask washed with 27 ml THF so that the total volume of the solution is now 227 ml. This was then irradiated for 2 hrs and subsequently worked up as described under 'General Procedure' . The crude product obtained was distilled (b.p. 140-150°(bath)/100 mm) to give 0.7 g(67 percent) of distillate and 0.25 g of residue.

III) Preparation and photoirradiation of Neryl Iodide

a) Neryl chloride: The experimental procedure here is the same as that used for geranyl chloride except that in this case the bath temperature was kept at -4 to -3°C during the addition of methanesulphonyl chloride. The yield of pure neryl chloride obtained was 2.80 g(80.5 percent; b.p.70-72°/ 2.6 mm).

PMR: three $\underline{CH_3}$-C=(9H; 3H singlets at 1.61, 1.68 and 1.78 ppm); $\underline{CH_2}$-Cl (2H; d, 4.0 ppm, J=8 Hz); $\underline{HC}$=C(1H, ill resolved m, 5.08 ppm); =$\underline{CH}CH_2Cl$(1H, t, 5.42 ppm) J= 8 Hz).

b) Neryl Iodide:- To 2.05 g (0.01 mole) Neryl chloride was added 8.7 g (0.058 mole) NaI dissolved in dry acetone and the reaction flask kept at -2 to -1° under total exclusion of light for 25 mts. It was then poured over ice-cold water and extd. with Et_2O(50 ml x 3). The combined ether extracts washed with aq. $Na_2S_2O_3$(5 percent, 5 ml x 2), brine and dried (Na_2SO_4). Removal of ether at room temp. under reduced pressure gives the neryl iodide(1.6 g ,71 percent) which due to its instability was immediately taken up for photolysis.

PMR:- three $\underline{CH_3}$-C=C(9H, 3H singlets at 1.63, 1.7 and 1.74 ppm); CH_2-I(2H, d, 3.83 ppm, J=9 Hz); $\underline{HC}$ = (1H, ill resolved m, 5.11 ppm); =$\underline{CH}$-CH_2I(1H, t, 5.53, J=9 Hz).

c) Photoirradiation of Neryl Iodide in the presence of an 8.9×10^{-4} M conc.(in THF) of CuCl.

The amounts taken and the experimental procedure followed was identical to that described for geranyl iodide. Distillation of the crude product obtained(b.p.135-150°(bath)/100 mm) gave 0.68 g(57 percent) of the distillate and 0.2 g of the residue.

IV) Preparation and photoirradiation of 1-Iodo-5-Hexene

a) Preparation:- It was prepared as described earlier (see Chapter-I, Experimental).

b) Photoirradiation of 1-Iodo-5-Hexene in the presence of an 8.9×10^{-4} conc.(in THF) of CuCl.

2.0 g(0.01 mole) 1-iodo-5-hexene, 1.0 g (0.01 mole) Et_3N and 0.018 g CuCl in 50 ml THF were stirred vigorously for 5 min. followed by the addition of an additional 150 ml THF and further stirring for 15 min. At the end of this period the solution was removed and irradiated as described under 'General Procedure' for 2 hrs. Subsequent work-up procedure was the same as that described earlier(See Chapter-I, Experimental).

V) Photoirradiation of Neryl Iodide using(-) Menthyl amine as base

(-)Menthyl amine was readily prepared from (-)Menthone by the standard procedure[16].

3.0g(0.012 mole) Neryl Iodide, 1.86 g(0.012 mole) (-)Menthylamine(b.p.80-2°/12 mm; $[\alpha]_D^{25} = -34.0^\circ$,Lit.[6] $[\alpha]_D^{19} = -34.2^\circ$) and 0.0265 g CuCl in 300 ml THF were stirred for 15 min. and the resulting solution then irradiated for 2 hr and worked-up - the procedure being the same as that described under 'General Procedure'. The crude product was distilled(b.p.160-170° (bath)/ 110 mm) to give 0.20 g of the distillate(13 percent yield) and 1.6 g of residue.

VI) <u>Photoirradiation of Neryl Iodide using N-dimethyl-(-)-menthyl amine</u>.

N-dimethyl-(-)-menthylamine was prepared by the Clark-Eschweiler reaction according to standard procedure[7] ($[\alpha]_D^{25}$ = -54.34 (neat); Lit[17], $[\alpha]_D^{26}$= -51.20(neat))

2.0 g(0.008 mole) Neryl iodide, 1.5 g(0.008 mole) N-dimethyl-(-)-menthylamine and 0.018 g CuCl in 200 ml THF was stirred vigorously for 15 min. Subsequent procedure is the same as that described above. The crude product obtained was distilled(b.p.140-160° (bath)/ 110 mm) gave 0.55 g of distillate and 0.4 g residue.

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