CHAPTER - I

SOLUTION PHOTOCHEMISTRY OF ALKYL IODIDES - A MECHANISTIC STUDY

CONTENTS

ABSTRACT

This Chapter is divided in two sections. Section I traces the development of ideas regarding a mechanistic understanding of the photochemistry of aliphatic halides and terminates with the current views on this subject.

Section II discusses our own investigations into the mechanism of the photocyclization process in those aliphatic iodides containing a suitably situated π-linkage. Our studies in photoalkylation of aromatic systems and the photocyclization of 4-phenyl-1-butyl and the hex-5-en-1-yl system establish conclusively that the cyclic products are derived from the 'hot' carbocation and not an alkyl radical.

SECTION - I

INTRODUCTION : THE BACKGROUND

This section attempts an overview of the conceptual developments regarding the mechanism of photochemistry of aliphatic halides. Particular emphasis is laid on the photochemistry of alkyl iodides in solution phase as a prelude to the work described in Section-II. The photochemistry of aliphatic halides has been the subject of extensive study over the years and has been reviewed[1,2]. The earlier studies were conducted mainly in the gas phase[1] but in recent years more and more investigations have been conducted in solution. It is proposed to summarize first of all present ideas about the nature of the phototransitions, when a carbon-halogen bond is irradiated and then discuss results from both gas-phase and solution photochemistry.

A. SOME FUNDAMENTAL ASPECTS

The lowest unfilled molecular orbitals in haloalkanes are formed from the out-of-phase overlap of an sp^3 hybrid orbital of the carbon atom and a p orbital of the halogen atom. They are of the type σ^* and are $C \leftrightarrow X$ antibonding. The lowest energy electronic transition or the first absorption band of the C-X chromophore results from the promotion of a non-bonding p electron bound to the halogen atom into the lowest σ^* orbital. Such transitions are termed $n \rightarrow \sigma^*$[4].

The σ^* orbitals possess a large degree of p character and these transitions are forbidden by the Laporte selection rules. As a result the intensity for this transition is low (ε=100-500). The long wavelength absorption is broad and continuous and results in ready photodissociation with unit quantum efficiency. The second absorption band of C-X bond due to the excitation of halogen atomic orbital-Rydberg transitions- is more intense but it is in the inaccessible vacuum U.V region(eg:- for alkyl iodides $\lambda_{max} \sim$ 190 nm; $\varepsilon \sim 7700$) and is of little practical importance. With halogen substituted ethylenes the $\pi \rightarrow \pi^*$ absorption band of the olefin is shifted to longer wavelengths, presumably because of interaction between lone pair orbitals of the halogen atom and the π-orbitals of the ethylene. The lowest transition is still the $\pi \rightarrow \pi^*$ type though the nature of excited state is somewhat intermediate in character; both C-C and the C-X bonds have some antibonding character[3].

The absorption data and the C-X bond strengths for methyl halides are given below(Table-I)[2].

Table I : UV absorption properties of methyl halides.

Compound	λmax (nm)	ε max (mole^{-1} cm^{-1})	C-X bond strength (kg mole^{-1})
CH_3Cl	173	200	326
CH_3Br	203	264	280
CH_3I	258	380	213

From the above Table it is evident that for a given series of alkyl halides the absorption spectrum shifts to the red while the bond strength decreases from Cl→Br→I.

The energy of a photon is greatly in excess of the C-X bond dissociation energy which explains the ready photocleavage of the C-X bond into the $C^{'}$ and $X^{\cdot}$ species with unit quantum efficiency. This is the primary process in the photolysis of the halides.

$$RX + h\nu \rightarrow R^{\cdot} + X^{\cdot}$$

The presence of free halogen atoms has been inferred from the observation of the transient spectra due to

ClO, BrO or IO following flash photolysis of chloro-[5a], bromo-[5b], or iodomethanes[5c] in a large excess of oxygen as well as from Kinetic evidence[1]. The methyl radical has been identified by its absorption spectrum during the flash photolysis of methyl iodide and bromide[6]. The higher alkyl radicals from the corresponding iodides have however evaded detection.

After the primary dissociation of the C-X bond, unless some excellent trapping agent is present the reformation of RX may occur efficiently in the system as X_2 builds up.

$$R^{\bullet} + X_2 \rightarrow RX + X^{\bullet} \quad (I)$$

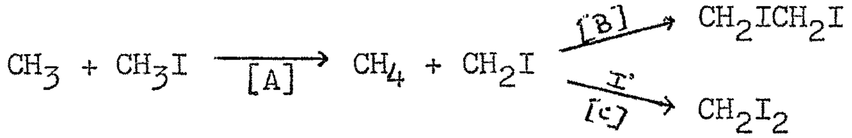
In solution phase studies direct recombination of the primary dissociation products may occur before escape from the solvent cage . Also traces of oxygen in the solvent have a pronounced effect on the yield of decomposition products[7].

The fate of the radicals ($R^{\bullet}$ and $^{\bullet}X$) generated in the primary process constitutes the secondary process of photochemical reactions leading to the products finally observed. It is these secondary processes which are of mechanistic interest.

B. GAS PHASE PHOTOCHEMISTRY

Since the most easily decomposed monohaloalkanes are the iodides they have been the most studied. The quantum efficiency of the primary dissociation to radicals is near or equal to unity. In the pure vapour phase however, this is effectively masked by the high probability of back reaction(Eq.I).

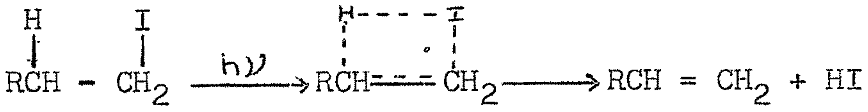
The principal products of the photodecomposition of methyl iodide in vapour phase are C_6H_6 and I_2 which can be easily rationalized. However, more strikingly it was found that CH_4, CH_2I_2 and CH_2ICH_2I are also among the products in comparable yields. These can only arise as a consequence of H atom abstraction from the parent molecule[8].



$$CH_3 + CH_3I \xrightarrow[{[A]}]{} CH_4 + CH_2I \begin{array}{l} \xrightarrow{[B]} CH_2ICH_2I \\ \xrightarrow[{[C]}]{I^{\cdot}} CH_2I_2 \end{array}$$

In order to explain the significant contribution of Step[A] it has been emphasized that the energy of the photon is greatly in excess of the H_3C-I bond dissociation energy(as discussed previously). For a photon at 2537 A some 57 K cal $mole^{-1}$ will remain after primary dissociation and a large portion of this energy will initially be concentrated in the methyl radical as translational and/or vibrational energy[9,10,11].

The gas phase decomposition of higher alkyl iodides has received relatively little attention and the contribution made by hot alkyl radicals is uncertain. For the photolysis of ethyl iodide it has been estimated that only <2 percent of the ethyl radicals produced in the primary process react as hot radicals[12]. During the flash photolysis of higher iodides, Thrush[13] observed strong bands due to HI. He suggested that this might be a primary product of an alternative, molecular mode of decomposition through a vicinal elimination of HI to give an alkene.



$$\overset{H}{RCH} - \overset{I}{CH_2} \xrightarrow{h\nu} \overset{H\cdots\cdots I}{RCH \cdots CH_2} \longrightarrow RCH = CH_2 + HI$$

Support is lent to this proposal by the observation that addition of radical scavengers such as I_2 and O_2 does not completely suppress the formation of alkene[12]. Furthermore the quantum yield of alkene increases at wavelengths shorter than 2250A suggesting increased contribution from molecular decomposition[14].

In gas phase photolysis of higher alkyl iodides the intermediacy of corresponding alkyl radicals has also been established by trapping with molecular oxygen[15].

C. SOLUTION PHOTOCHEMISTRY

a) Earlier ideas

Solution photochemistry of simple alkyl iodides showed differences from the corresponding gas phase photolysis in that there were evidences of solvent participation. For example the photolysis of methyl iodide in cyclohexane gave the products: I_2, HI, CH_4, cyclohexene and cyclohexyl iodide in the quantum yields 0.048, 0.009, 0.190, 0.057 and 0.085 respectively[16,17]. Methane was attributed to the reaction of hot CH_3 with solvent and to the thermal CH_3 with HI. Cyclohexene was attributed to a diffusion controlled reaction between the resulting cyclohexyl radical and I.

The mechanism postulated was

$$\begin{aligned}
CH_3I + C_6H_{12} + h\nu &\rightarrow (\dot{C}H_3^{*} + \dot{I} + C_6H_{12}) \\
(\dot{C}H_3^{*} + \dot{I} + C_6H_{12}) &\rightarrow CH_4 + (\dot{C}_6H_{11} + \dot{I}) \\
&\rightarrow (\dot{C}H_3 + \dot{I}) + C_6H_{12} \\
&\rightarrow \dot{C}H_3 + \dot{I} + C_6H_{12}
\end{aligned}$$

$(\overset{\circ}{C}H_3 + {}^{\bullet}I) \rightarrow CH_3I$

$({}^{\bullet}C_6H_{11} + {}^{\bullet}I) \rightarrow C_6H_{10} + HI$

$\rightarrow C_6H_{11}I$

$\rightarrow {}^{\bullet}C_6H_{11} + {}^{\bullet}I$

${}^{\bullet}CH_3 + HI \rightarrow CH_4 + {}^{\bullet}I$

${}^{\bullet}CH_3 + I_2 \rightarrow CH_3I + {}^{\bullet}I$

${}^{\bullet}C_6H_{11} + HI \rightarrow C_6H_{12} + {}^{\bullet}I$

${}^{\bullet}C_6H_{11} + I_2 \rightarrow C_6H_{11}I + {}^{\bullet}I$

${}^{\bullet}I + {}^{\bullet}I \rightarrow I_2$

Parentheses indicate substances which may react before reaching the stationary state and CH_3 denotes a hot methyl radical.

Further studies with higher alkyl iodides gave evidence of the presence, atleast partly, of the molecular decomposition mechanism to the olefins(Eq.I)[18,19]. The photodecomposition of liquid n-propyl iodide gives apart from the usual products a rearranged product, isopropyl iodide[20]. Both tracer studies with I^{131} and trapping experiments suggest that the rearranged iodide is formed from the alkene and hydrogen iodide[20,21].

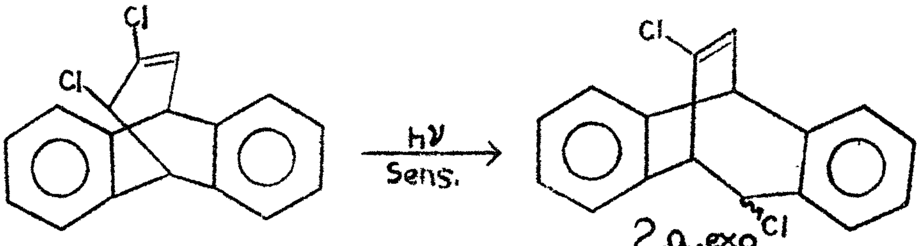
$$CH_3CH = CH_2 + HI \longrightarrow CH_3CHICH_3$$

In summary therefore, upto the mid-sixties or so the photochemistry of alkyl halides in liquid or solution phase, alkin to the gas phase, was thought to involve essentially the alkyl and halide radicals. The products obtained were rationalized within this framework.

b) The new paradigm

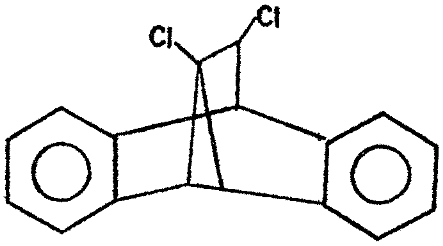
One of the first deviation from the above approach was from Cristol and co-workers- in their study of the sensitized photoisomerization of 3,4-dichlorodibenzobicyclo[3.2.2] nonatriene-2,6,8(1) a bridgehead polycyclic compound[22]. They observed that the photoinduced rearrangement of (1) gave predominantly the thermodynamically unstable(2) and lesser amounts of (3).

Products obtained from the allylic radical species(4) which would result from the initial homolytic cleavage were absent. The predominance of (2) also precludes a benzo-vinyl bridging type mechanism[23]. The authors concluded that the triplet state of(1) probably decays to a vibrationally excited singlet which then dissociates to a $[R^+Cl^-]$ ion pair which could then recombine to give(2).



1.

2,a, exo
b, endo



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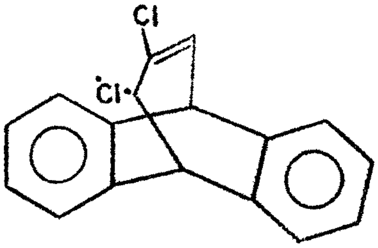
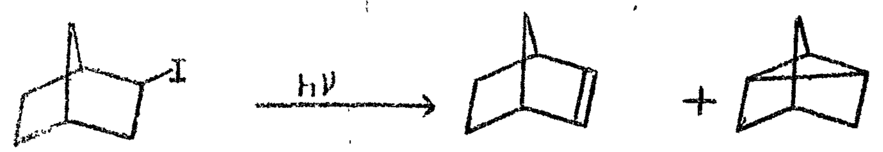


4.

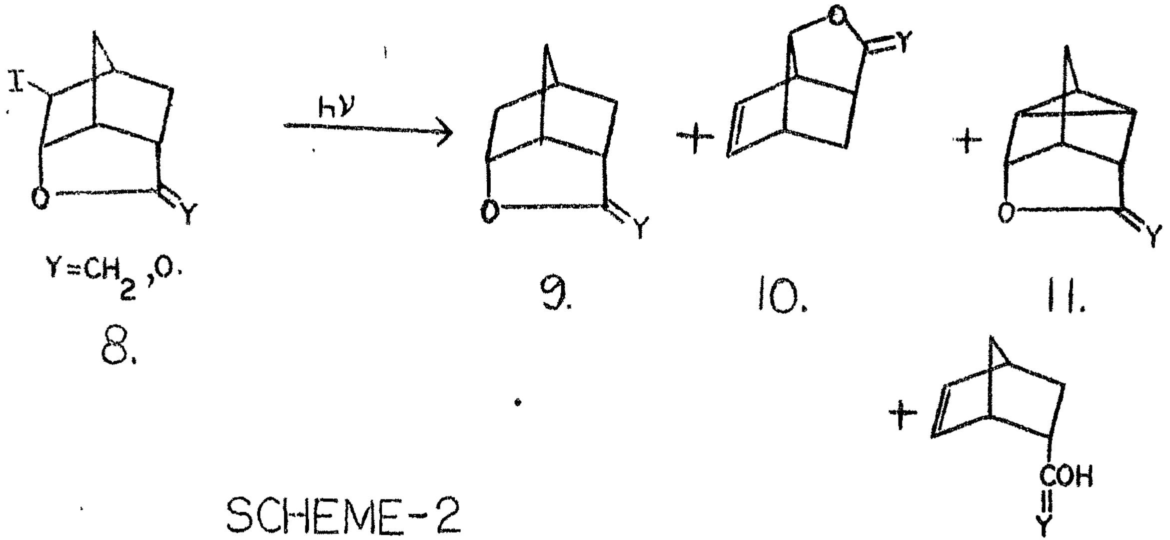
It was only a few years later, however, that more conclusive evidence regarding an ionic character to the photochemistry of alkyl halides in solution was obtained. Kropp et al[24] observed that the irradiation of 2-exo-iodonorbornane(5) both in methanol and nortricyclene(7) to a lesser extent(Scheme-1). Irradiation of the iodoether(8) in ether gave a mixture of products(9-12) (Scheme-2). A marked solvent effect was noted. In methanol only a single principal product was formed, the ring opened system(12). The occurrence of Wagner-Meerwein shifts in both cases, 1,3 elimination and nucleophilic substitution prompted the authors to conclude that a cationic intermediate was involved. The concurrent formation of the reduction product(9) and the ionic products(10 and 11) seemed to suggest as initial homolytic cleavage of the C-I bond followed by an electron transfer process leading to the ion pair (R^+I^-). The product formation could then be accounted for from the formation of the transition states(13) and (14).

A similar conclusion was arrived at by Sukh Dev et al in their study of intramolecular photocyclization of purely aliphatic iodides with a suitably substituted ethylenic or some other labile linkage[25]. Longibornyl iodide(15) on irradiation in heptane gave 44 percent of



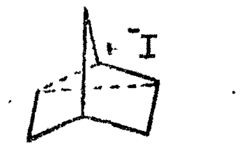
5. 6. 7.

SCHEME -1.



8. 9. 10. 11. 12.

SCHEME-2



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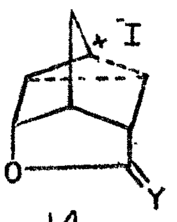
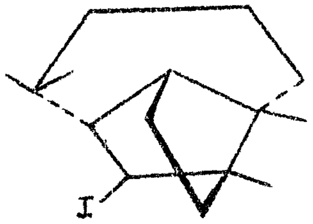


14.

longicyclene(16) while citronellyl iodide(17) gave 31-54 percent of the cyclized products(18a-d) depending on the experimental conditions employed[26]. The formation of longicyclene(16), the effect of solvent polarity on the photocyclization of citronellyl iodide(17) and the near absence of the reduced product in this case could be best explained in terms of a 'hot' carbocationic intermediate. This study was subsequently extended to some allylic iodide systems[27] and it was found that the (Z)- isomer gives a larger proportion of the cyclic products in comparison with the corresponding(E)- isomer. Thus while geranyl iodide(19) gives only 6.7 percent of the cyclic products(20), neryl iodide(21) gives 33 percent of (20).

A significant difference in photochemical behaviour between alkyl iodides and their corresponding bromides was noticed[24]. The photoproducts from the bromides were typical of radical derived products. The corresponding bromide of (8)afforded exclusively(9). The difference in behaviour between bromides and iodides was attributed to the difference in reactivity of Br and I. As the former is a hot radical the authors suspect rapid hydrogen abstraction from the solvent cage leading to radical-derived products. On the other hand $I^{\bullet}$ being incapable



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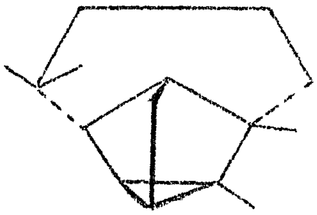

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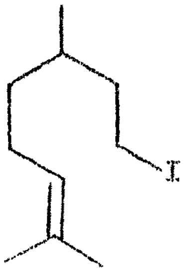

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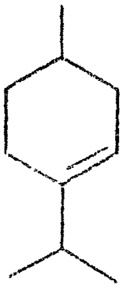
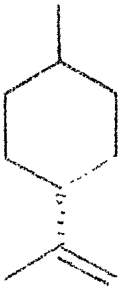
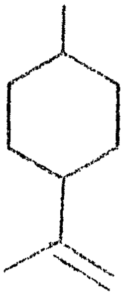


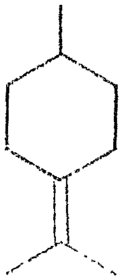
18a.



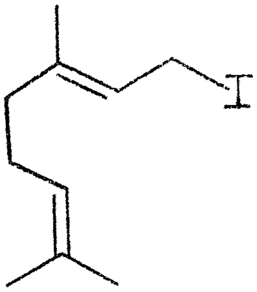
18b.



18c.



18d.



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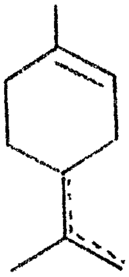

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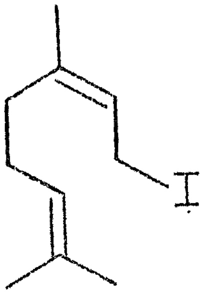


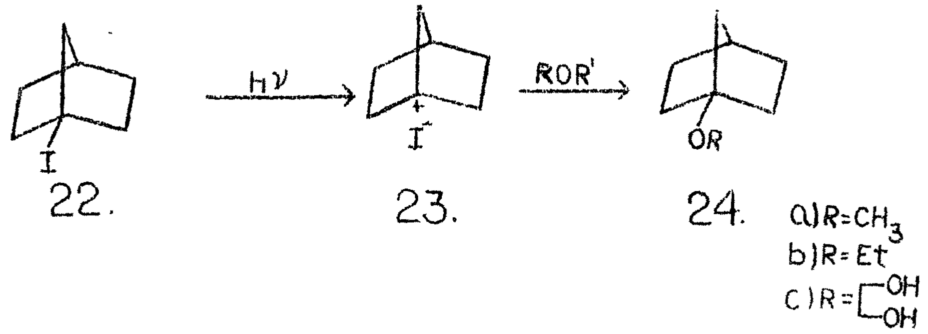
21.

of abstracting hydrogen atoms from most solvents, the radical pair would have a sufficient lifetime for the electron-transfer to occur.

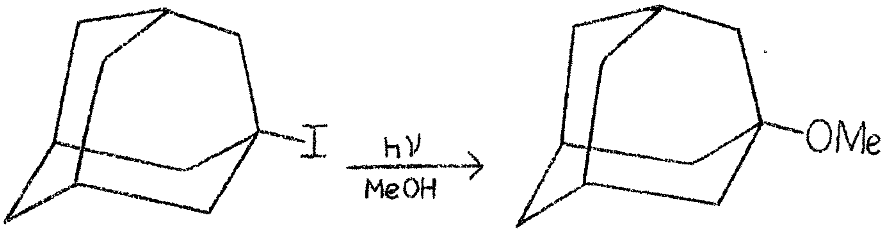
Further evidence regarding the intermediacy of an alkyl cation has been obtained by trapping of the 1-norbornyl cation(23) generated by the photolysis of 1-iodonorbornane(22)[28,29]. Irradiation of (22) in methanol or ether under an atmosphere of nitrogen afforded predominantly the nucleophilic substitution product(24)[29]. Irradiation of (22) in methanol saturated with oxygen gave significantly lowered yields of (24a) supporting the earlier proposal that cationic intermedieates from alkyl halides arise via initial homolytic cleavage followed by electron transfer. The corresponding bromide of (22) also exhibits similar behaviour except that the reduced product predominates suggesting that the difference in behaviour involves differences in relative rates of competing radical and ionic pathways rather than mutually exclusive ones. Based on the overall evidence a generalized mechanism could be represented as[31]

$$\begin{tikzcd}
R\text{-}I \arrow[r, "h\nu"] & (R\text{-}I)^{*} \arrow[r] & (R^{\circ}\ I^{\circ}) \arrow[r] \arrow[d, "\text{electron transfer}"] & \text{Radical products} \\
 & & (R^{+}I^{-}) \arrow[d] & \\
 & & \text{Carbocationic products.} &
\end{tikzcd}$$

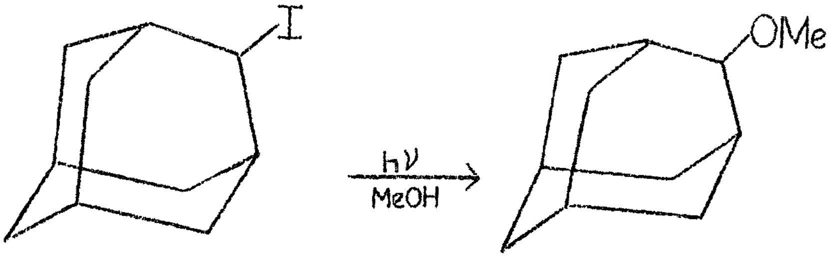
Cations thus generated at the bridgehead positions afford exclusively nucleophilic substitution products. Elimination is inhibited in these systems due to inherent strain of the resulting bridgehead olefin. Thus irradiation of 1-iodoadamantane(25) gives exclusively(26) and 2-iodoadamantane(27) gives (28)[30,31]. Similar results are obtained with diiodoadamantane(29)[30]. On the other hand the cation generated by the photolysis of 1-iodooctane gives almost exclusively the elimination product 1-octene[31]. This preference for elimination over nucleophilic substitution is characteristic of 'free' cations generated by high energy processes with little or no solvent participation[32]. The photochemistry of several homologous bridgehead iodides has been studied by Kropp and his group and in all cases the mechanism proposed earlier has been vindicated[33]. In the case of 2-iodoadamantane(27) however, it has been found that the ether product(28) is not a result of direct nucleophilic attack on the generated 'hot' bridgehead cation by the solvent[34]. Studies with methanol-O-d have shown that the primary products are 2,4-dehydro-adamantane(29a) and protoadamantene(30) which subsequently react with the solvent to give (28)



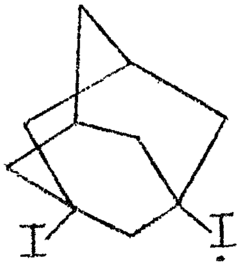
22. 23. 24.



25. 26.



27. 28.



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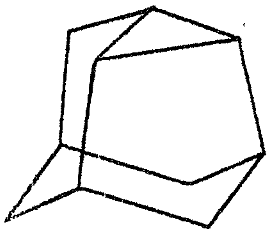
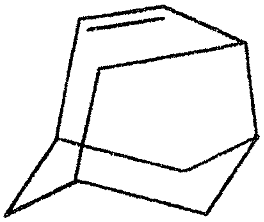
In contrast to 2-iodoadamantane, 2-iodo-2-nitroadamantane(31) on photolysis in isopropylalcohol gives as a major product, the radical derived one viz:- 2-nitroadamantane(32)[35]. The reason here is probably the presence of electron withdrawing $-NO_2$ group which prevents heterolytic removal of the iodine by destabilizing the resultant carbonium ion. The facile double elimination from (33) on photolysis is also interpreted in terms of an ionic mechanism[36]. C-I homolysis followed by rapid electron transfer gives the carbocation which results in the product(34).

The photochemistry of alkyl iodides in the presence of aromatic substrates has also been studied in order to gain an insight into the mechanism. The photolysis of methyl iodide in an excess of various aromatic compounds gave the ring methylated aromatics(35)[37]. The observed orientation ($o/2 \approx m/2 \approx p$) was abnormal when compared with that in methyl radical substitutions($o/2>p>m/2$). Furthermore iodine and oxygen had no effect on the reaction which suggests the absence of any direct radical attack. The authors suggest that the photolysis may proceed via a complex between methyl iodide and the alkyl benzene formed either in the ground state or via photoinduced electron transfer from the aromatic to the methyl iodide,



29a



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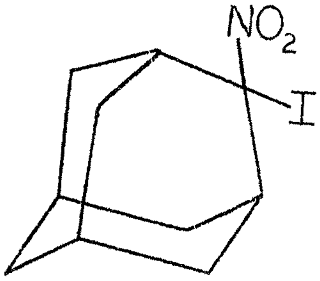

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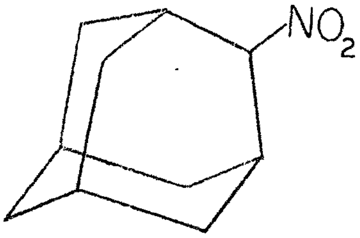

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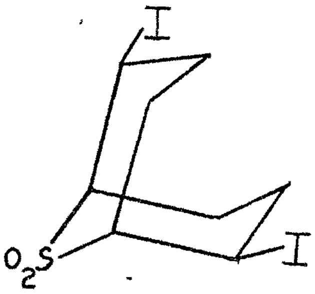

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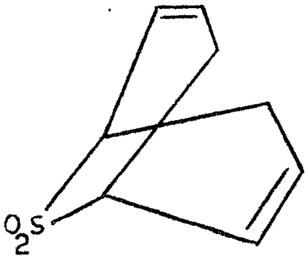
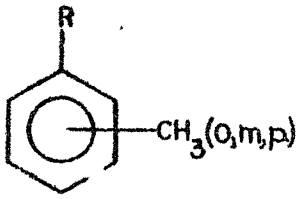


34.

leading to the observed product ratios.

$$\mathrm{MeI} + \mathrm{PhR} \longrightarrow \underset{\text{complex}}{[\mathrm{MeI{-}PhR}]} \xrightarrow{h\nu} \mathrm{MeC_6H_4R} + \mathrm{HI}$$

A closely similar study involves the photolysis of allyl iodide in various aromatic solvents wherein also the low reactivity of the ortho position of the aromatic substrate w.r.t. homolytic substitutions was observed[38]. The photolysis of 4-phenyl-1-iodobutane (36) in benzene or acetonitrile gives 4-phenyl-1-butene(37) as the major product and 1-phenyl butane(38)[39,40]. In the presence of oxygen the yield of alkene(37) was approximately halved suggesting that about 50 per cent of the initially formed radical pairs give alkene while the remainder become free of the solvent cage[39]. In contrast 4-phenyl-2-iodomethyl-1-butene(39) gives mainly the ionic product . The intermediacy of a carbonium ion is established by trapping with the solvent(acetonitrile) resulting in the corresponding amide(40)[40].



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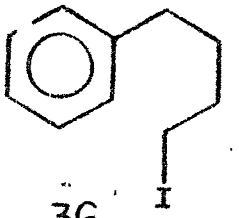

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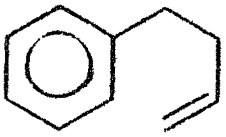

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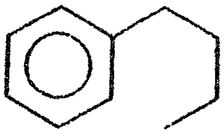

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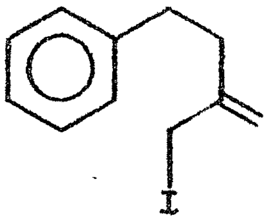

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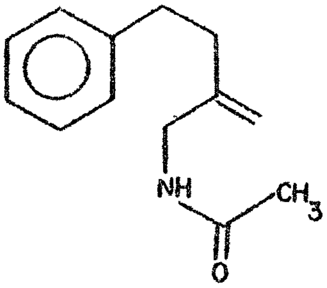

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c) Photochemistry of related halides

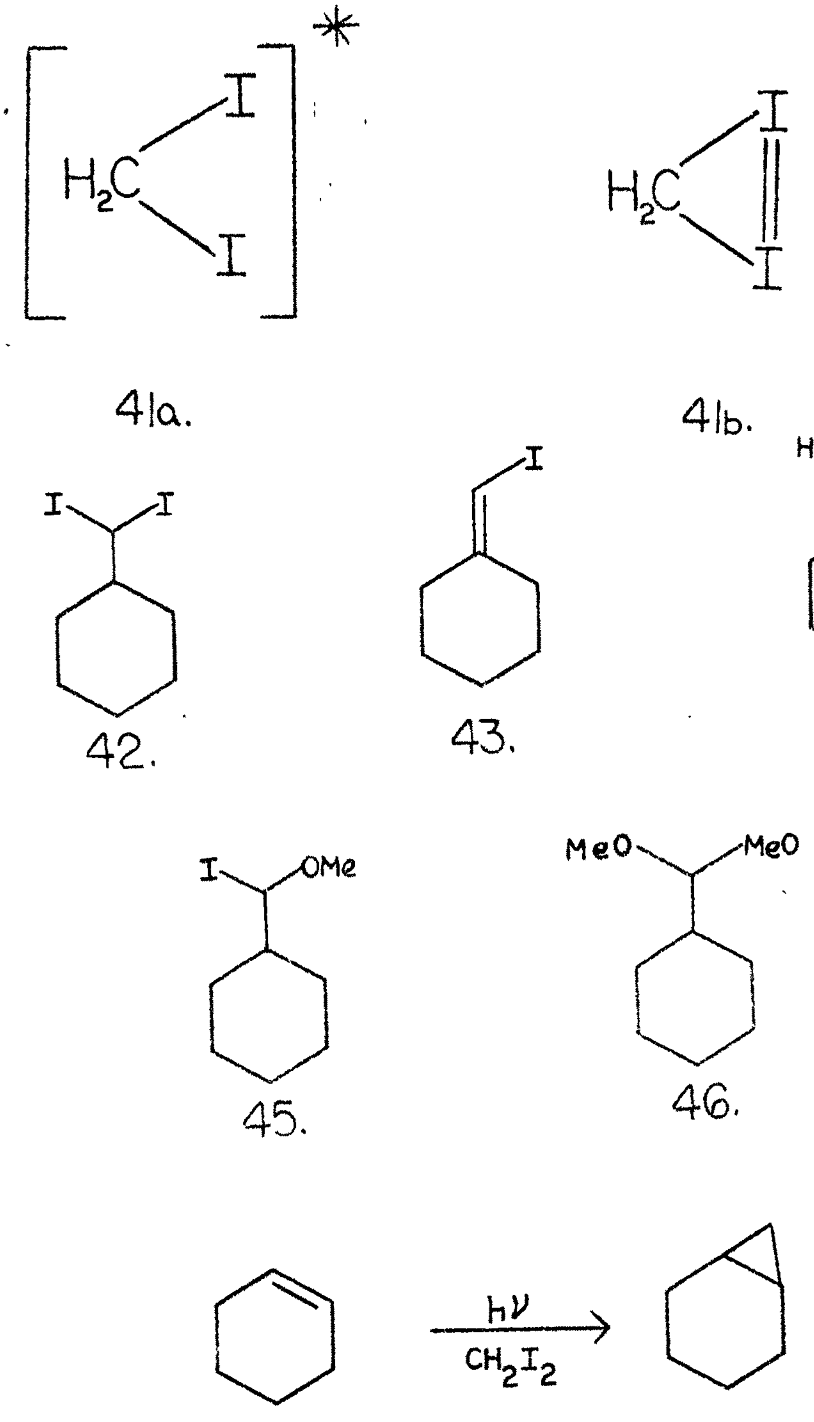
(i) Benzyl halides: There appears to be some divergence in the results of photolysis of benzyl halides under sensitized and non-sensitized conditions by two schools of research. Cristol and Greenwald[41] reported that only products arising via radicals(viz:- $PhCH_2CH_2Ph$, $PhCH_2CH_2OH$) are obtained under direct photolysis of benzylchloride whereas the cation-derived products ($PhCH_2OMe$) was obtained in the presence of triplet sensitizer(acetone) on methanol. On the other hand McKenna's group report[42,43] both radical and ion-derived products in alcohol media under direct as well as sensitized irradiation. They propose that interconversion of loose triplet and singlet radical pairs followed by electron transfer in the singlet pair to give a solvent separated ion-pair is a vital sequence in the mechanism.

(ii) Geminal dihaloalkanes: Early ideas regarding the photochemical decomposition of geminal diiodoalkanes seemed to consider the formation of a carbene intermediate[44] as was indicated by subsequent trapping experiments with olefins to give cyclopropanes[45]

$$RCHI_2 \xrightarrow{h\nu} RCH: + I_2$$

However on the basis of product distribution and stereochemical studies it was concluded that the main product forming intermediate was probably an excited state methylene(41a, 41b) rather than free methylene. Subsequent investigations by Kropp's Group[46], in the light of their new proposal[31], led to the conclusion that gem-diiodides also exhibit cationic behaviour on irradiation though under appropriate conditions carbenoid behaviour also prevails depending on the solvent. Irradiation of (42) in a variety of polar solvents yields principally the ionic product(43) with small amounts of the radical product(44). In methanol the nucleophilic substitution products(45) and (46) were formed in substantial amounts at the expense of (43). The behaviour of gem-diiodides is therefore analogous to that observed for monoiodides[31].

The photolysis of gem-diiddides structurally incapable of undergoing competing elimination to a vinyl iodide has been found to be a convenient method for the cyclopropanation of olefins(Scheme-3). This method affords an improvement over the traditional

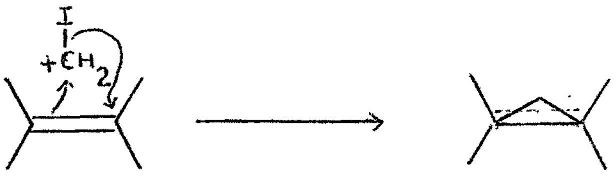


SCHEME -3

Simmons-Smith reaction[47]. A variety of olefins have been cyclopropanated by this method. It is proposed, in analogy with monohalides, that independent photobehaviour by the two halogen substituents of CR_2I_2 gives the α-iodocation(A)

$$CH_2I_2 \xrightarrow{h\nu} [\dot{C}H_2\dot{I}\ ] \xrightarrow[\text{transfer}]{\text{electron}} [{}^+CH_2I\ I^-] \rightleftharpoons \underset{[A]}{{}^+CH_2I} + I^-$$

It is this α-iodocation which is proposed as the reactive species in photocyclopropanations.

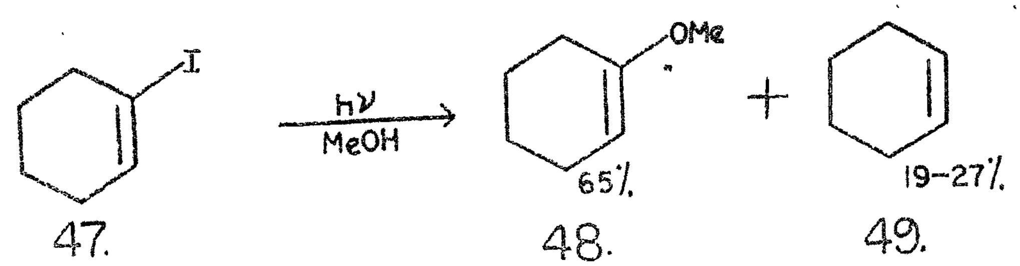


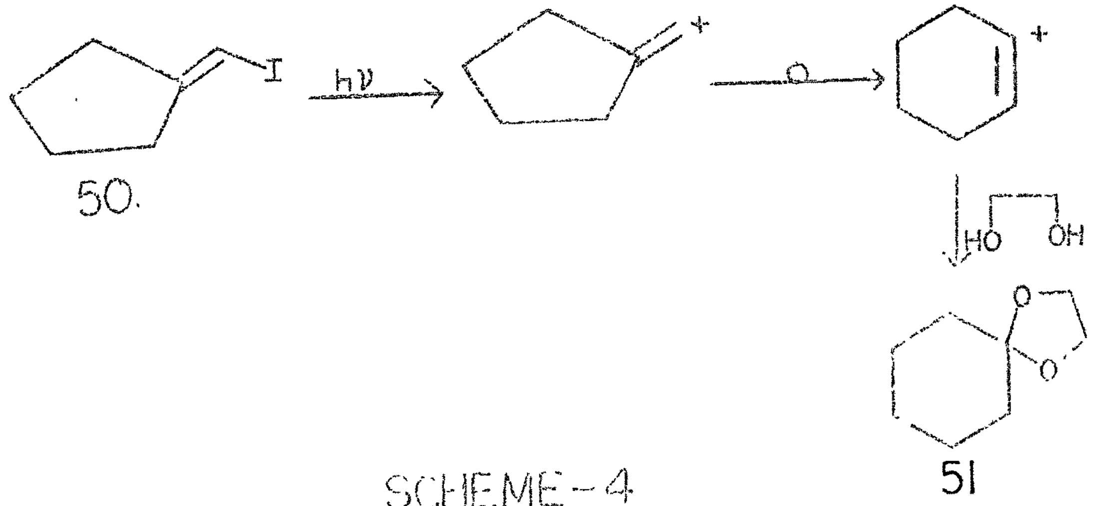
The intermediacy of an α-iodocation has been asserted by trapping experiments with LiBr which afforded iodobromomethane and some dibromomethane.

iii) <u>Vinyl halides</u>: Contrary to earlier views[48] Kropp et al have shown that electron transfer following the initial homolysis of C-I bond also takes place for these substrates[49]. Irradiation of vinyl iodide is thus a facile route to the difficultly accessible vinyl cations.

Thus irradiation of 1-iodocyclohexene(47) in methanol gives principally the nucleophilic substitution product (48) and smaller amounts of the radical derived product (49). Primary vinyl cations have also, for the first time, been obtained by this route. Irradiation of (iodomethylene) cyclopentane(50) in ethylene glycol gives 30 per cent of the cationic product(51) and 50 per cent of the reduction product(52). The ionic product here is ring expanded as the cyclic cation, being secondary, is more stable(Scheme-4). In contrast the cation derived from the cyclobutyl analogue principally undergoes fragmentation to 1-penten-4-yne(53) on irradiation in methylene chloride.

Subsequent to this pioneering work a host of other examples have appeared in literature[50-52] where the carbocation mechanism has been invoked in the photochemistry of vinyl halides. A novel ortho -substituent effect has also been noted[53]. Introduction of a substituent into the ortho position of β-aryl substituent in a vinyl bromide results in preferrential formation of a vinyl cation in the photolysis. Steric repulsion of the β-aryl group is believed to force the molecule into a conformation convenient for an electron transfer from the aromatic ring to the halogen atom in the radical pair.





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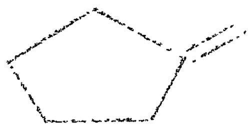

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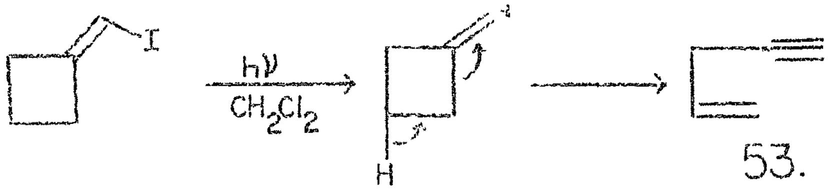
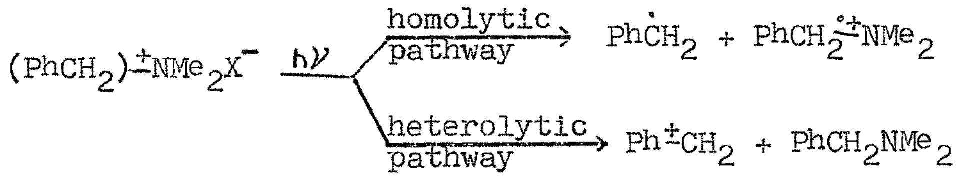


Another interesting development has been the enhancement of vinyl cation formation in the photolysis of vinyl bromides by the use of Cu(II) salts[54]. The Cu(II) species is thought to act by oxidizing the radical to the cation.

d) Alternative approaches to the mechanism

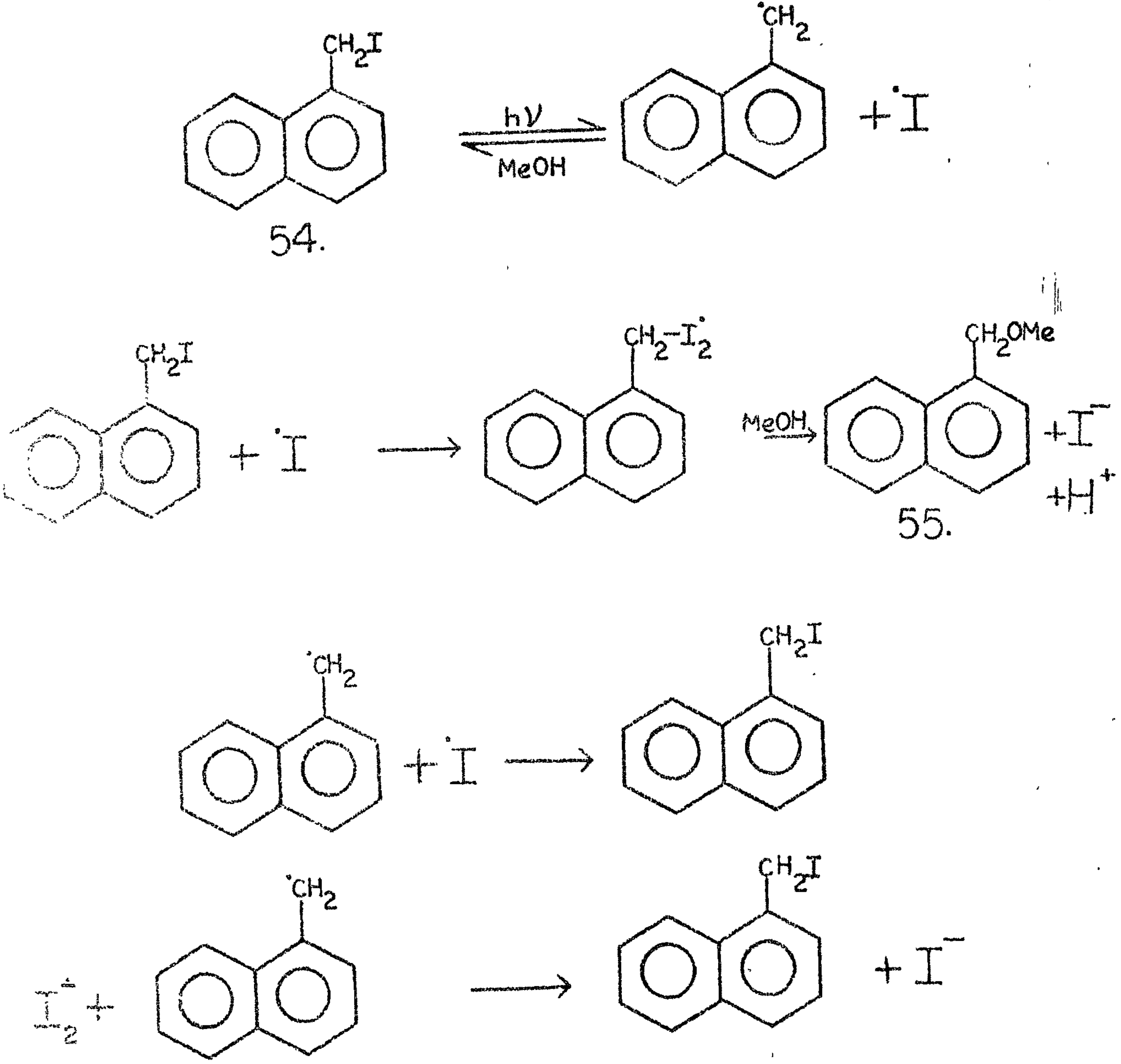
In the mechanism proposed by Kropp *et al*[31], the photolysis of alkyl iodides in solution results initially in a homolytic cleavage of the carbon-halogen bond giving a radical pair. The radical pair may undergo radical reactions or may suffer intracomplex electron transfer to give an ion pair which would then undergo carbonium ion reactions.

An alternative to the seriatim formation of the carbonium ion has been mooted by Ratcliff and Kochi[55]. In their work on the photolysis of benzylammonium salts they obtained products arising both from the radical and cation. They proposed that the two pathways were independent and designated them as homolytic and heterolytic pathways.



Their observation that benzylchloride gives products from benzyl radical on direct irradiation while it gives products from the benzyl cation on photosensitized irradiation led Cristol and co-workers[41] to favour this mechanism. Subsequently however[56], on the basis of available evidence, they preferred the intimate ion-radical pair concept proposed by Walling[57] as a mean of the earlier two positions. Walling et al describe the intimate ion-radical pair as 'an intermediate in which electronic interactions between the fragments is still extensive and ionic and paired diradical formulations merely represent contributing structures of a resonance hybrid'. They further suggest that as the fragments become separated by solvent or as conformational or rotational processes in solution occur, ionic and radical structure, become increasingly distinct species. This concept was later applied by Nozaki et al[58] to the photochemistry of benzhydryl esters.

More recently[59], laser spectrophotometric analysis of the photochemistry of(iodomethyl) naphthalene(54) has thrown new light on the mechanism. No evidence was found for the direct photochemical generation of carbonium ions or for their formation by electron transfer from the naphthylmethyl radical to iodine atoms in the conversion of (54) to the ether (55). The authors propose a mechanism involving the formation of a complex between the iodine atom and(iodomethyl) naphthalene(Scheme-5). Kropp[60] however contends that this mechanism is restricted to aralkyl iodides and apparently does not apply to alkyl systems. The observed decrease in formation of the ether(24) in the presence of oxygen cannot be accounted for by this mechanism. Further, observations that the conversion of 1-iodooctane is independent of the concentration and that the iodide(22) is inert to $I^{\cdot}$ in a methanolic solution also, in Kropp's view, precludes the generality of this mechanism.


CH₂I
hν
MeOH
•CH₂
+ •I
54.
CH₂I
+ •I
CH₂–I₂•
MeOH
CH₂OMe
+ I⁻
+ H⁺
55.
•CH₂
+ •I
CH₂I
I₂•⁻ +
•CH₂
CH₂I
+ I⁻

SCHEME-5

D. CONCLUSION

It has now been established that competing ionic and radical mechanisms prevail in the solution photochemistry of aliphatic halides particularly the iodides though the finer aspects remain elusive. The facile generation of difficultly accessible cations like vinyl, bridgehead and α-halocations open up possibilities in synthetic organic chemistry. Other developments include photocyclopropanations and photocyclizations of aliphatic systems. Further studies are likely to be along the lines requiring a closer look at the mechanism on the one hand and an exploration of the synthetic utility of these reactions on the other.

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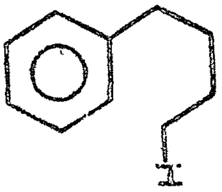
SECTION - II

PRESENT WORK

It is obvious from what has been discussed in the previous section that alkyl iodides display a rich array of photochemical behaviour much of it having synthetic interest eg. cyclizations[1,2,3]. In the course of a study of the photocyclization of purely aliphatic iodides containing a suitably substituted ethylenic linkage[2] eg. citronellyl iodide, it had been suggested that the cyclic products obtained are from a hot carbonium ion generated in the photoreaction. An optimisation of parameters conducive to cyclization led to the following experimental conditions:- temp. 50^{o}; solvent, THF; intensity of radiation, 400 watts(Med.press. Hg vapour lamp). In the wake of this report another report appeared wherein the postulation of a cationic intermediate in the photocyclization was questioned[4]. The photolysis of 4-phenyl-1-iodobutane(1) gave the elimination product 4-phenyl-1-butene(2) as the major product presumably via the hot cation. Only traces of the cyclized product, tetralin(3) were obtained. On the basis of this result the authors noted that evidence of a 'hot' cation leading to cyclization was lacking.

In the light of this report it was felt that a more thorough investigation into the mechanism of photocyclization was called for and the work described subsequently gives an account of our attempts in this direction.



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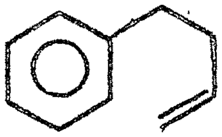

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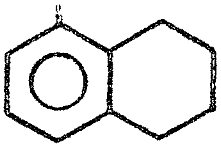

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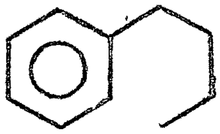

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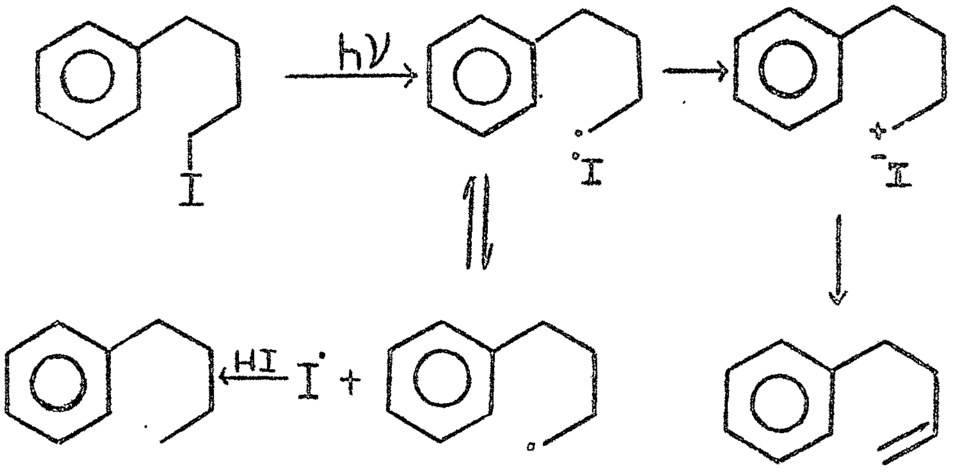


SCHEME-I

A. Photochemistry of 4-Phenyl-1-Iodobutane(1)

As noted above the photoirradiation of (1) under varying conditions in benzene as solvent was found to give (2) as the major product[4]. The minor product obtained was the reduction product 1-phenyl butane(4). The mechanism proposed by the authors is illustrated in Scheme 1.

As evidence for the cation entering into a cyclization reaction was lacking the authors raised doubts as to the interpretation of Gokhale *et al*[2] of the photocyclization of citronellyl iodide as a cationic process. They suggested the equal likelyhood of a free radical mechanism.

In a study of the effect of temperature, solvent and intensity of radiation on the total yield of cyclization products arising from photoirradiation of citronellyl iodide[3] a definite solvent effect was noted. In more polar solvents (THF, Et_3N) the reaction was faster and higher proportions of the cyclic products were obtained - suggestive of an ionic intermediate in this pathway.

In order to evaluate this in the present context, 4-phenyl-1-iodobutane(1) was first irradiated in benzene at 50° under a blanket of nitrogen. The product distribution obtained after work-up was essentially similar to that reported[4] ie a negligible amount of the cyclization product(3)(Table-I). On the other hand, photolysis of (1) in THF at 50° in the presence of a molar equivalent of triethylamine as scavenger yielded 20 percent of the cyclised product(3) (Table I) (Fig. 1a).

Table I :- Photolysis of (1) in Benzene and THF

Product	%obt. (solvent = Benzene)	%obt. (Solvent = THF)
2.	80.0	58.0
4.	13.5	22.0
3.	3.0	20.0

The dramatic improvement in cyclization in THF as compared to benzene is again indicative of an ionic intermediate in the mechanism. A closer look at Table-I reveals that while the proportion of reduction product(4) in both cases is fairly comparable, the cyclization product(3) in THF has been formed at the expense of the elimination product(2).

It logically follows therefore that the cyclization process competes with elimination from a common intermediate which can only be the hot cation generated by the electron transfer in the radical cage (Scheme-1, see also Sec.I). Such an effect of solvent is precisely what one would expect if a 'hot' free cation is generated on electron transfer. In a nonpolar solvent like benzene the elimination product which results is from the unencumbered cation[5] while in THF there would be a gradual relaxation of the 'hot' cation by the polar solvent molecules, increasing its lifetime thereby facilitating cyclization.

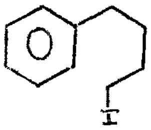
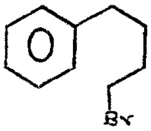
In order to establish on firmer grounds that a large part of the cyclic product(3) is derived from the 'hot' carbonium ion rather than the radical intermediate it would be necessary to differentiate between the two pathways.

The photochemistry of alkyl bromides has been studied in comparison with the corresponding iodides[6]. The observation was that while the photochemistry of iodides involves cationic intermediates, the photoproducts from bromides were typical of radical-derived products(with the exception of benzylic[7] and bridged bromides[8]). This difference was attributed to the difference in reactivity of $Br^{\cdot}$ and $I^{\cdot}$.

While the former is a hot radical which undergoes rapid hydrogen abstraction from the solvent cage leading to radical-derived products the latter is incapable of abstracting hydrogen atoms from most solvents. In the absence of an efficient competing process in the latter case the radical pair has sufficient time for electron transfer to occur. On this basis it was thought the photolysis of 4-phenyl-1-bromobutane would give products derived predominantly from the 4-phenylbut-1-yl radical. Added to this was also the report[8] that the solution photolysis of 1-bromooctane gave exclusively n-octane while 1-iodooctane gave predominantly a mixture of 1-(56 percent), 2-(4 percent) and 3-octene(2 percent).

Thus if the photolysis of 4-phenyl-1-bromo butane proceeds predominantly by the free radical pathway one would expect the reduction product(4) to predominate and only a trace if any of the elimination product(2). The photolysis of 4-phenyl-1-bromobutane in THF in the presence of a molar equivalent of Et_3N was carried out and the expected result was obtained(Fig. 1b). The major product was(4) (~72 percent) and(2) was present in only 9 percent. In addition the cyclised product(3) was present in 18.3 percent. Comparison of these results with the previous two cases along with the reduction to cyclization ratios are given in Table-II.

Table II:- Comparison of the results from the photolysis of 4-phenyl-1-iodobutane and the corresponding bromide.

Products			
	in Benzene %	in THF %	in THF %
2	80.0	58.0	9.0
4	13.5	22.0	71.7
3	3.0	20.0	18.3
$\frac{\text{Reduction}}{\text{Cyclisation}}$	4.5	1.1	3.92

GLC of the photo products of 4-phenyl-1-iodo and 4-phenyl-1-bromo-butane

GLC Conditions

Column length - 12'
Stationary phase - 10% Carbowax
Temperature - 160°
Carrier gas - Hydrogen
Flow rate - 60 ml/min

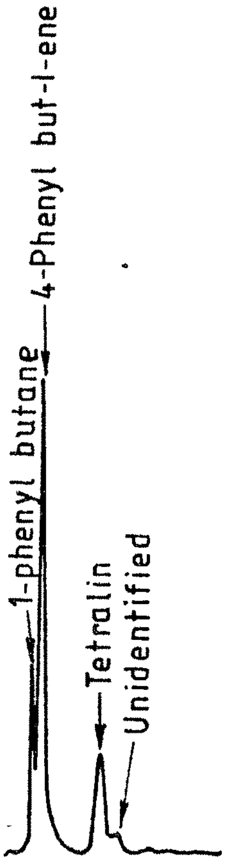


Fig.1a: 4-Phenyl-1-iodobutane

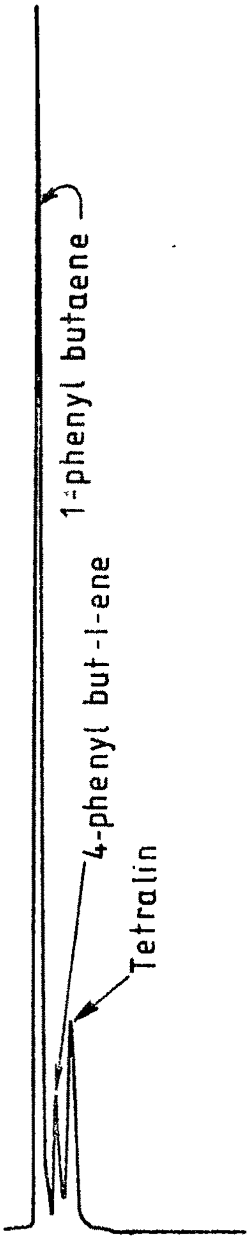
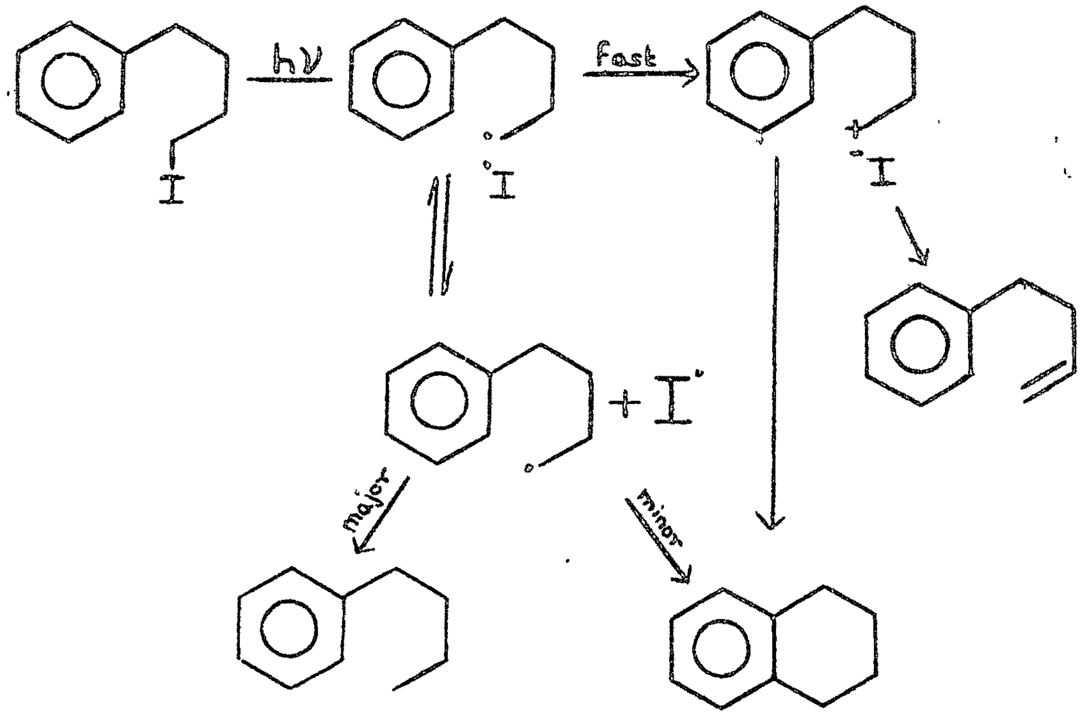


Fig.1b: 4-Phenyl-1-bromobutane

Comparing between the results obtained from the bromide and iodide in THF one can see that the reduction to cyclization ratio increases by 3.6 times in going from the iodide to bromide. Or conversely there is an almost four-fold decrease in the amount of cyclized product. The only difference between the photochemistry of bromide and iodide being the relative extent of competing radical and cationic pathways it follws that in the photolysis of the iodide(in THF) a substantial part of the cyclized product(3) is derived from the hot cation rather than the radical. If we assume that an exclusively free radical pathway operates in the bromide(which need not be the case considering the 9 percent of (2) obtained) and compute this datum with that for the iodide(in THF) we can say that approximately 80 percent of the cyclic product(3) is derived from the hot carbonium ion and only about 20 percent is derived from the radical.

We have said earlier that in the photolysis of the iodide in benzene the cationic intermediate goes over exclusively to the elimination product(2). If this is so then the 3 percent of tetralin(3) obtained (Table I) would be entirely from the radical intermediate. This argument too is substantiated by the comparable reduction/cyclization ratio with the bromide case where the cyclic product is predominantly radical derived(Table II).

Thus, on the basis of all the data discussed above it is possible to conclude that the electron transfer process in the radical pair in the solvent cage is a fast process giving rise instantaneously to a 'hot' unencumbered cation. The subsequent fate of this cation depends on the polarity of the solvent as may well be expected[5]. Of the radical pairs which become kinetically free of the solvent cage a major portion goes over to the reduction product by abstraction of a hydrogen atom. Photocyclization, as the evidence indicates, is predominantly derived from the 'hot' carbocation intermediate and is in competition with elimination. Judging from the relative proportion of (2) and (3) one can deduce that elimination is a faster process than cyclization. The overall picture is illustrated in Scheme-2.



SCHEME-2

a) Solvent effects on the photochemistry of (1)

Contrary to the results obtained by us in tetrahydrofuran, Charlton and Williams[4,9] report that 4-phenyl-1-iodobutane does not cyclize to tetralin(3) on irradiation in either benzene or acetonitrile. The results in benzene may probably be rationalized, as against ours, in terms of lower polarity of the solvent resulting in a lesser contribution of the intermediate carbocation to the overall mechanism. This argument too has its failings in that the relative cyclisation to elimination ratio ought not to be seriously affected by polarity of the solvent if both the processes are in competition from the same carbocation. Solvent polarity is only expected to affect the extent of generation of the cation.

That cyclization results in tetrahydrofuran though not in acetonitrile is however surprising. Acetonitrile being the more polar(for $CH_3CN = 37.5$ and for THF = 7.58)[10] is expected to give a greater amount of the cation-derived product. This is indeed borne out by the nearly quantitative(99 percent) yields of the olefin(2) obtained[9]. On the other hand irradiation in THF results in a significant amount (22 percent) of the reduction product(4). It is obvious therefore that some other solvent dependent factor rather than polarity plays an important role in photocyclizations.

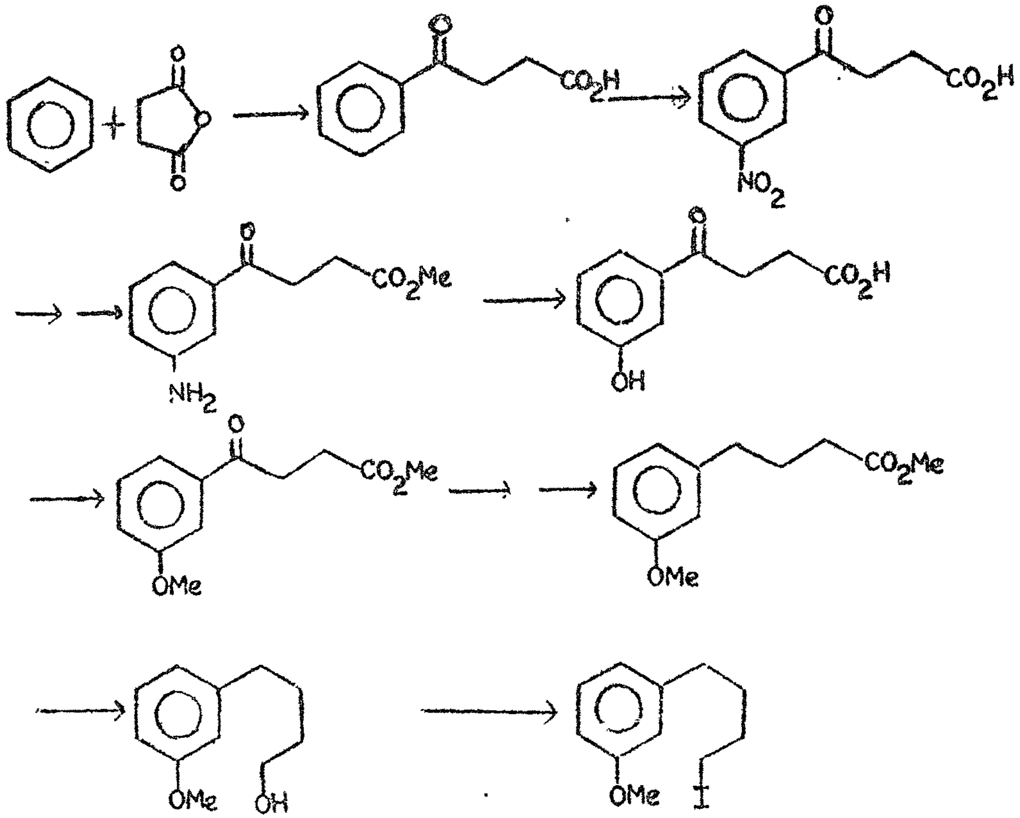
It is known that initial homolysis of the C - I bond followed by rapid electron transfer gives rise to an unencumbered cation. It is the subsequent fate of this cation which would decide the extent of cyclization vis-a-vis elimination if any. The unencumbered cation is expected[5] to be very unstable, rapidly decomposing to the olefin[8]. A relaxation of the unencumbered cation by the solvent would increase its life-time thereby enabling side reactions - cyclization in the present case. THF having a greater necleophilic solvating power(Lewis basicity = 142) than acetonitrile(Lewis basicity = 101)[11] is expected to be the more efficient in relaxing(by solvation) the unencumbered cation. We therefore suggest that it is the nucleophilicity rather than the polarity of solvent which determines the extent of cyclisation. Nucleophilic trapping by solvent of the more stable cations[8,9] and previous studies with citronellyl iodide[3] where triethyl amine gives the maximum cyclisation would seem to bear this out. It also follows that while the elimination product(2) is derived from the unencumbered cation[8] the cyclised product is derived from a somewhat encumbered one.

B. Photochemistry of 4-(m-methoxyphenyl)-1-iodobutane(5)

In order to study the effect of substitution on this cyclisation the photochemistry of 4-(m-methoxyphenyl)-1-iodobutane(5) was investigated and synthesized by a eleven step sequence via the corresponding alcohol as shown in Scheme-3.

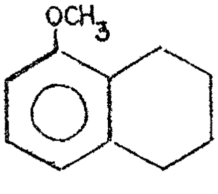
A 1 percent soln. of (5) was irradiated in THF in the presence of a molar equivalent of Et_3N at 50°. After work-up the product mixture was found to consist of atleast eight components(GLC) of which only 4.4 percent corresponded to the cyclic products(6) and (7) (3.1 percent of (6) and 1.3 percent of (7)).

Though we expected a methoxy substituent to enhance cyclization at para position ie(7) this as can be seen is not the case. The reason, however, is not very clear.



5.

SCHEME-3



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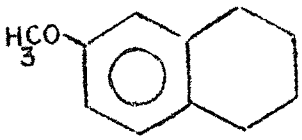
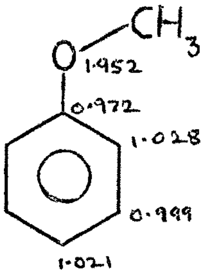


7.

C. Photosubstitutions on Anisole

The presence of a methoxy group on the benzene ring activates it towards electrophiles especially in the ortho and para positions. Calculations have been made of the electron density on the various carbon atoms in the ground state which are shown below



An electrophilic substitution by a methyl group on anisole gives almost exclusively the para -isomer(p-methyl anisole)[13]. On the other hand homolytic substitution by a methyl group on anisole gives the ortho isomer as the major product (74 percent) while the meta and para isomers were obtained in 15 percent and 11 percent respectively[14]. This striking difference in product distribution offers convenient method for differentiating between an electrophilic(cationic) and a homolytic (free radical) substitution. Thus the products obtained on photosubstitution should give a clear picture as to the nature of the alkyl moiety involved.

Anisole was irradiated with methyl iodide both in the presence and absence of a radicale scavenger(Et_3N). A 5 percent solution of iodomethane in anisole was irradiated with a 400 W med. pressure Hg lamp for 2 hrs. For the experiment with Et_3N a molar equivalent of Et_3N was also added. Work-up(see experimental) gave a small amount of anisole enriched in the methyl anisoles(~4 percent in 9 ml of the solution). The products were characterised and their percentages calculated by quantitative NMR (Table III).

Table III:- Photoirradiation of Iodomethane with Anisole.

Compound	with Et_3N	without Et_3N
o-methyl anisole	37.19	39.27
m-methyl anisole	26.70	31.87
p-methyl anisole	36.12	28.72

A comparison of these results with those for homolytic and electrophilic substitution is revealing. A striking feature seen in Table-III is the comparable proportion of all the three isomers(o, m and p). Taking into account the statistical factor viz:- the presence of only one para site for two ortho and meta sites in anisole, it follows that in the photosubstitution the para site is the most reactive towards the methyl species. These results indicate therefore that a large proportion of the photoreaction follows an electrophilic pathway ie. via a methyl cation. The presence of significant amount of the meta substituted product is indicative of a competing radical pathway which might well be expected. A comparison of the meta/para ratio of the products obtained by photoirradiation with that by homolytic aromatic substitution of the methyl radical[14] substantiates this argument (taking also into account the reduced proportion of the ortho product) (Table-IV).

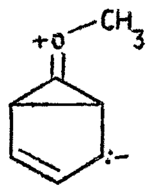
Table-IV: m/p ratios in the methylation of Anisole

	Homolytic methylation	Photomethylation	
		with Et_3N	without Et_3N
m/p	1.4	0.756	1.11

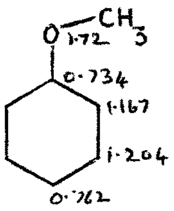
It may also be noted from Table-IV that the meta/para ratio in photomethylation decreases when Et_3N is used as scavenger.

In the above argument it has been assumed that the photomethylation reaction proceeds from the ground state anisole. This however, need not be the case. It is possible that irradiation results in an electronic excitation of the anisole molecule which subsequently undergoes the methylation.

It is known that while in the ground state anisole the ortho and para sites are activated, a photochemical $\pi \rightarrow \pi^*$ transition results in an activation of the ortho and meta sites[15]. The valence bond diagram of the first excited singlet state is shown below(A) while (B) shows the distribution of electron density over the various atoms in this state.



A



B

On this basis, a methylation from the photoexcited anisole would be expected to lead to a predominance of the meta substituted product and to a lesser extent the ortho substituted product at the expense of para substitution. The results obtained therefore lead to two important conclusions (i) a large part of the photosubstitution is electrophilic in nature ie a methyl cation is involved.

(ii) Under the experimental conditions a substantial proportion of the reaction is from the ground state anisole.

Further confirmation was obtained from the photocyclohexylation of anisole with cyclohexyliodide. In the homolytic cyclohexylation of anisole[14], 67 percent of ortho-, 28 percent of meta- and 5 percent of paracyclohexyl anisoles were obtained. For the electrophilic substitution a 1:1 molar mixture of anisole and cyclohexanol was stirred with PPA for a period of 35 min at room temp.[16]. Subsequent work-up gave the product which after distillation was analysed(GLC). The product ratio obtained was 60 percent of the para- and 40 percent of the ortho- cyclohexylated isomers.

Photoirradiation of cyclohexyliodide with anisole in the presence of triethyl amine gave the product ratio shown in Table-V.

A comparison of the meta/para ratio indicates the dramatic difference between the homolytic and photosubstitution(Table-VI).

It is obvious that the results obtained in this case only serve to augment the inferences deduced earlier.

Table-V:- Photoirradiation of Cyclohexyl Iodide with Anisole

Compound	Photosubstitution	Homolytic substitution	Electrophilic substitution
o-Cyclohexyl anisole	41	67	40
m-Cyclohexyl anisole	16	28	-
p-Cyclohexyl anisole	23	5	60

Table -VI :- m/p ratios in the Cyclohexylation of Anisole

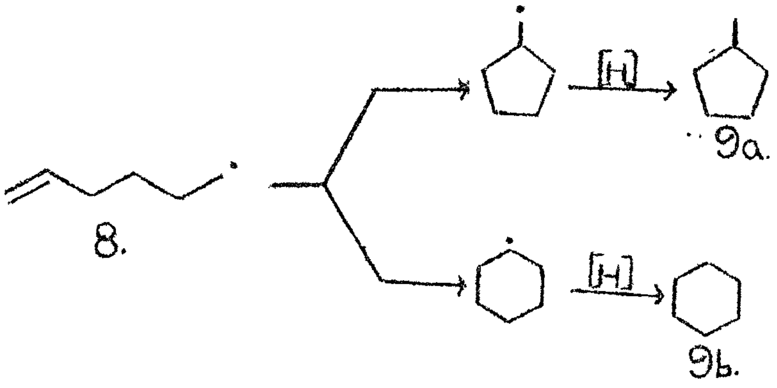
	Homolytic cyclohexylation	Heterolytic cyclohexylation
m/p	5.6	0.7

D. Photochemistry of 1-Iodo-5-Hexene(10)

The cyclisation of 5-hexen-1-yl radical(8) has been an area of much study[17]. In these investigations it has been found that methylcyclopentene(9a) was the major product while cyclohexane(9b) was present only in trace amounts (Scheme-4).

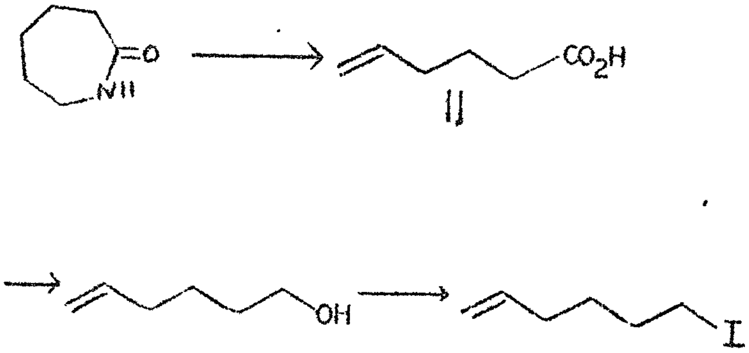
The preferential closure to a five membered ring is surprising since it is contrary to the usual direction of radical addition to double bonds and is energetically unfavourable both because of ring strain and the greater stability of secondary vs. primary radicals. Subsequently it was found that the ring closure is an irreversible one and kinetically controlled[17]. The rate of closure to the five membered ring (9a) was found to be much faster than to the six membered ring (9b). The reason for this appears to be a combination of both entropy and enthalpy factors[18,19]. In contrast the 5-hexen-1-yl cation is known to cyclize to a six membered ring[20].

In the light of the above data it was felt that 1-iodo-5-hexene(10) would be an ideal substrate for our investigation into the mechanism of photocyclisation as the radical and cationic pathways lead to distinct products. An analysis of the five vs six membered ring products obtained on the



SCHEME-4

10.



SCHEME-5.

photolysis of (10) was expected give a quantified picture of the relative predominance of the radical and ionic pathways for cyclization.

a) Preparation of 1-iodo-5-hexene(10)

(10) was prepared from 5-hexenoic acid which in its turn was obtained by the diazotization of caprolactam(Scheme-5).

According to a German patent[21], nitrosation of caprolactam with $NaNO_2/HCl$ leads to a major product of $Cl(CH_2)_4COOH$ (210 parts) and a minor product of 5-hexenoic acid(40 parts). Another report claims[22] claims that the products obtained were many and identified as 5 and 6-chlorocaproic acid, 6-hydroxycaproic acid, caprolactone and $Cl(CH_2)_5\ COO(CH_2)_5COOH$. Use of sulphuric acid instead of HCl gave the corresponding terminally hydroxy substituted products. In the light of these results the nitrosation of caprolactam does not appear to be a good method for the preparation of 5-hexenoic acid(11). However it was found that using H_3PO_4 instead of HCl or H_2SO_4 for the nitrosation gives 5-hexenoic acid(11) as the major product(~70 percent purity) which could be easily purified. Subsequent transformation of (11) to 1-iodo-5-hexene was easily accomplished by standard procedure(see Experimental).

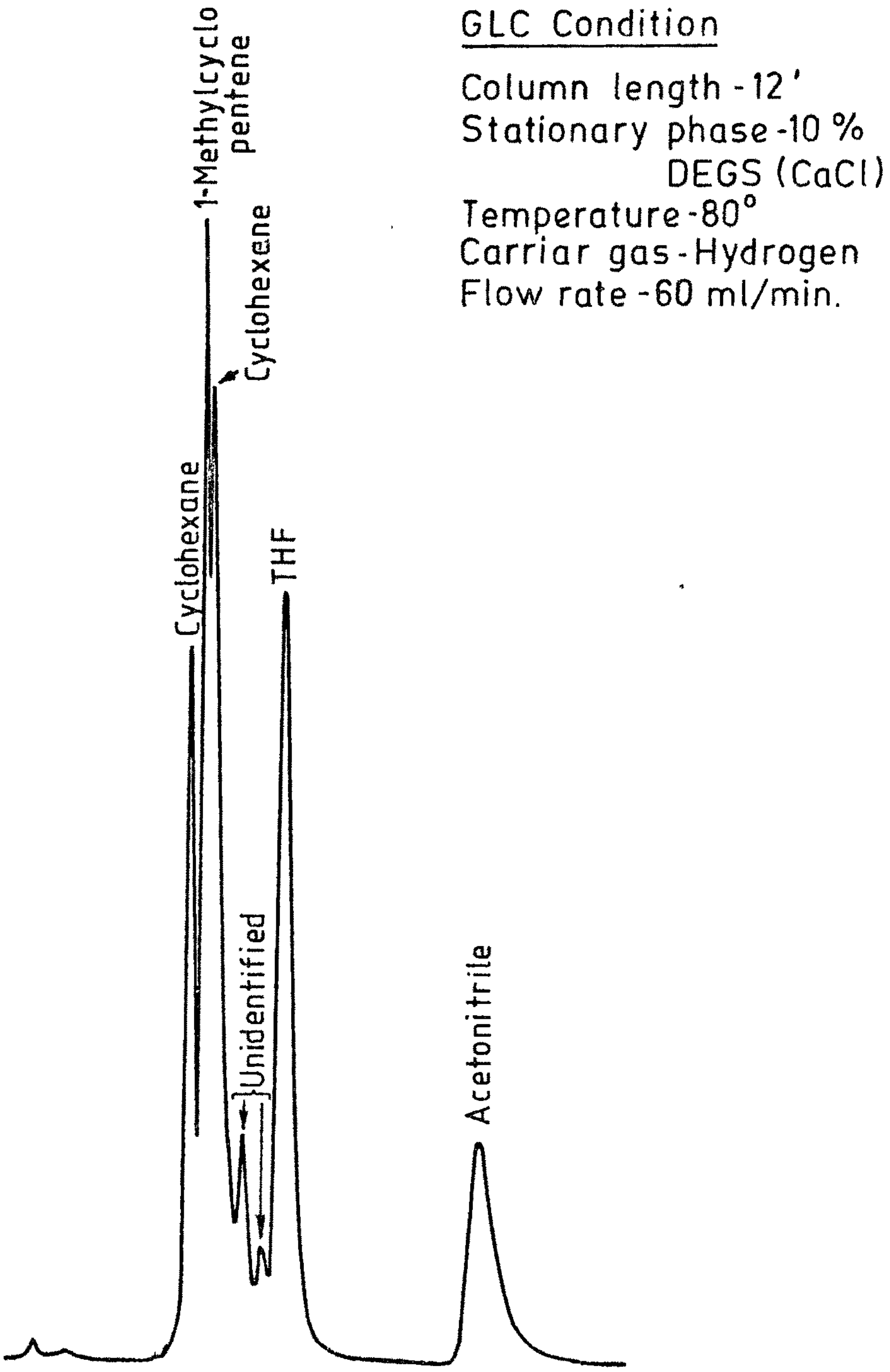
b) Photolysis

The photolysis of 1-iodo-5-hexene in THF in the presence of an equimolar amount of Et_3N was carried out using a 400 W med. pressure Hg vapour lamp. After an intricate work-up procedure(see Experimental) the product mixture was analysed by GLC. Identification of the individual components was by mixed injection with authentic samples on two columns(10 percent DEGS, 10 percent DEGS-CuCl).

The products and their ratios obtained are given in Table VII.(Fig.2)

Table VII: Products of the Photolysis of 1-Iodo-5-Hexene

Product	Structure	%
Cyclohexane		28.08
1-Methylcyclopentene		32.96
Cyclohexene		29.80
Unidentified	—	6.2
Unidentified	—	3.0



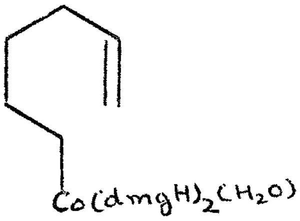
GLC Condition

Column length - 12'
Stationary phase - 10 % DEGS (CaCl)
Temperature - 80°
Carriar gas - Hydrogen
Flow rate - 60 ml/min.

Fig.2 : Photoproducts of 1-Iodo-5-hexne

The most nòticeable feature of the above results is the predominance of the total six membered ring products(cyclohexane + cyclohexene) over the five membered ring product (1-methyl cyclopentene) (58 percent of the total prod. mixture).

If the photocyclization was derived only from the radical intermediate one would expect exclusively the five membered ring product. The photolysis of hex-5-enyl cobaloximes(12) generates the hex-5-enyl radical which is known to cyclize~~d~~ to a five membered ring[23]. This rules out the possibility of hot radical generated by photolysis leading to a different mode of cyclization vis-avis the thermodynamically generated one.



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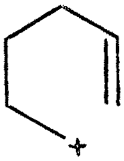


13.

Solvent effects may also be ruled out as the hex-5-enyl radicals are known to cyclize in THF to the five membered ring[24]. All these lead to the iference that the six membered ring products in the photolysis of (10) arise from the hex-5-enyl cation(13).

The predominance of the six membered ring products over the five membered one establishes unequivocally the predominant contribution of the 'hot' carbocation to the photocyclization process as opposed to the contribution from the 'hot' radical.

E. Conclusion

In conclusion therefore it can be generalized that in the photocyclization of aliphatic iodides with a suitably situated ethylenic linkage, the major contribution is from the 'hot' carbocation which is generated on electron transfer in the solvent cage within the radical pair. A lesser contribution from the radical intermediate also exists. The two pathways (ionic and radical) are not directly dependent on each other and can in some cases lead to different products as with 1-iodo-5-hexene.

EXPERIMENTAL

All b.p.'s are uncorrected. All solvent extracts were finally washed with brine before drying(Na_2SO_4).

The following instruments were used for spectral/ analytical data: Perkin-Elmer infrared spectrophotometer, model 267; Perkin-Elmer, model R 32(90 MHz) NMR spectrometer; Varian Mat CH-7 mass spectrometer(70 , direct inlet system); Hewlett-Packard 5712A(analytical) gas chromatograph (Al columns, 360 cm x 0.6 cm; support, 60-80 mesh Chromosorb W; stationary phases used-Carbowax, Diethylene glycol succinate and SE-30; carrier gas N_2). IR spectra were recorded on smears or in CCl_4 solution. All PMR spectra were recorded with 15-20 percent soln. in CCl_4 with TMS as internal standard; signals are reported in ppm(δ); while citing PMR data following abbreviations have been used-s, singlet; d, doublet; t, triplet; q,quarted; m,multiplet; b,broad.

Solvents

Solvents used for photoirradiation were purified as under:

Tetrahydrofuran:- by refluxing and distilling over LAH[25]

Triethylamine:- by refluxing with KOH pellets and distilling over Na[26].

NaI was dried by azeotropic distillation with xylene till 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) Photoirradiation of alkyl iodides in anisole

A 5 percent(by volume) solution of the alkyl iodide (CH_3I or $C_6H_{11}I$) in anisole was irradiated for the required period. For experiments with triethylamine a molar equivalent of triethylamine(w.r.t. iodide) was also added. The solution was then removed and most of the anisole distilled off. The residue was fractionated for enrichment of the ring alkylated products.

b) Photoirradiations in THF

1 percent solution of the substrate in THF containing a molar equivalent of triethylamine was irradiated. The reaction was monitored by T.L.C(10 percent benzene in pet. ether). When the photostationary state was reached(2-6 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[27] 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 atleast two or three of the following stationary phases: 5 percent and 10 percent carbowax, 10 percent SE-30, 10 percent diethylene glycol succinate(DEGS) and 10 percent DEGS-CuCl[39].

Photoirradiation of Iodomethane in anisole

A solution of 12.5 ml(~29 g) of Iodomethane in 250 ml anisole was irradiated as described under General Procedure . In a separate experiment 28.9 ml (~21 g) of triethyl amine was added to the solution as HI quencher. In this case white crystals($Et_3\overset{+}{N}CH_3I^-$) separate out and the mixture irradiated as such. At the end of irradiation the solution was washed with water to remove the remaining ammonium salt, foll. by aq. 10 percent $Na_2S_2O_3$ solution(25 ml x 3) and finally with brine, water and then dried(Na_2SO_4). Most of the anisole was distilled off and the residue(~30 g) was fractionated carefully (1 atoms) through a vigreaux column(6 inches length) and collected in three portions. The third cut (~9 ml) was refractionated and collected in ~2 ml fractions. The last fraction showed enrichment of methyl anisoles(GLC, 10 percent SE-30, 150^o). The relative ratio of o-, m- and p-methyl anisoles was calculated by quantitative NMR. The values reported are the mean of three such calculations.

Preparation of cyclohexyl iodide[28]

In a 500 ml three-necked RBF equipped with a thermometer, a sealed Hershberg stirrer and a reflux condenser were placed 16.3 g phosphoric oxide(P_2O_5) and 58 g(34 ml) of 85 percent orthophosphoric acid. When the stirred mixture cooled to room temp. 83 g KI and 25 g distilled cyclohexanol were introduced. The mixture was heated with stirring at 100-120° for 2-3 hrs and then cooled to room temp. followed by addition of 75 ml water and 125 ml ether. The ether layer was separated, decolourized by shaking with 25 ml 10 percent $Na_2S_2O_3$ soln.(aq.), washed with 100 ml cold sat. brine solution and dried(Na_2SO_4). Removal of ether and distillation of the residue gave pure cyclohexyl iodide(45 g, 90 percent yield; b.p. 67-69°/9 mm).

Irradiation of cyclohexyl iodide in anisole

A mixture of 250 ml distilled anisole, 12.5 ml(~19 g) cyclohexyl iodide and 13.7 ml(10.1 g) triethylamine was irradiated as described earlier(General Procedure) for 24 hrs when GLC(10 percent SE-30, 170°) showed no more cyclohexyliodide. The solution was then washed with 10 percent aq.$Na_2S_2O_3$(25mlx3) followed by brine and water and dried(Na_2SO_4). Most of the anisole was distilled off and the residue (~4.0 g) was fractionated carefully through a vigreaux column(length, 6 inches). Three fractions were collected in the range 140-170°/7 mm. The first two fractions consisted only of anisole

(GLC, 10 percent SE-30, 200°) while the last fraction contained 20 percent anisole and 80 percent of the cyclohexylated anisoles. The peaks corresponding to the o-,m- and p- subst. products were identified by mixed GLC with authentic samples(10 percent CW, 10 percent SE-30 and 10 percent DEGS). The authentic samples were prepared by known procedures[29,30]. The o-, and p-isomers were separated by column chromatography(SiO_2-gel/IIB; eluant, pet.ether + 5 percent benzene).

Preparation of 4-phenyl-1-iodobutane

(i) γ-Phenyl butyric acid:- 5 g(0.028 moles) of β-benzoyl propionic acid[31] was dissolved in 50 ml methanol. To it was added 0.6 g of 5 percent palladised charcoal and the mixture was shaken under an atmosphere of hydrogen (1 atmos) at room temperature till no more hydrogen is absorbed(~ 4 hrs). The solution was then filtered to remove the charcoal and the solvent removed to furnish crude γ-phenyl butyric acid. Distillation(b.p.178-181/19 mm) afforded the pure acid(4.3 g, 94 percent yield).

(ii) 4-Phenyl-1-butanol:- A suspension of LAH(1.2 g, 0.03 moles) in 10 cc dry ether was stirred at room temp. and to it was added a solution of γ-phenyl butyric acid(4 g, 0.0244 moles) in 5 cc dry ether at such a rate that a gentle reflux is maintained. After completion of addition the stirring is continued for 3 hrs at the end of which the reaction mixture was decomposed with icecold water followed by cold 10 percent H_2SO_4(5 ml). The resulting solution was extracted with ether(10 ml x 3), washed with brine followed by water and dried (Na_2SO_4). Evaporation of the ether and distillation of the residue gives pure 4-phenyl-1-butanol(3.5 g, 95 percent yield; b.p.140°/ 14 mm).

PMR: two C-$\underline{CH_2}$-C(4H, m, 1.4 to 1.8 ppm); Ar-$\underline{CH_2}$(2H, t, 2.57 ppm, J=7 Hz); CH_2-OH(2H, t, 3.51 ppm, J=6 Hz); Ar-H(5H, m, 7-7.3 Hz)

IR(CCl_4): O-H 3370 cm^{-1}.

(iii) 4-Phenyl-1-butyltosylate:- 2g(0.0133 mole) of the alcohol was dissolved in 10 cc dry pyridine and cooled to 0°. To it was added in portions 3.6 g(0.019 mole) p-toluenesuphonyl chloride while shaking. After addition the reaction mixture was kept at 4° for 20 hrs during which crystals of pyridine hydrochloride separate out. The reaction mixture was then poured into crushed ice, extracted with ether(10 ml x 3) and the combined extract washed with 10 percent HCl (5 ml x 3) followed by water and dried (Na_2SO_4). The solvent was flushed off at room temp.(~35°)

under reduced pressure to afford the pure(single spot on TLC) tosylate (4g, 100 percent)

PMR: two C-$\underline{CH_2}$-C(4H, m, 1.5 to 2 ppm); Ar-$\underline{CH_2}$(2H, t, 2.63, J=7 Hz); $\underline{CH_2}$-OTs(2H, t, 3.56 ppm, J=6 Hz), $\underline{CH_3}$-Ar(3H, s, 2.45 ppm)

IR: (CCl_4) C-SO_2-O-C 1350, 1175 cm^{-1}

(iv)4-Phenyl-1-iodobutane:- To the tosylate(3 g, 0.0099 mole) dissolved in dry acetone(30 cc) was added dry NaI(7.5 g) and the reaction mixture stirred at room temp.(~35°) for 12 hrs. The bulk of the solvent was stripped off, the residue treated with water(30 ml) and the product taken up in Et_2O(20 ml x 3). The combined ether extract was washed with 10 percent aq. $Na_2S_2O_3$(10 ml x 2) and water. The solvent was distilled off and the residue (2.3 g) passed through a column of silica gel(1.5 cm x 25 cm, IIB). The pet.ether eluate was collected. Removal of the solvent furnished the pure iodide(2.1 g, 82 percent yield).

PMR: two C-$\underline{CH_2}$-C(4H, m, 1.5 to 2.0 ppm); Ar-$\underline{CH_2}$(2H, t, 2.57 ppm , J= 7 Hz), $\underline{CH_2}$-I(2H, t, 3.09 ppm, J=6.5 Hz); Ar-H(5H, m, 7 to 7.25 Hz).

Photoirradiation of 4-phenyl-1-iodobutane in THF

2 g (0.008 mole) of 4-phenyl-1-iodobutane and 0.8 g (0.008 mole) of triethylamine were dissolved in 200 cc dry THF and irradiated for 2 hrs when G.L.C.(10 percent SE-30, 170°) showed no more iodide. The total reaction product was worked up (see General Procedure and distilled to afford a colourless liquid(0.50 g; b.p.128-130°(bath)/ 20 mm) and a residue (0.49 g). Two of the three products obtained, 1-phenylbutane and tetralin were identified by mixed GLC with authentic samples on two columns(10 percent CW and 10 percent SE-30, 170°) while 4-phenyl-1-butene was identified by comparing the PMR of the product mixture with the reported spectrum[32]. In addition, quantification of this compound from the NMR spectrum and tallying with the GLC obtained value was also done for confirmation.

Photoirradiation of 4-phenyl-1-iodobutane in benzene

2 g (0.008 mole) of 4-phenyl-1-iodobutane in 200 ml of thiophene-free benzene was irradiated for 2 hrs and worked up as described above. wt. of distilled material obtained = 0.40 g, wt. of residue = 0.19 g.

Preparation of 4-phenyl-1-bromobutane

To 3 g (0.02 mole) of 4-phenyl-1-butanol in a 100ml RBF equipped with a stirring needle was added at room temp.

(~35°) 10 ml of 60 percent HBr. The mixture was magnetically stirred and heated gradually over a period of half an hour to 120°. The bromide separated out as a dark brown layer on top. The mixture was then cooled, diluted with water (30 ml) and extracted with ether(25 ml x 3). The combined ethereal extract was washed with aq. 10 percent Na_2CO_3 soln., water and dried(Na_2SO_4). Evaporation of the ether afforded the crude bromide which on distillation gave the pure material (3.4 g, 80 percent yield; b.p. 130-132°/12 mm).

PMR: two $C-\underline{CH_2}-C$(4H, m, 1.6 to 2.0 ppm); $Ar-\underline{CH_2}$(2H,t,2.6 ppm, J=7 Hz); $\underline{CH_2}-Br$(2H, t, 3.32 ppm, J= 6 Hz); Ar-H(5H, m, 7.0 to 7.3 ppm).

<u>Photoirradiation of 4-phenyl-1-bromobutane in THF</u>

2.8 g (0.013 mole) of 4-phenyl-1-bromobutane was dissolved along with 1.33 g(0.013 mole) Et_3N in 280 mol THF (dry) and irradiated for 2 hrs. Further procedure is the same as that described for 4-phenyl-1-iodobutane.

<u>Preparation of 4-(m-methoxyphenyl)-1-iodobutane</u>

(i) 3-(m-nitrobenzoyl)-propionic acid:- 60 cc con.H_2SO_4 was taken in a beaker equipped with a mechanical stirrer and an alcohol thermometer and cooled in an ice-salt bath to -10°. 18 g(0.1 mole) β-Benzoyl propionic acid was gradually added(~5 min) under stirring such that the temperature does not rise above 10°. After completion of addition the stirring was continued and the soln. transferred to a liquid nitrogen-ethyl acetate bath. When the temp. reached -40° a previously cooled(5-10°) solution of nitrating mixture(12 cc 95 percent H_2SO_4+ 9 cc fuming HNO_3) was added rapidly(~2 min) under vigorous stirring. After addition the mixture was stirred for an additional 10 min. It was then warmed to room temp. and poured over 100 g crushed ice under vigorous manual stirring. A faint yellow solid separated out which was filtered and washed thoroughly with ice-cold water. Recrystallization from hot water gave 17.3 g(80 percent yield) of pure m-nitro-β-benzoylpropionic acid(mp. 142-144°)

PMR : $C\underline{H}_2$-COOH(2H, t, 2.69 ppm, J= 7 Hz); $C\underline{H}_2$-COAr(2H, t, 3.32 ppm, J= 6 Hz)

IR(Nujol): C-NO_2 1535, 1350 cm^{-1}; $\text{Ar-}\overset{O}{C}$ 1693 cm^{-1}; $\overset{\overset{O}{\|}}{C}OH$ 1715 cm^{-1}.

(ii) Methyl ester:- 10 g of the above acid(0.045 mole) is dissolved in 150 ml methanol to which is added under cooling 2 ml conc. H_2SO_4 and the mixture refluxed on a water bath for 5 hrs. Removal of methanol followed by addition of 100 ml water, ether extraction(25 ml x 3), washing the combined ethereal extract with water drying (Na_2SO_4) and removal of ether gives the ester(8 g, 80 percent yield, m.p.57-58°)

PMR:- CH_2COOMe(2H, t, 2.78 ppm, J= 7 Hz); $C\underline{H}_2COAr$(2H, t, 3.33 ppm, J = 7 Hz); $C\underline{H}_3$-O(3H, s, 3.7 ppm)

IR(Nujol): C-NO_2 1523, 1348 cm^{-1}; ArC 1690 cm^{-1}, COMe 1735 cm^{-1}

(iii) Methyl-3-(m-aminobenzoyl)-propionate:- 8 g(0.034 moles) of the above ester was dissolved in a min. amount of acetone (~3 ml) and added during one hr. to a well stirred suspension of iron filings(10 g) in water(60 cc) and acetic acid(4 cc) at 75°C. The mixture was then boiled gently for half an hour with continued stirring and filtered hot, the amino compound separating rapidly as the filtrate cooled. It was extracted with ether (3 x 50 ml) and the ethereal solution shaken thoroughly with 50 ml, 15 percent HCl soln.(cold). The aq. layer was cooled in an ice bath and neutralized with 10 percent aq. NaOH solution. Extraction with Et_2O(20 ml x 4), washing of the combined ethereal extract with water, drying (Na_2SO_4) and removal of ether furnishes the crude amino compound (5 g, 72 percent yield) which was taken as such for the next step.

PMR: $\underline{CH_2}COOMe$(2H, t, 2.7 ppm, J = 7 Hz); $\underline{CH_2}COAr$(2H, t, 3.23 ppm, J= 7 Hz); CH_3O(3H, s, 3.67 ppm).

IR(Nujol): C-NH_2 1262 cm^{-1}; ArC 1680 cm^{-1}; COMe 1725 cm^{-1}

(iv) 3-(m-methoxybenzoyl)-methylpropionate:- 25 g of crude 3-(m-aminobenzoyl)-methyl propionate dissolved in a solution of 85 ml conc. H_2SO_4 and 300 cc water was diazotised with a solution of 18.8 g $NaNO_2$ in 70 ml water at -8° over 30 min. 70 cc water was then added and the solution boiled to give a brown tar which soon solidifies. Ether extraction(50 ml x 3) followed by the usual work-up procedure gives 15 g of a dark brown solid(3-(m-hydroxy benzoyl)-propionic acid). A mixture of this solid (15 g) and 28 g potassium carbonate(anhydrous) was taken in 100 ml acetone and to it was added, dropwise, 18.75 g (0.143 mole) dimethyl sulphate (distd.) and the mixture refluxed on a water bath for 10 hrs. The acetone was then distilled off and 50 ml water added to the residue. The aqueous soln. was extracted with Et_2O(50 ml x 3), the ether extracts combined and washed with water, dried(Na_2SO_4) and evaporated to give the crude 3-(m-methoxy benzoyl)-methyl propionate. Distillation (b.p. 195°/12 mm) affords the pure material as a pale yellow oil (15 g, 90 percent yield; acid m.p. 108-109°, Lit.[33] m.p.110°).

(v) 4-(m-methoxyphenyl)-methylbutyrate:- 5 g(0.023mole) of the above compound was mixed with 25 ml 85 percent $N_2H_4 \cdot H_2O$ and 5 ml ethylene glycol in a 100 ml RBF and heated for 1 hr at 100° and the resulting clear solution cooled. KOH pellets(10 g) were added portionwise during 10 min at room temp. and the mixture slowly heated to 200° and kept at that temp. for 2 hrs. The reaction mixture was then cooled, diluted with water(20 ml) and acidified with conc.HCl. The acidic solution was extracted with Et_2O(25 ml x 4), the combined extracts washed with water and dried(Na_2SO_4). Removal of ether funishes a mixture of 4-(m-hydroxy phenyl)- and 4-(m-methoxy phenyl)-butyric acids(3 g) as a dark viscous material. This mixture was methylated with dimethylsulphate(4.2 g, 3.14 mole)as described under(iv) to give the 4-(m-methoxy phenyl)-methyl butyrate which gave a single spot on TLC(solvent, benzene) (3.5 g, 74.4 percent yield; acid mp 43-45°, Lit[34] m.p. 42-46°)

PMR: $C\text{-}\underline{CH_2}\text{-}C$(2H, m, 1.8 to 2.1 ppm); $Ar\text{-}\underline{CH_2}$(2H, t, 2.22 ppm, J= 7 Hz); $\underline{CH_2}COOMe$ (2H, t, 2.56 ppm, J = 7 Hz); two $\underline{CH_3}\text{-}O$(3H, s, 3.6 and 3.72 ppm)

IR(CCl_4): $\overset{O}{\overset{\|}{C}}OMe$ 1740 cm^{-1}

(vi) 4-(m-methoxyphenyl)butan-1-ol:- To a suspension of LAH (1 g, 0.025 moles) in dry ether(10 ml) was added the above ester (3.5 g, 0.0169 mole) in dry ether(5 ml) at 0°, dropwise, during 15 min. at such a rate that a constant reflux is maintained. After stirring for 4 hrs the complex is decomposed with cold water followed by 5 ml of 10 percent HCl. The usual work-up gave 2.7 g of the alcohol which was distilled(b.p.130°/2 mm; Lit[35] 112°/0.5 mm) to give 2.5 g (85 percent) yield of the pure alcohol.

PMR: C-$C\underline{H}_2$-C(4H, m, 1.5 to 1.8 ppm); Ar-$C\underline{H}_2$(2H, t, 2.6 ppm, J= 7 Hz); $C\underline{H}_2$-OH(2H, t, 3.59 ppm, J=6 Hz)

IR(Neat) 3380 cm^{-1}

(vii) Mesylation[36]:- To an approximately 0.2 M solution of the alcohol in methylene chloride containing a 50 percent molar excess of Et_3N(2 g alcohol+10 ml CH_2Cl_2+ 1.7 g Et_3N) at 0 to -10° was added an excess of 10 percent methane sulphonylchloride(1.4 g) over a period of 10 minutes. Stirring for an additional half hour completes the reaction (TLC; solvent, benzene+2 percent EtOAc). The reaction mixture was transferred to a separatory funnel with the aid of more CH_2Cl_2 and washed with water, cold 10 percent HCl, sat. $NaHCO_3$ brine. Drying(Na_2SO_4) followed by removal of CH_2Cl_2 gave the pure mesylate(single spot on TLC; 2.9 g,~100)

(viii) 4-(m-methoxy phenyl)-1-iodobutane:- To a soln. of 5 g dry NaI in dry acetone (40 ml) was added the mesylate(2.5 g, 0.01 mole) and the mixture stirred for 14 hrs at room temp. (~35°) when TLC(solvent benzene) shows no more starting material. The acetone was removed in vacuo, 20 ml water added to the residue and the resulting solution extd. with Et_2O(10 ml x 3). The combined ether extracts washed with aq. $Na_2S_2O_3$(10 percent, 5 ml x 2), water and dried (Na_2SO_4). Evaporation of the ether gives the pure iodide(single spot on TLC; 2.3 g, 70 percent yield). A small portion of it decomposed on attempted distillation, hence it was used without further purification for photoirradiation.

PMR: $C-\underline{CH_2}-C$(4H, m, 1.6 to 1.9 ppm); $Ar-\underline{CH_2}$(2H, t, 2.59 ppm, J=7 Hz) ; $\underline{CH_2}-I$(2H, t, 3.16 ppm, J=7 Hz)

Anal : Found; C, 81.02; H, 9.35, $C_{11}H_{15}O$ requires C, 80.98, H, 9.2

Photoirradiation of 4-(m-methoxyphenyl)-1-iodobutane

A soln. of 2.3 g(0.08 mole) 4-(m-methoxyphenyl)-1-iodobutane and 0.8 g(0.008 mole) Et_3N in 230 ml THF was irradiated for 6 hrs(monitored by TLC; solvent, benzene) and worked-up as described under General Procedure . The residue distilled to afford a colourless liquid(1.2 g; b.p. 130-140^{o}(bath)15 mm) and a residue(0.30 g).

The cyclic products(6) and (7) were identified by coinjection with authentic samples on three columns(10 percent SE-30, 10 percent CW and 5 percent CW, 180^{o}). The elimination product was isolated by column chromatography (10 percent $AgNO_3$ on SiO_2 gel; eluant, pet.ether and 10 percent benzene in pet.ether) and identified from its PMR spectrum($=C\underline{H}$(1H, m, 5.4 to 6.1 ppm); $-\underline{CH_2}=$(2H, m, 4.8 to 5.2 ppm); Anal., found; C, 81.60; H, 8.72. $C_{11}H_{14}O$. requires C, 81.48; H, 8.64). The reduction product was identified by mixed GLC with authentic sample on three columns(10 percent and 5 percent CW and 10 percent DEGS; 160^{o}).

Preparation of 1-iodo-5-hexene

(i) 5-hexenoic acid:- 11g $NaNO_2$ in 23 cc water is added at 0^{o} to caprolactam (17 g, 0.17 mole) in 25 cc water contg. 85 percent orthophosphoric acid (53 g) while stirring at 0^{o} after addition the mixture is gradually allowed to attain room temp. and then heated to 80^{o} until all the nitrogen is evolved. The solution is then cooled to room temperature and diluted with water (25 ml) and extracted with ether(10 ml x 3). The ethereal extract washed with water and dried (Na_2SO_4). Evaporation of ether leaves a residue (16 g). The residue is fractionally distilled and the fraction boiling between 100-105°/ 13 mm^{37} collected. The 5-hexenoic acid thus obtained is 85 percent pure(12 g, 70 percent yield based on caprolactam)

PMR: =C$\underline{H}$-(1H, m, 5.37 to 6.02 ppm); C$\underline{H}_2$=C(2H, m, 4.86 to 5.19 ppm)

IR(Neat): $\overset{\overset{O}{\|}}{C}OH$ 1710 cm^{-1}

(ii) Ethylhex-5-enoate: 10 g(0.088 mole) of the acid in 120 ml abs. EtOH contg. 1.8 g con.H_2SO_4 was refluxed on a water bath for 4 hrs. The usual work-up gives the ethylhex-5-enoate(crude, 10 g, 80 percent yield).

IR(CCl_4): $\overset{\overset{O}{\|}}{C}OEt$ 1735 cm^{-1}

(iii) 5-Hexen-1-ol:- To a cooled (0°) suspension of LAH (1.3 g, 0.033 moles) in 50 cc dry Et_2O is added with stirring 6 g of the crude ethyl hex-5-enoate in 10 cc dry Et_2O . After addition stirring is continued for 4 hrs. The usual work-up gave the crude 5-hexen-1-ol which was distilled for purification(2 g, 50 percent yield; bp^{38}.74°/20 mm,n_D^{20} = 1.4364)

PMR: two $C-C\underline{H}_2-C$(4H, m, 1.3 to 1.8 ppm); $C\underline{H}_2-C=$ (2H, m, 1.9 to 2.3 ppm); $C\underline{H}_2-OH$72H, t, 3.56 ppm, J= 6 Hz); $C\underline{H}_2=C$(2H, m, 4.8 to 5.14 ppm); =CH-(1H, m, 5.3 to 6.04 ppm)

IR(CCl_4): O-H, 3320 cm^{-1}; C=C, 1640 cm^{-1}

(iv) Mesylation[36]:- To an approximately 0.2 M solution of the alcohol in methylene chloride contg. a 50 percent molar excess of Et_3N(2 g alcohol+ 100 cc CH_2Cl_2 + 3 g Et_3N) at 0 to -10° was added a 10 percent excess (2.54 g) of methane sulphonyl chloride over a period of 5-10 min. Stirring for an additional 10 min. completes the reaction (TLC; solvent, 5 percent ether in pet. ether). The reaction mixture was transferred to a separating funnel with the aid of more CH_2Cl_2 and washed with water, cold 10 percent HCl, sat. $NaHCO_3$ soln.(aq.) and brine. Drying (Na_2SO_4) followed by removal of CH_2Cl_2 gave the pure mesylate(3.5 g, ~100 percent)

PMR: $C\underline{H}_3SO_2$ (3H, s, 2.9 ppm); CH_2-OSO_2(2H, t, 4.2 ppm), J= 6.5 Hz).

(v) 1-Iodo-5-hexene:- To a solution of 7 g NaI(dry) in dry acetone (35 ml) was added the mesylate (3.5 g, 0.018 mole) and the solution stirred at room temp. for 6 hrs. when by TLC(solvent, pet.ether) no more mesylate remains. The acetone is removed in vacuo and the residue dissolved in water(25 ml), the solution extd. with Et_2O(10 ml x3) and the combined ethereal extracts washed with aq. 10 percent $Na_2S_2O_3$(5 ml x 2), water and dried (Na_2SO_4). Evaporation of ether gives pure (TLC) 1-iodo-5-hexene(3.3 g, 80 percent yield). A portion of it was distilled in a bulb for its spectra (bp. $95-100^{\circ}$(bath)/15 mm)

PMR: two $C-\underline{CH_2}-$ and $\underline{CH_2}-C=C$ (6H bet.1.3 and 2.2 ppm); $\underline{CH_2}-I$(2H, t, 3.15 ppm, J=7Hz); $\underline{CH_2}=C$(2H, m, 4.8 to 5.17 ppm); CH=(1H,m, 5.27 to 6.01 ppm)

IR(Neat): C=C 1648 cm^{-1}

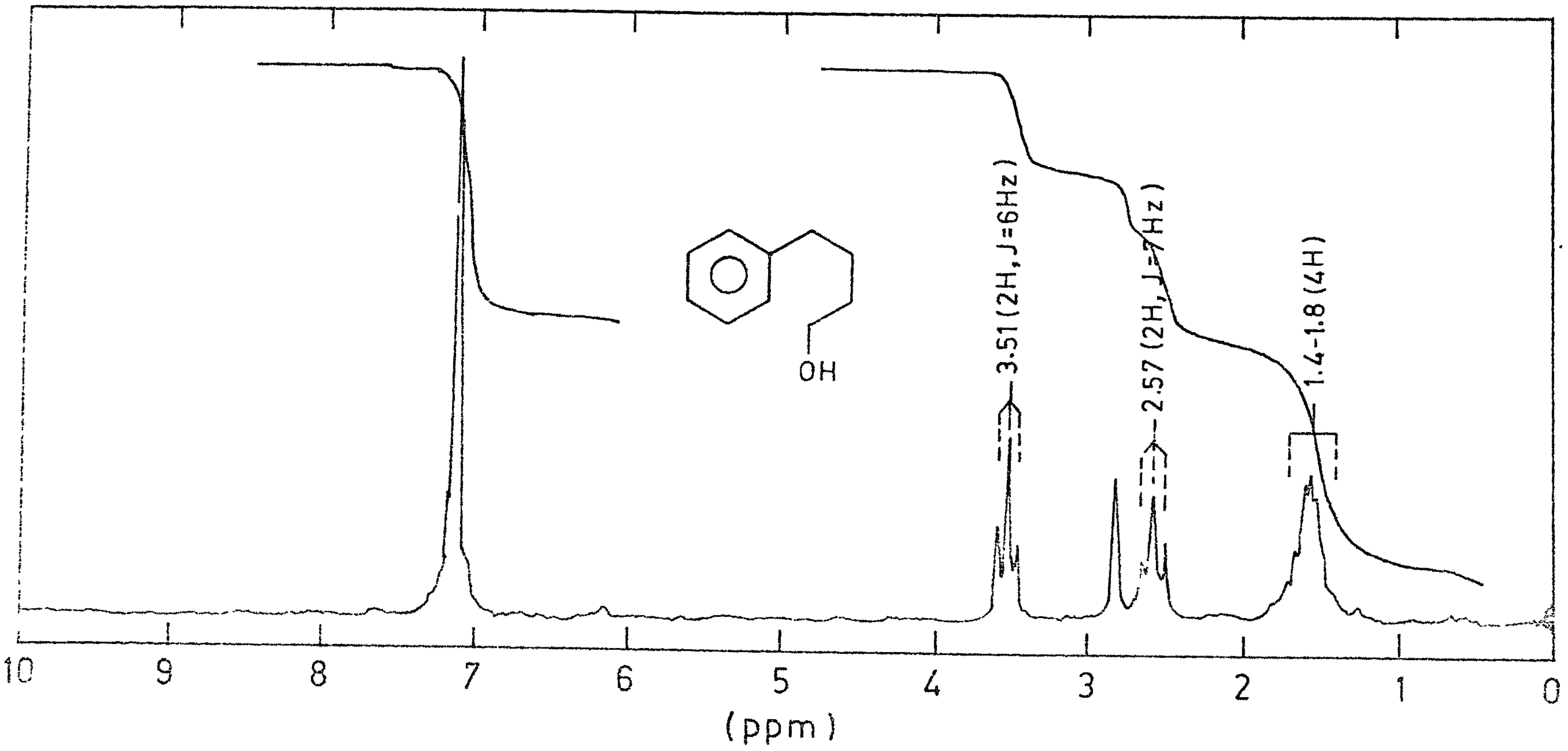
MS: m/e 210(M^+, 20 percent), 83(65.3 percent),54(100 percent), 41(61.2 percent).

Photoirradiation of 1-iodo-5-hexene

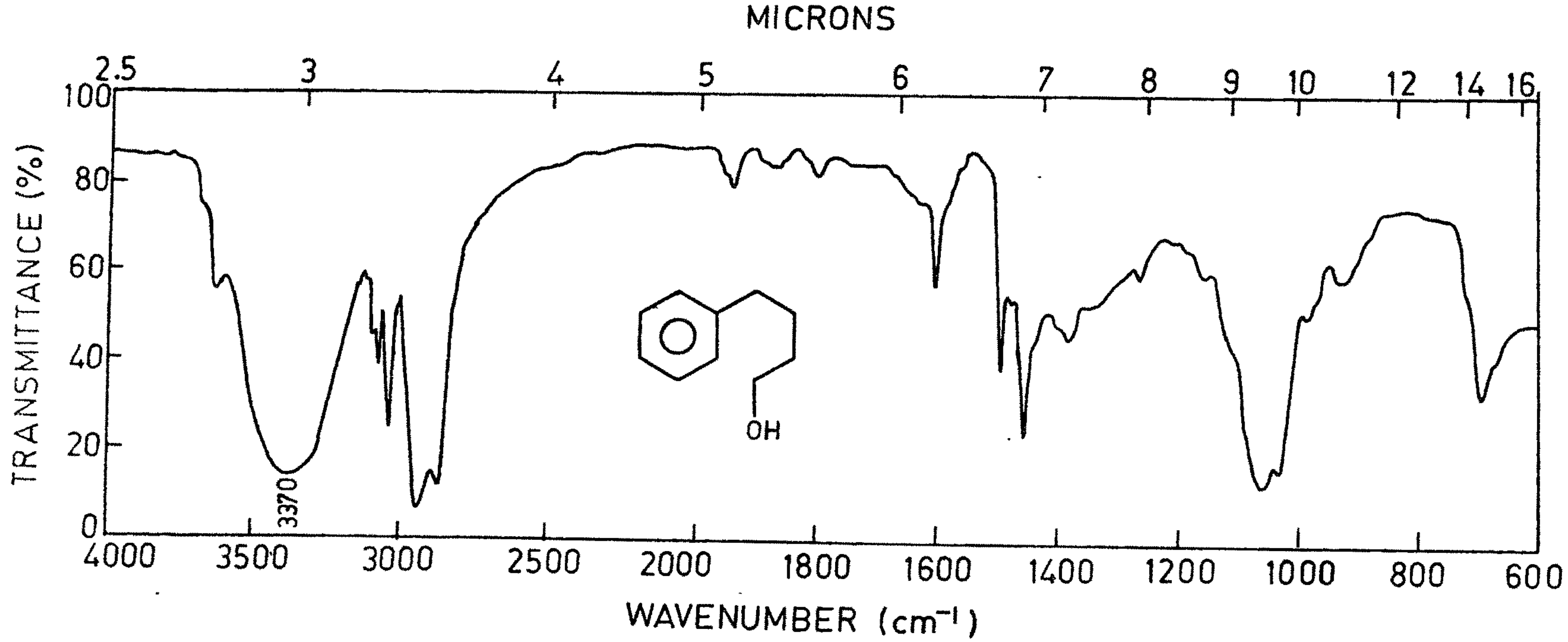
A soln. of 2.1 g(0.01 mole) 1-iodo-5-hexene and 1 g(0.01 mole) Et_3N in 210 ml THF was irradiated(see General Procedure) for 2 hrs. when TLC(solvent, pet. ether) shows no more starting material.

Work-up:- 20 cc of the above solution was dissolved in 40 cc dist. water. To this was added solid$(NH_4)_2SO_4$ in small portions with shaking till a small layer(~2 ml) is salted out (this must be done with care that the min. amt. of $(NH_4)_2SO_4$ is added). This layer was then removed with a fine dropper. Similarly two more portions of ~2 ml each were obtained and all the three portions combined. This was dissolved in water(10 ml) and extd. with xylene (2 ml). The xylene layer was separated and distilled over a water bath. The distillate obtained(~ 1 ml) was dissolved in 1 ml acetonitrile and extracted with 1 ml. pet. ether(b.p.120°). The pet. ether extract was again distd. on a water bath and the distillate(~0.6 ml) thus obtained was kept at ~4° for seven days when two layers separate. The upper layer is enriched in the reaction products(~70°) as per GLC(10 percent DEGS, 80°).

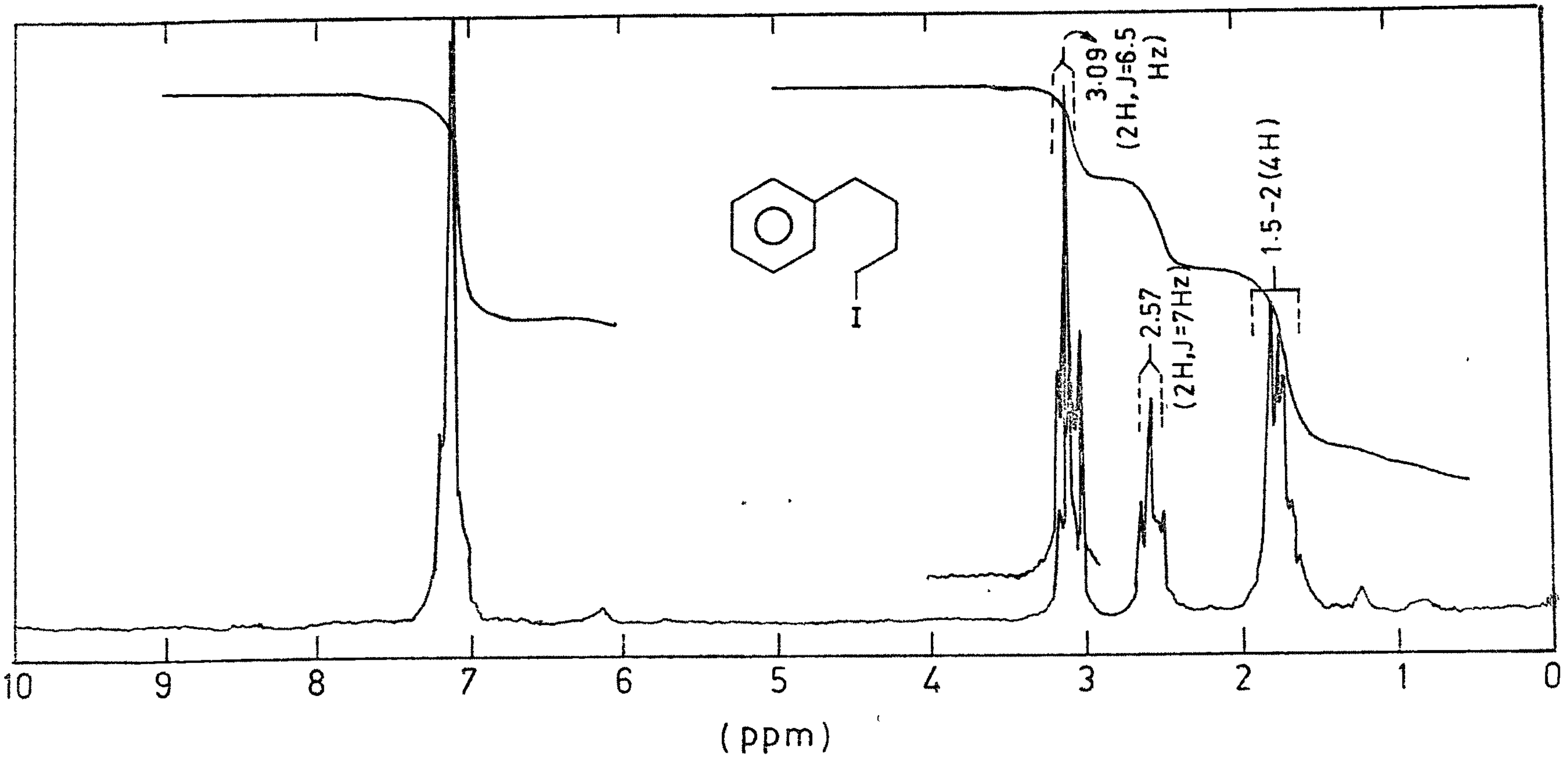
The produts were identified by mixed GLC with authentic samples on three columns(10 percent CW,10 percent DEGS and 10 percent DEGS-CuCl[39]; temp. 80°).



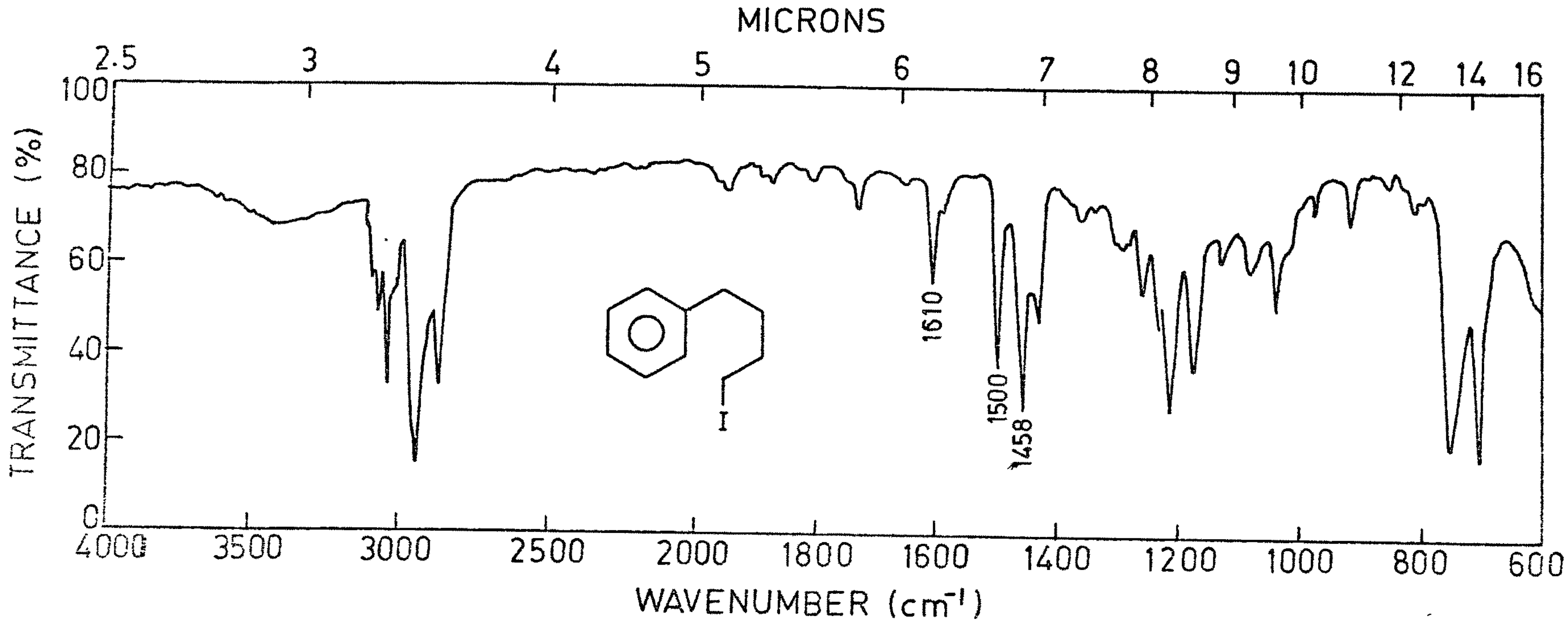
Sp.A.1a: PMR spectrum of 4-phenylbutan-1-ol



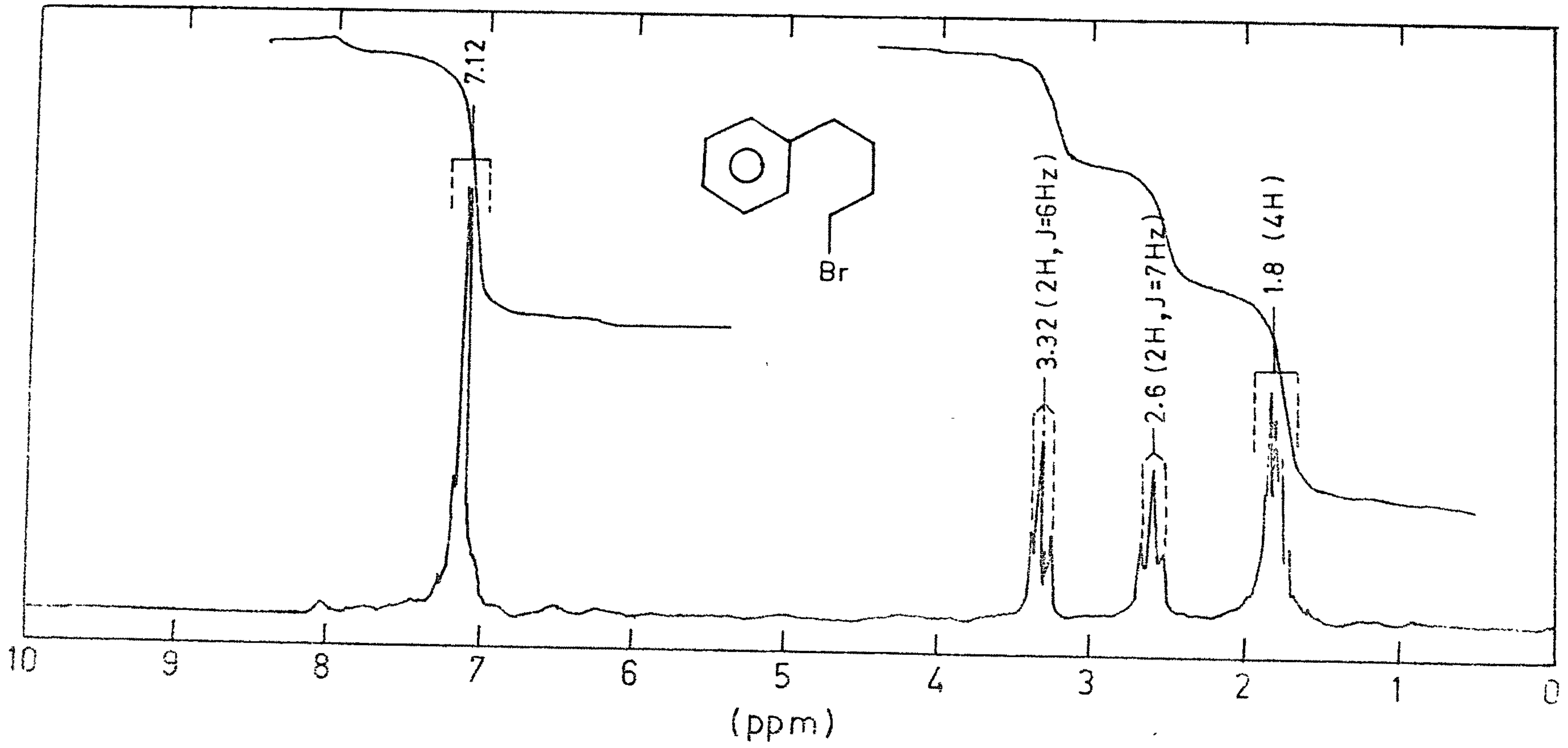
Sp.A.1b: IR spectrum of 4-Phenylbutan-1-ol



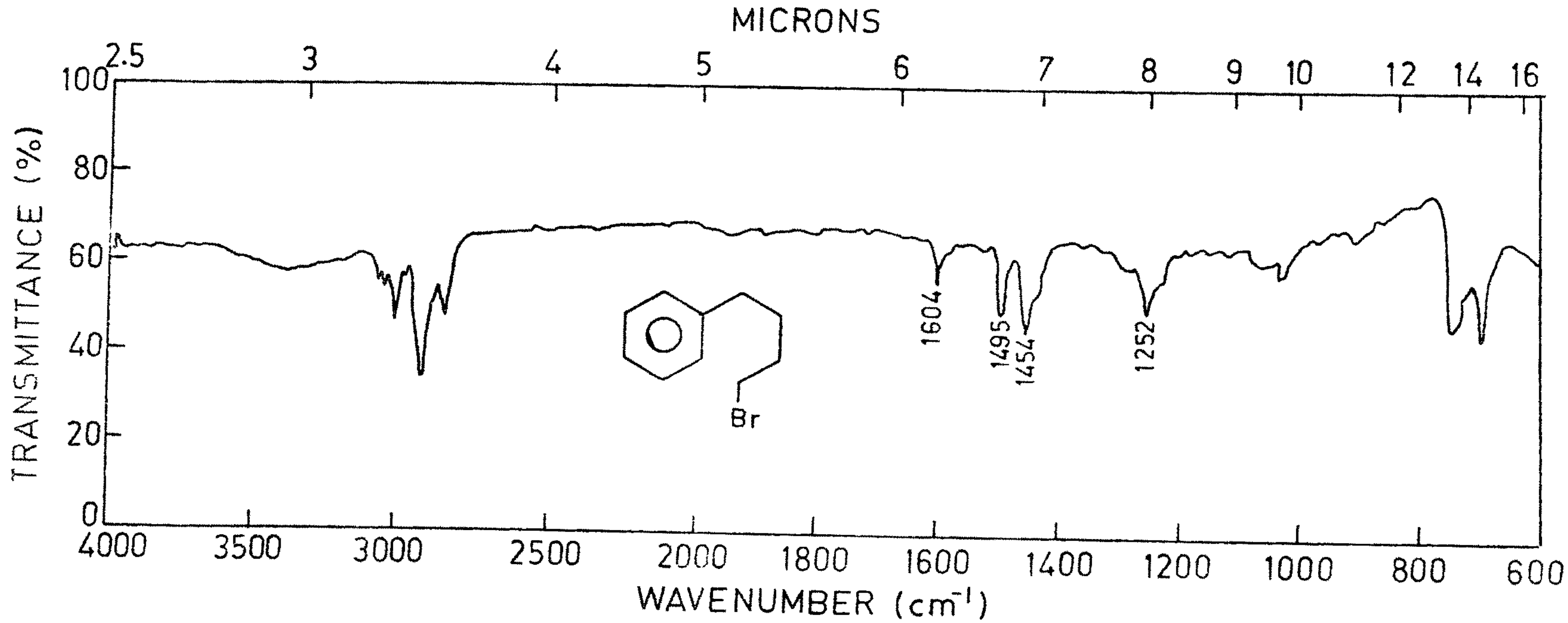
Sp.A.2a: PMR spectrum of 4-Phenyl-1-iodobutane(1)



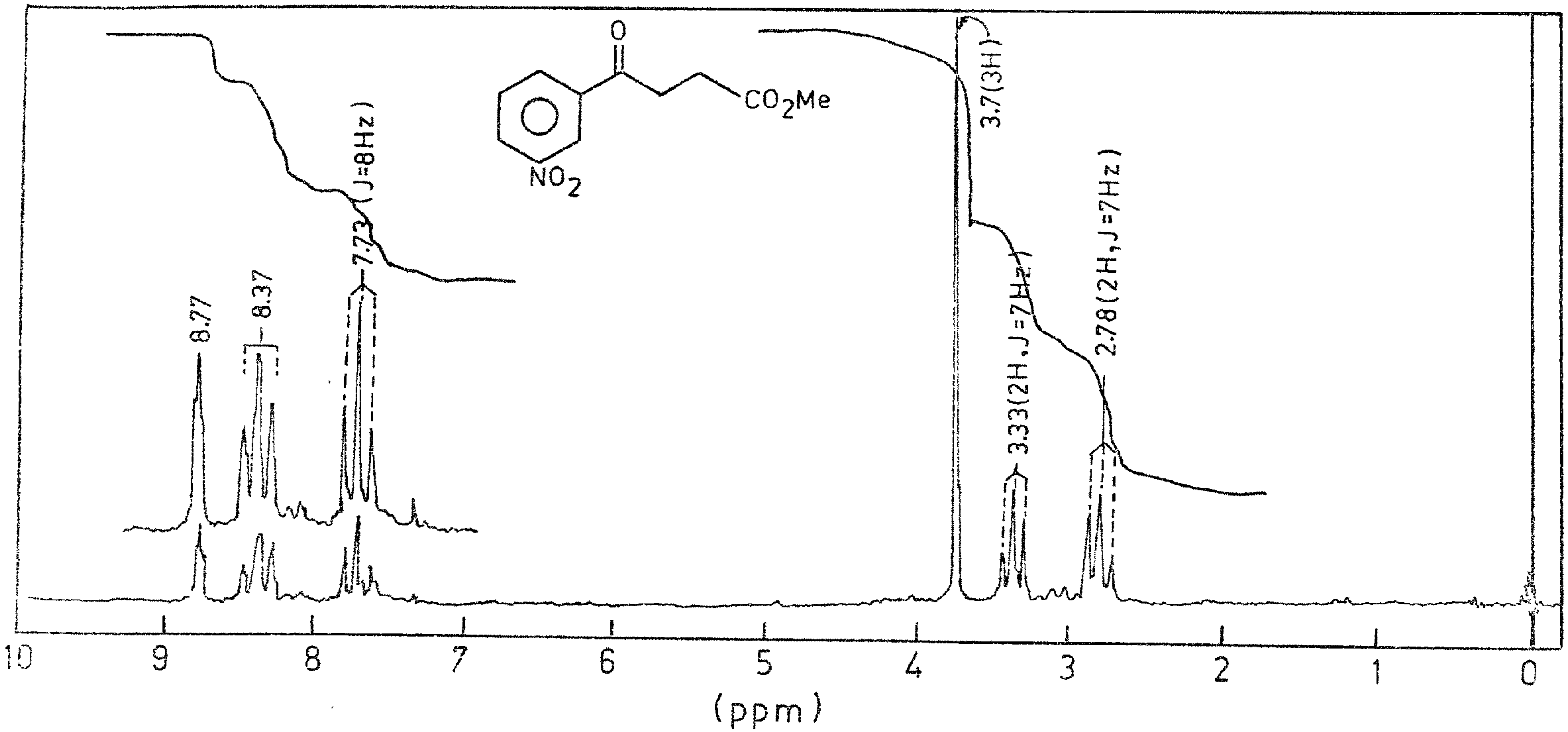
Sp.A.2b: IR spectrum of 4-Phenyl-1-iodobutane(1)



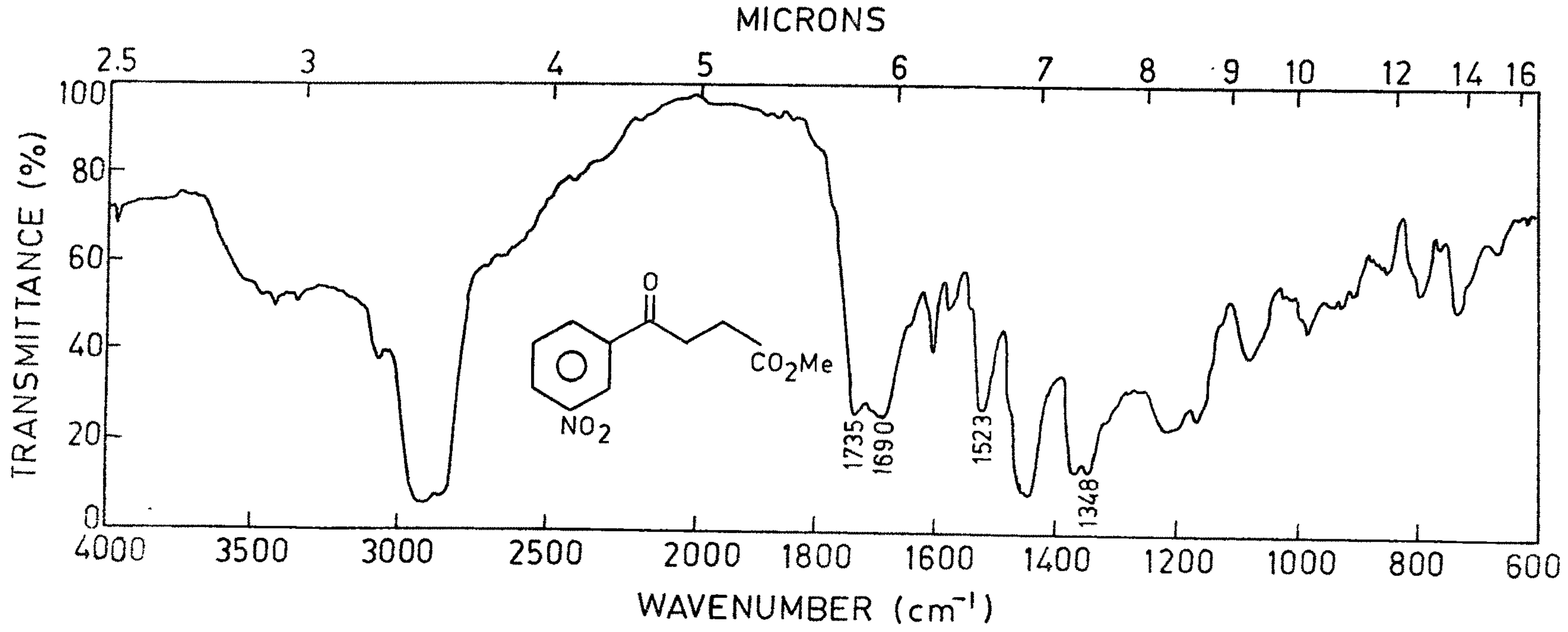
Sp.A.3a: PMR spectrum of 4-Phenyl-1-bromobutane



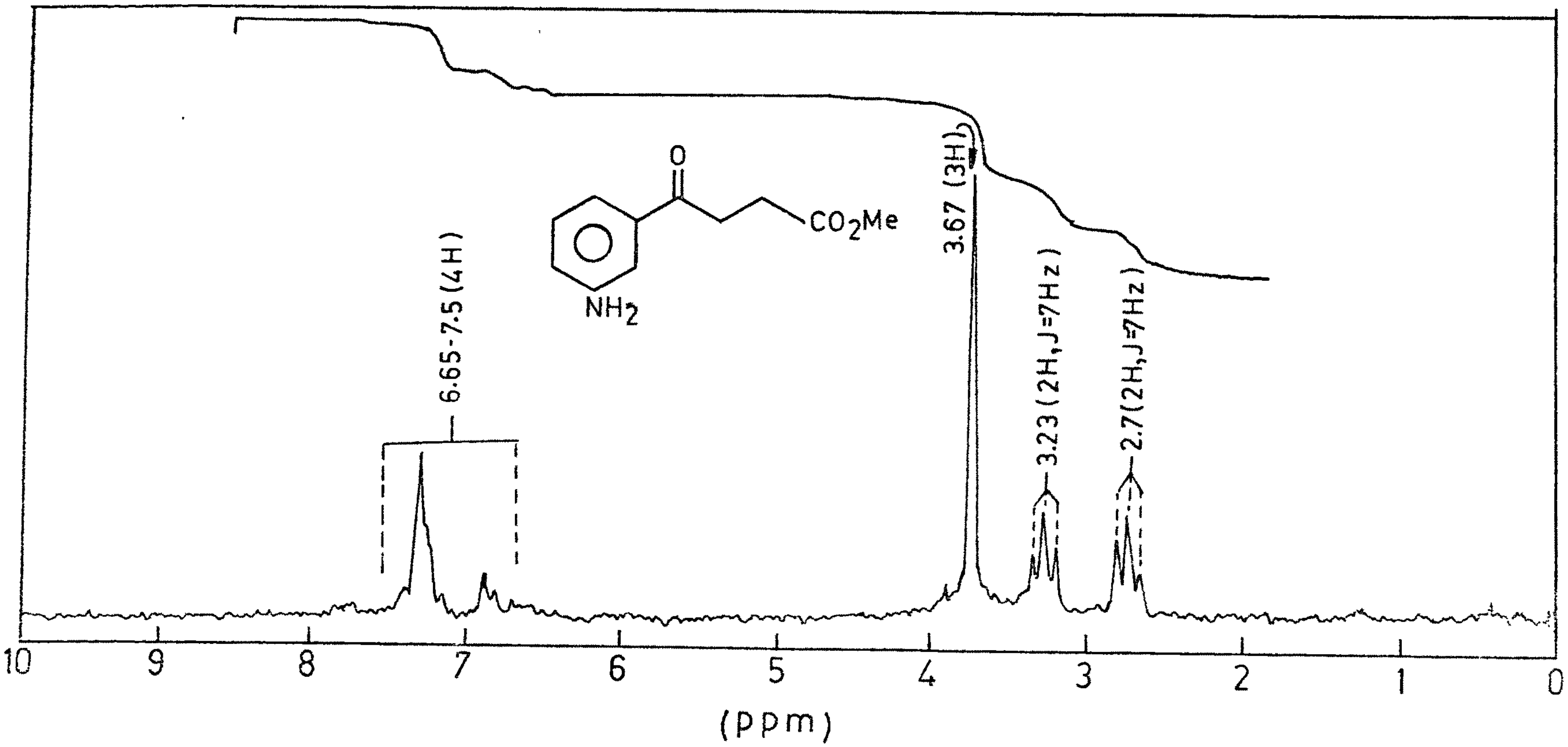
Sp.A.3b: IR spectrum of 4-phenyl-1-bromobutane



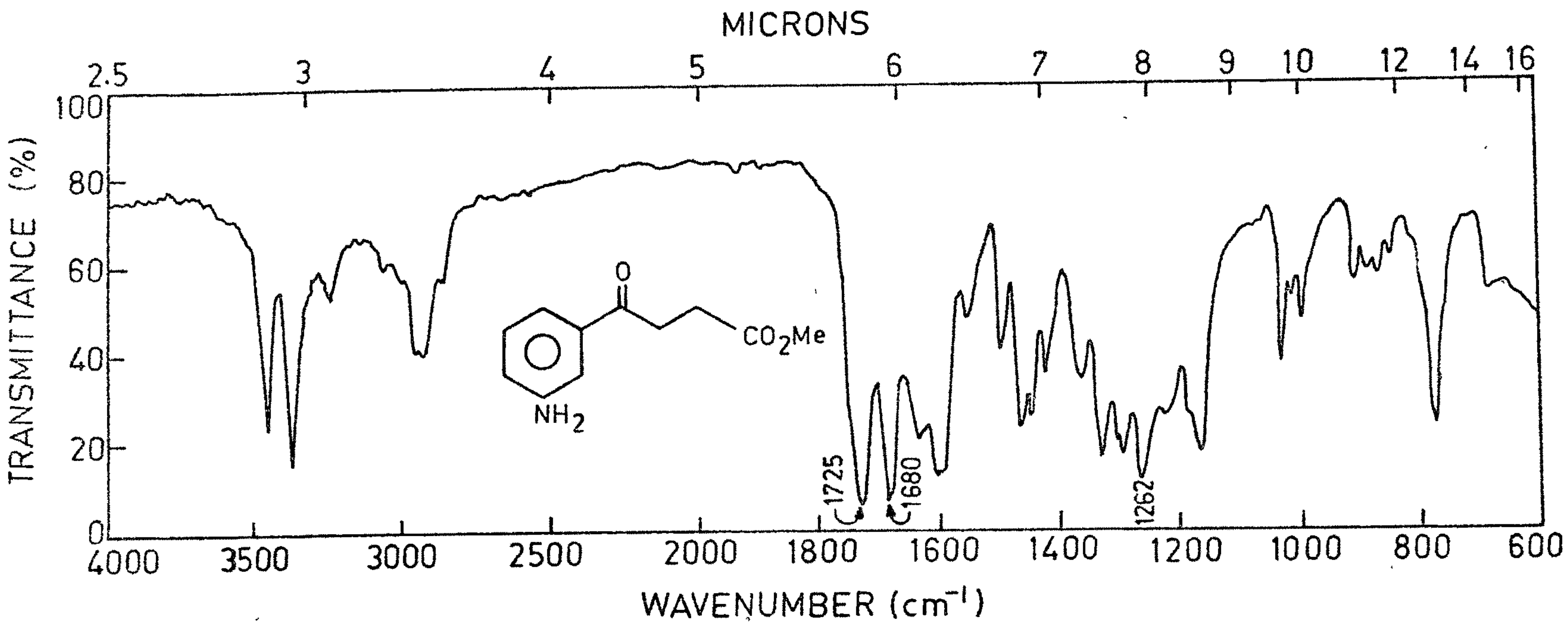
Sp.B.1a: PMR spectrum of Methyl-3-(m-nitrobenzoyl)-propionate



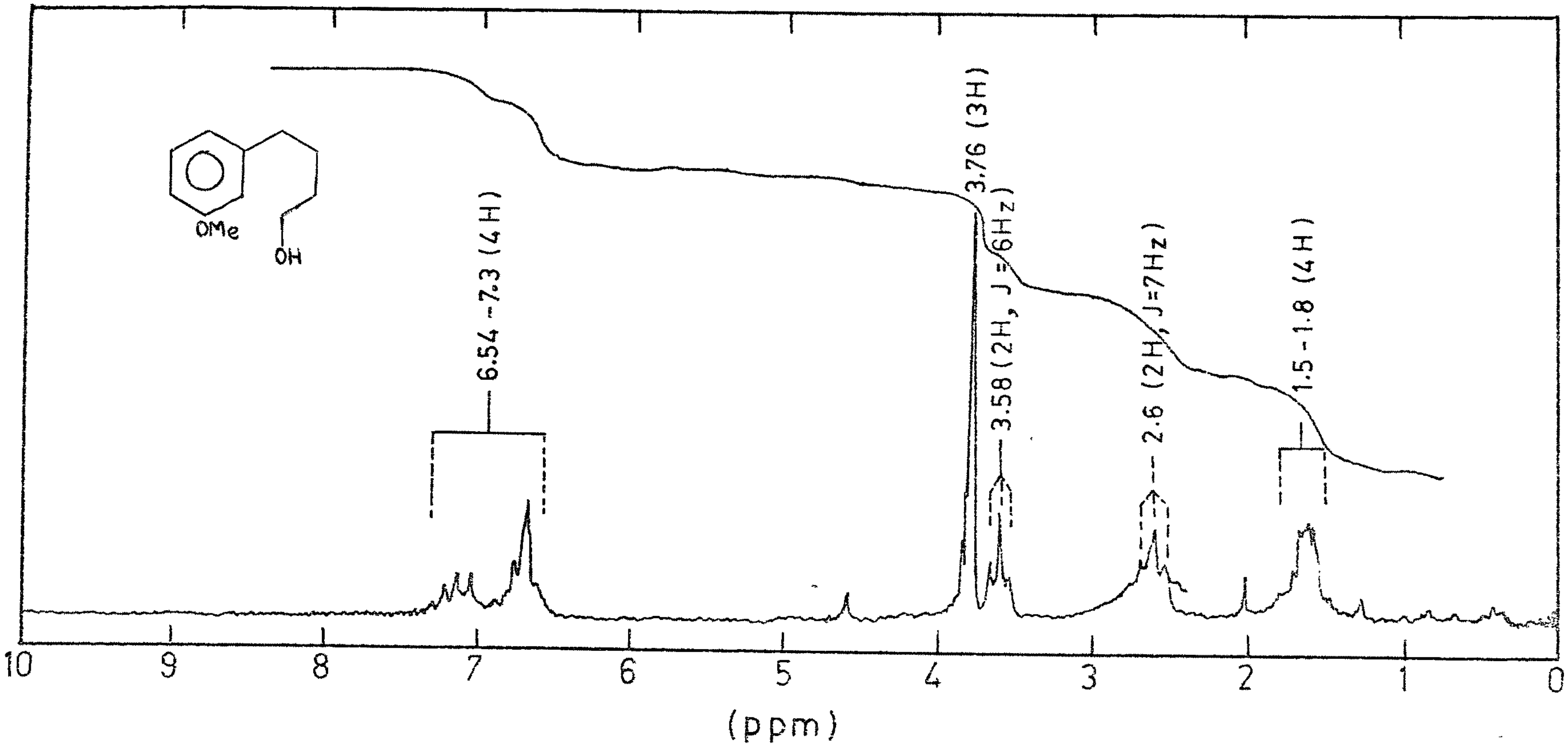
Sp.B.1b: IR spectrum of Methyl-3-(m-nitrobenzoyl)-propionate



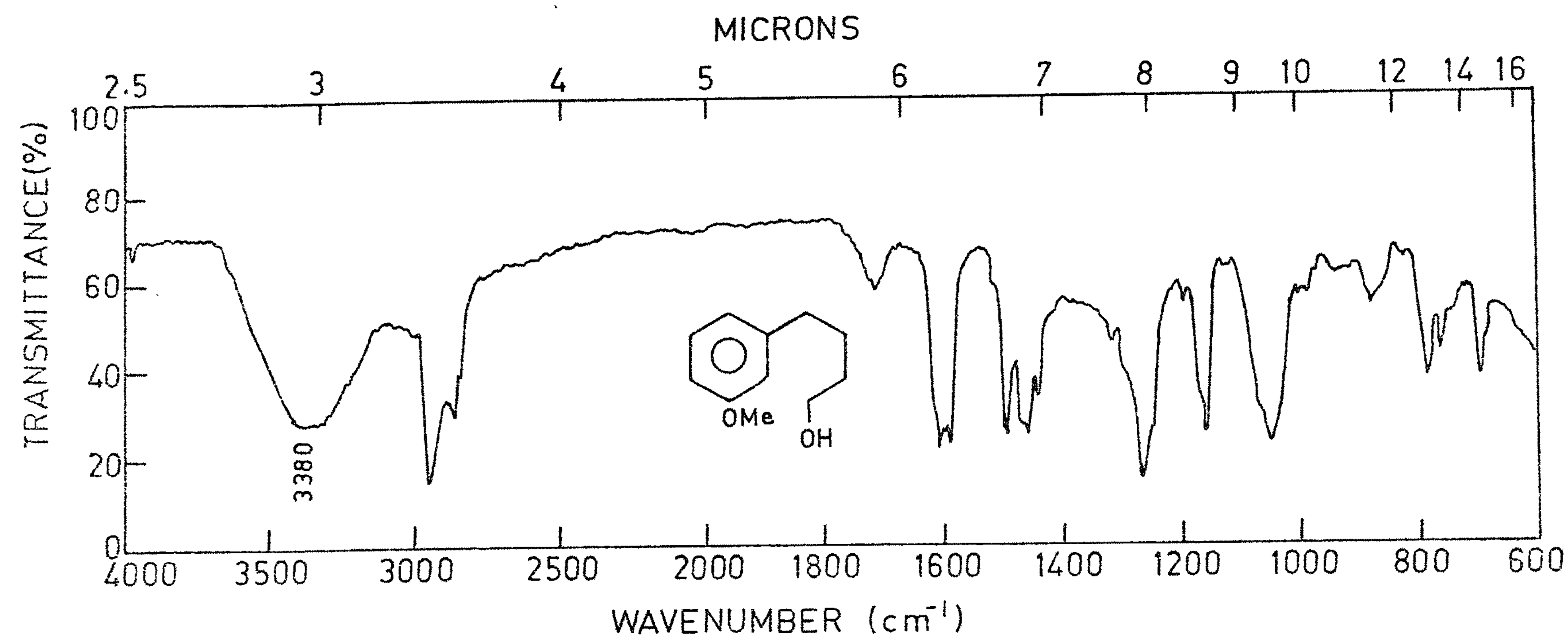
Sp.B.2a: PMR spectrum of Methyl-3-(m-aminobenzoyl)-propionate



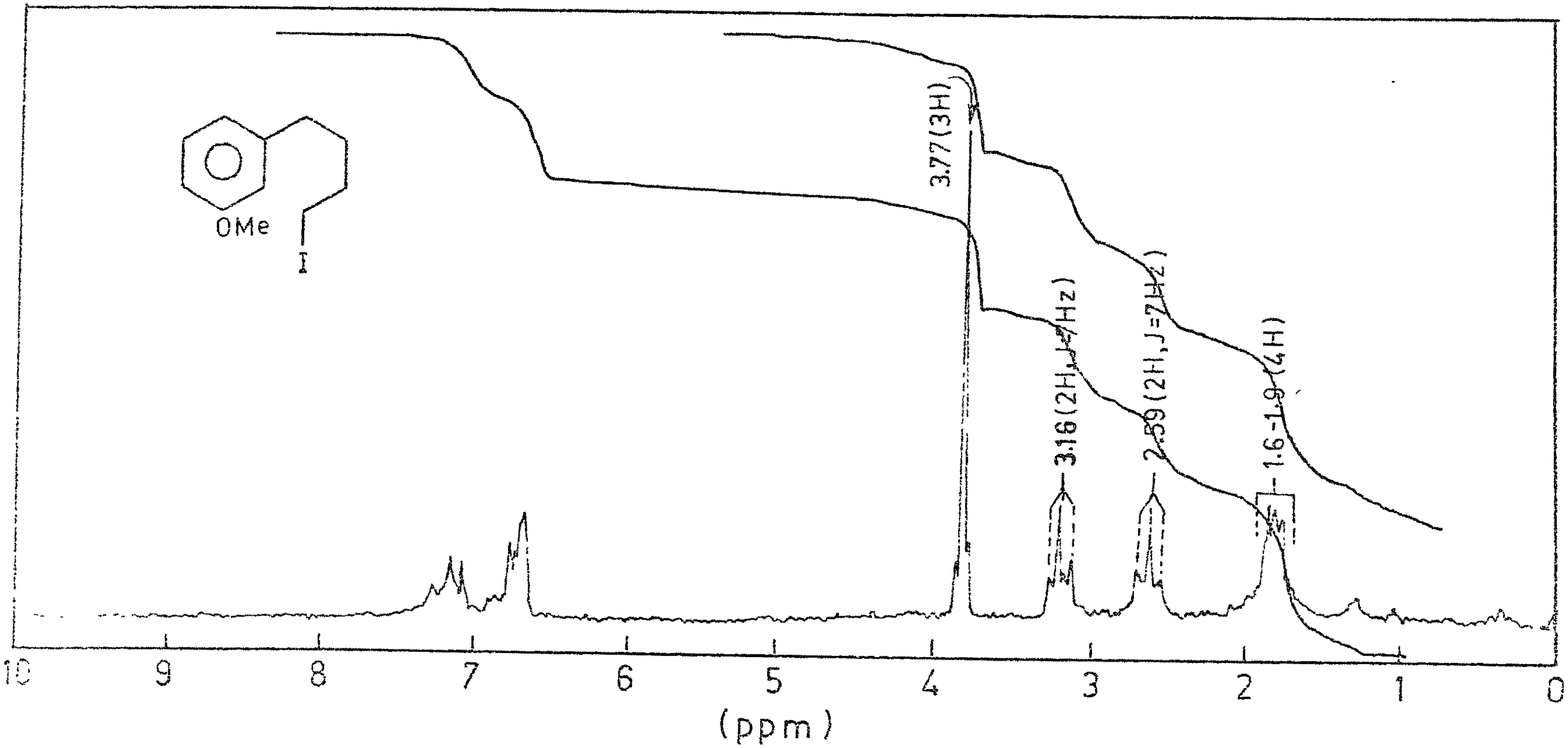
Sp.B.2b: IR spectrum of Methyl-3-(m-aminobenzoyl)-propionate



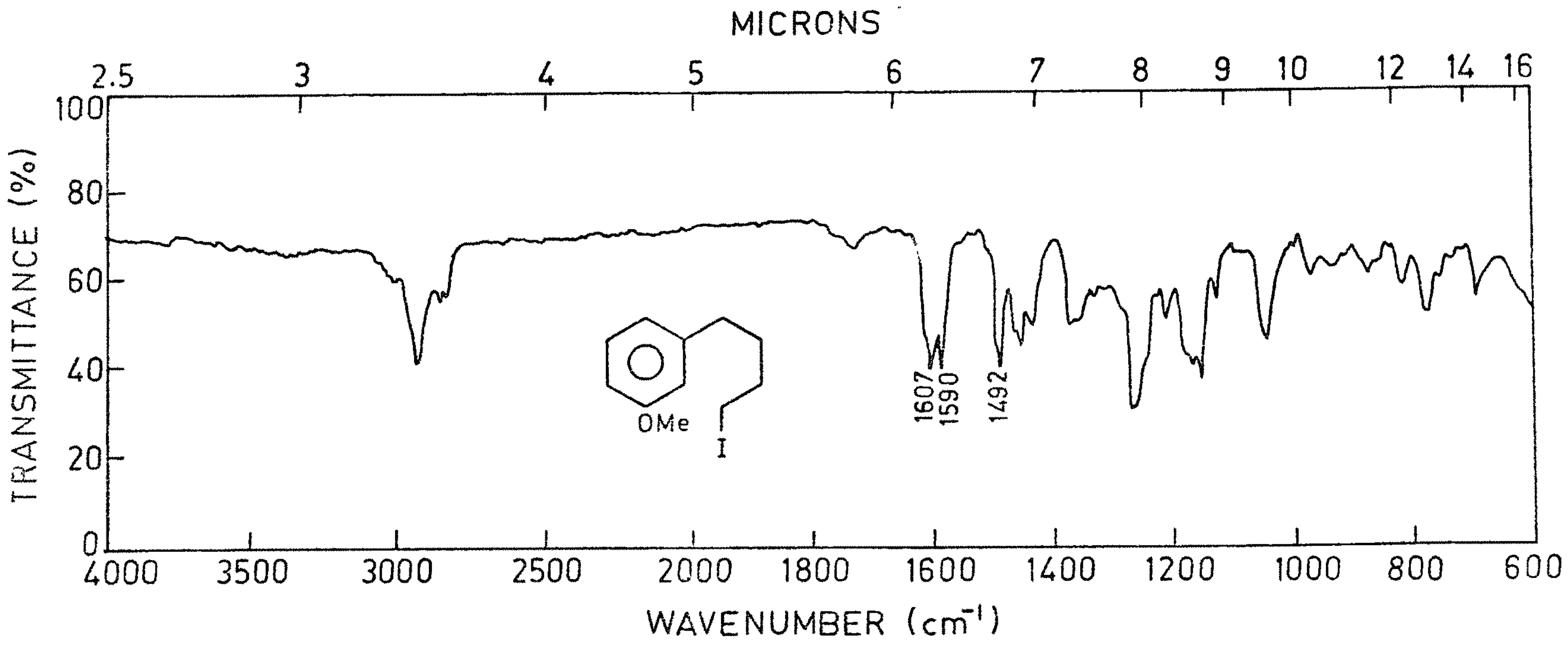
Sp.B.3a: PMR spectrum of 4-(m-methoxyphenyl)butane-1-ol



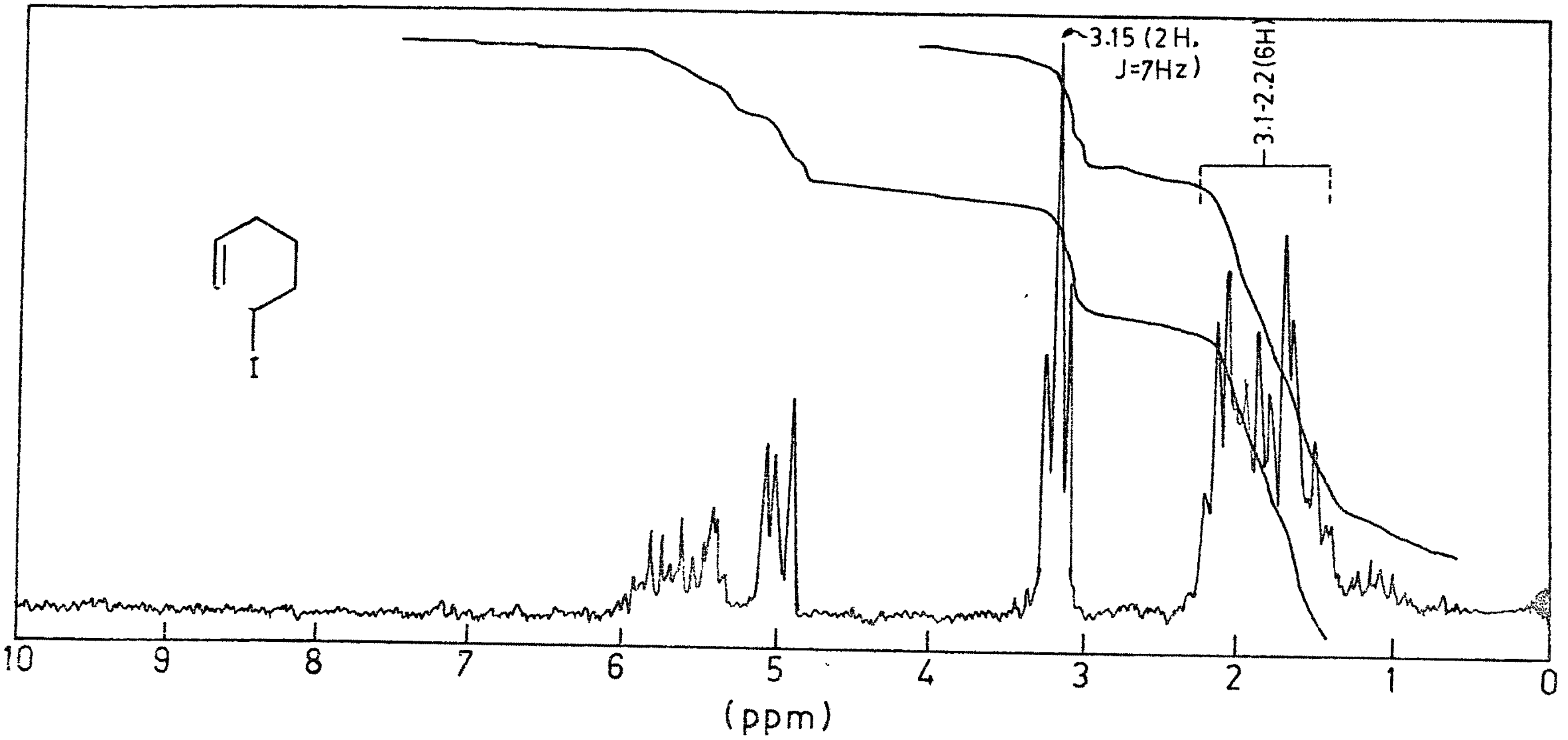
Sp. B.3b: IR spectrum of 4-(m-methoxyphenyl)butan-1-ol.



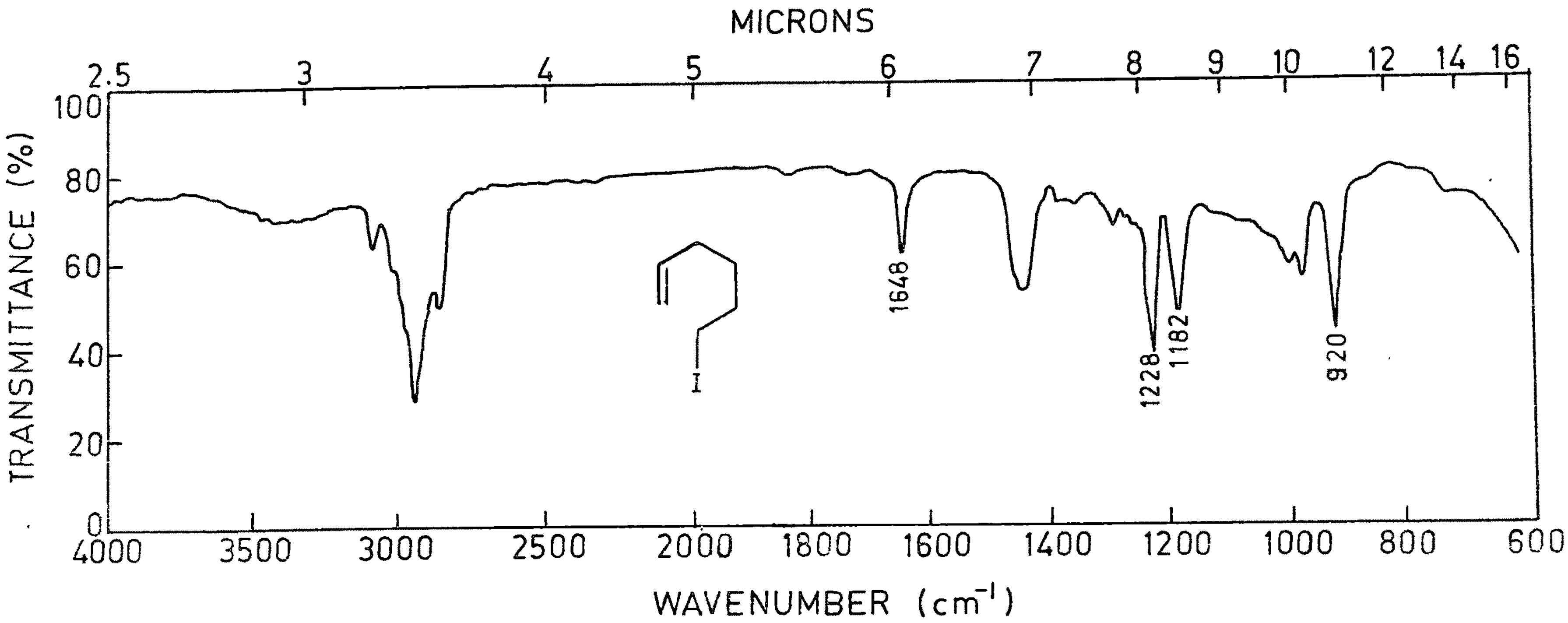
Sp.B.4a: PMR spectrum of 4-(m-methoxyphenyl)-1-iodobutane(5)



Sp.B.4b: IR spectrum of 4-(m-methoxyphenyl)-1-iodobutane(5)



Sp.D.1a: PMR spectrum of 1-Iodo-5-hexene(10)



Sp.D.1b: IR spectrum of 1-Iodo-5-hexene(10)

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