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THE OXIDATION OF PHENYLPROP-1-ENES

USING MERCURY (II) CHLORIDE

BY

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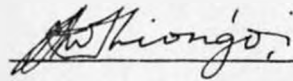
A thesis submitted in part fulfilment
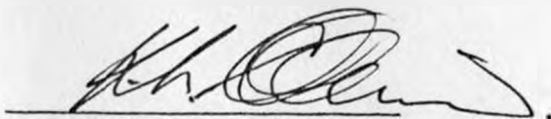for the Degree of Master of Science
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This thesis is my original work and has not been presented for a degree in any other University.
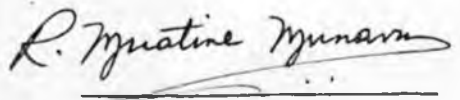
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Dedication

To my wife, Njeri Thuku, to our son
Thiong'o Thuku and to my mother,
Wangari Thiong'o.

ACKNOWLEDGEMENTS

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LIST OF ABBREVIATIONS

1.	DMF	Dimethylformamide
2.	THF	Tetrahydrofuran
3.	HMPT	Hexamethylphosphoric triamide
4.	Et_2O	Diethyl ether
5.	EtOH	ethanol
6.	DMSO	dimethyl sulphoxide
7.	$PrNH_2$	Propylamine
8.	$\bar{C}Hal_3$	Trihalomethyl Carbanion

ABSTRACT

The project consists of three sections: the synthesis of 3,4-methylenedioxyphenylprop-1-ene, the oxidation of phenylprop-1-enes using mercury (II) chloride and finally an attempt to follow the mechanism of this oxidation reaction.

Several methods were used in an attempt to synthesize 3,4-methylenedioxyphenylprop-1-ene and the route described below was ultimately successful.

3,4-Methylenedioxybenzaldehyde (piperonal)

3,4-Methylenedioxyphenylpropan-1-ol

3,4-Methylenedioxyphenyl-prop-1-ene (Isosafrole)
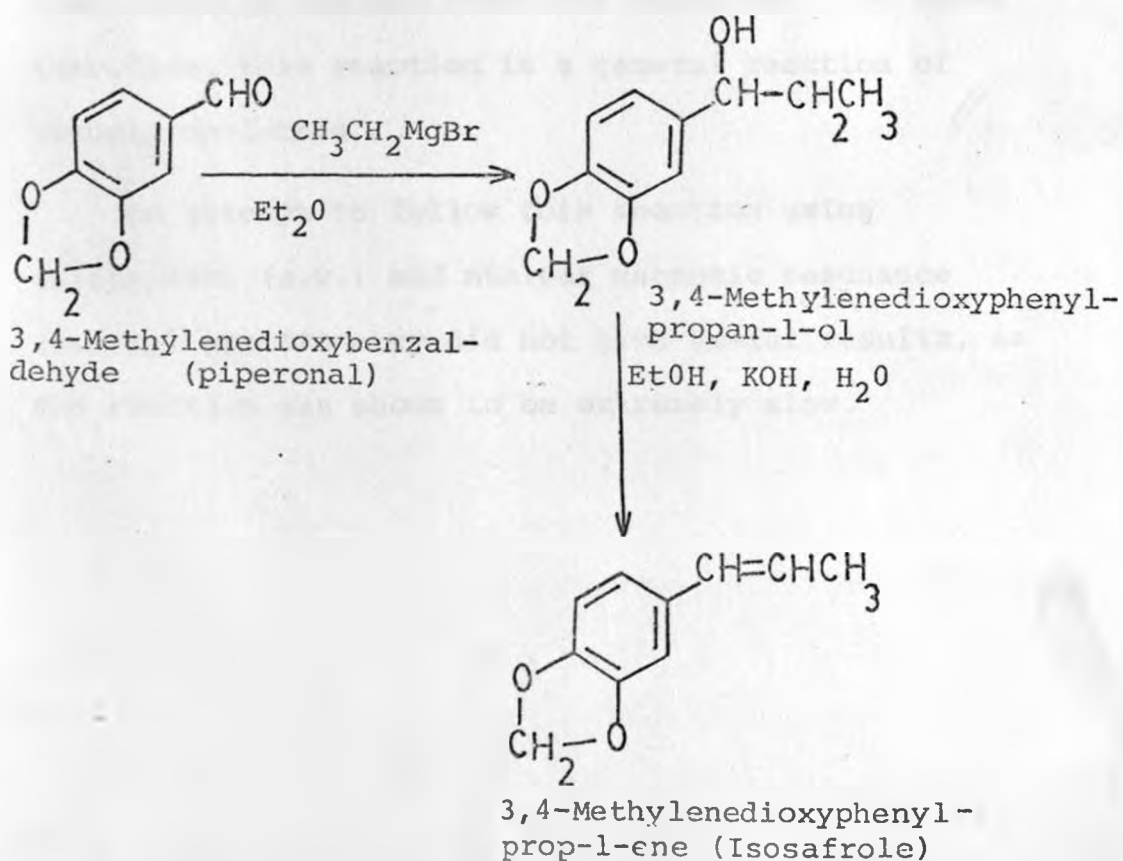
Five different phenylprop-1-enes were oxidized by mercury (II) chloride in a variety of solvents and the products of these reactions were investigated by thin layer chromatography. The products were shown to be the appropriate benzaldehyde, sometimes obtained as its corresponding acetal; and ethanal. In some cases, under the reaction conditions, further oxidation took place to form the corresponding carboxylic acid. The non conjugated phenylpropene, 3,4-methylenedioxyphenylprop-2-ene, did not undergo this reaction and was recovered unchanged. It seems, therefore, this reaction is a general reaction of phenylprop-1-enes.

An attempt to follow this reaction using ultraviolet (u.v.) and nuclear magnetic resonance (n.m.r.) spectrometry did not give useful results, as the reaction was shown to be extremely slow.

CHAPTER ONE

1.0 PREVIOUS WORK IN THE FIELD

As early as 1830, Zeise[1] isolated the first
addition compound of an olefin and a metal. This
compound analysed for $KCl.PtCl_2.C_2H_4$ and it was soon
followed by many similar but less stable compounds
involving metals such as palladium, silver and copper.
These compounds are now regarded as true co-ordination
complexes, the olefin occupying one place in the
co-ordination sphere of the metal and acting as if it
had a lone pair of electrons to donate to the metal.
Understandably, the compounds are much less stable than
the ammine complexes, which are able to donate a lone
pair of electrons.[2]

The first report, of a study of organomercury
compounds, was made in 1852 by Frankland.[3] Dialkyl-
mercurials (R_2Hg; R = alkyl), were prepared in 1858
and in 1870, Dreher and Otto prepared arylmercurials.[3]
In 1892 Kucherov reported, that mercuric salts were
able to add to olefins, however, the subject was not
really developed until 1900-1908, when Hofman and Sand
described the conditions necessary for the formation
and isolation of oxymercury adducts.[5] Hofman and Sand
recognised the compounds to be of two distinct types
but could not decide if the compounds were coordination
complexes or true addition compounds. Adams and Mills,[6]

were finally able to show, that these compounds were addition compounds and this observation, was later confirmed by nuclear magnetic resonance (n.m.r.) studies.

The first paper concerned with the (n.m.r.) spectra of an organomercury compound was published by Cotton and Leto[7] in 1958 and dealt with hydroxy- and methoxy-mercury derivatives.

Cotton and Leto investigated proton magnetic resonance spectra (p.m.r.) of $CH_3OCH_2CH_2HgOCOCH_3$ and $HCCH_2CH_2HgOH$ in tetrachloromethane and basic deuterated water consecutively. From the chemical shifts, peak area ratios and spin-spin hyperfine coupling, they were able to conclude that the addition of HgX_2 across the double bond, gives σ-bonded organomercury compounds, rather than π-complexes of mercury salts with olefins. These conclusions were verified in papers reported by Brownstein,[8] Wells and Kitching[9] and Kiefer et al.[10] Verification was done by observation of proton-mercury spin-spin coupling in molecules.

In the early part of this century, organomercurials started to be used as fungicides and since then an enormous number of compounds containing mercury-carbon bonds has been prepared, largely in the hope of finding substances of pharmacological value.[11] It is also important to point out, that mercury poisoning was recognised as early as 1865[4] and today extensive studies of mercury toxicology and the environmental

chemistry of organomercurials, continues to be an important active research area.

Mercury-carbon bonds are formed with significantly greater ease, than bonds of many metals and carbon. The essential feature is that, once formed, mercury-carbon bonds tend to remain intact, whereas, organometallic compounds are distinguished by high-sometimes strikingly high reactivity. The bond is highly covalent (1.9 on the Pauling Scale), it is polarizable (with carbon assuming a limited carbanion character); however, the intrinsic nucleophilicity is low. Hence unactivated carbon-mercury bonds are generally unreactive towards typical organic electrophiles such as, alkylhalides, carbonyl compounds and epoxides.

Most organomercurials are stable to water and alcohols. Primary alkylmercurials and arylmercurials are essentially unreactive towards oxygen, however, secondary and tertiary alkyl, allyl, and benzyl derivatives, do react and care should be taken with these compounds to avoid prolonged contact with air.

For RHg-X, where X is an electronegative group such as ClO_4^- , NO_3^- , ionic compounds result, which have an appreciable solubility in water and polar solvents but little solubility in hydrocarbons. The Hg-X bond becomes more polar in polar solvents and if the alkyl group present is electronegative. Solvents

which have the ability to stabilize cations by solvation also increase the polarity. Diorganomercurials R_2Hg will act as electron acceptors only if R is very electronegative.[12]

Highly polarizable Hg-X bonds are good electrophiles and can interact with electron-rich organics such as alkynes and alkenes.[12]

1.1   OXIDATION STATES

Mercury shows +2 and +1 oxidation states but +2 is more developed, however, mercury (I) σ-bonded compounds of the constitution, R-HgHg-R have been frequently cited as short-lived species in electro-chemical reductions at mercury surfaces.[13] A report[14] that di-n-hexyldimercury, was produced by electrochemical reduction, was regarded with some scepticism, since a subsequent study suggested polymeric mercury (II) products could have been formed from similar reactions.[15]

There is good evidence for σ-bonded organo-mercury (I) derivatives of ketenes.[16] Ketene derivatives of mercury II, have also been obtained.

Mercury (I) ketenides are involatile, infusible, and insoluble solids in common solvents and as such, have been difficult to characterise, except by infrared and Raman spectroscopy.

Mercurous ion $[Hg_2]^{2+}$ is not particularly stable, it shows a strong tendency to disproportionate, to yield metallic mercury and mercuric compounds. This explains the fact that the mercurous chloride, bromide and iodide darken on exposure to light, with the production of mercury.[17] The electrode potentials predict a spontaneous process for the mercurous ion disproportioning into mercury and mercuric ion. i.e.

$$Hg^{2+} + 2e^- \longrightarrow Hg^o \qquad - 0.85V \qquad (1)$$

$$2Hg^{2+} + 2e^- \longrightarrow Hg_2^{2+} \qquad - 0.92V \qquad (2)$$

$$Hg_2^{2+} \rightleftharpoons Hg + Hg^{2+} \qquad + 0.1150V$$
$$\text{at } 25^oC \qquad (3)$$
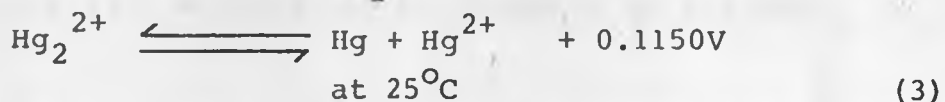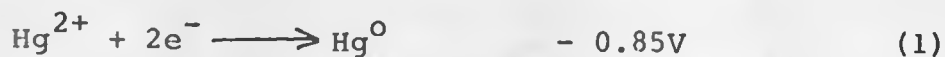
1.2 ORGANIC CHEMISTRY OF MERCURY (II)

The organic chemistry of mercury (II) is expected to be similar to that of thallium (III) and lead (IV) since they are isoelectronic and neighbours in the Periodic Table. Mercury (II) reactions produce stable organomercury compounds unlike thallium (III) and lead (IV). This is shown, by the fact that, very few oxythallation and no oxylead adducts have been isolated and characterised.

Generally mercury (II) is less reactive than thallium (III) and lead (IV), however, thallium (III) is more selective in its reactions than mercury (II)

and lead (IV). Grinstead[18] has reported that
thallium (III), mercury (II), and lead (IV) may undergo
some reactions in a similar manner.

In glacial ethanoic acid, for example,
mercury (II) chloride undergoes the following reaction
with ethene:-

$$C_2H_4 + Hg(OAc)_2 \longrightarrow AcOC_2H_4HgOAc \qquad (4)$$
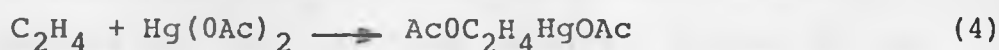
However, the reaction of pent-2-ene with
mercury (II) nitrate may be effected as follows:

$$CH_3CH = CHC_2H_5 + 2Hg^{2+} \longrightarrow CH_3COC_3H_7 + 2Hg^+ + 2H^+$$
$$\sim 2M \qquad\qquad\qquad (5)$$
$$\text{nitric acid}$$
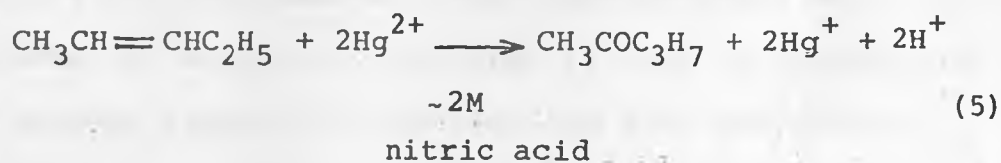
This oxidation is possible with lead (IV) and in
addition to the carbonyl compounds glycol derivatives
are also formed. The reaction with thallium (III)
also produced both carbonyl and glycol derivatives
according to the following reactions:-

$$RCH = CHR' + Tl^{+++} + 2H_2O \rightarrow RCH(OH)CH(OH)R' +$$
$$Tl^0 + 2H^+ \qquad (6)$$
$$RCH = CHR' + Tl^{+++} + 2H_2O \rightarrow RCOCH_2R' + Tl^+ + 2H^+ \qquad (7)$$
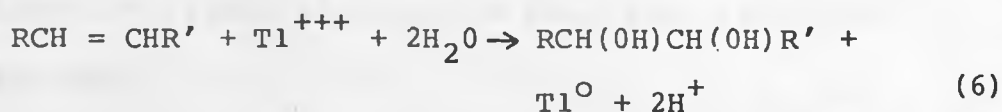
The organic chemistry of mercury (II) bears little resemblance to that of zinc and cadmium which are elements of the same group of the Periodic Table. Mercury-carbon bonds are less reactive and in particular are generally inert towards oxygen and water,[19] however, zinc, cadmium and mercury are similar, in that they form volatile, covalent organometallic compounds and that the bond is simply formed by the metal and the organic group; each contributing an electron.[20] All the three elements are of great importance in synthetic organic chemistry; in particular, zinc is used extensively in the Simmons-Smith and Reformatsky reactions. Cadmium is used in preparation of ketones from acid chlorides and acid anhydrides.

1.3 GENERAL FORMATION OF σ-BONDED ORGANOMERCURIALS

The principal methods for making organo-mercurials are based upon the electrophilic behavior of mercuric salts in substitution reactions (such as: transmetallation, mercurideprotonation) or addition reactions (such as oxymercuration). Thermal and radical initiated elimination reactions have also been used.

1.3.1   TRANSMETALLATION

The general reactions are given in the
equations below:-

$$R - M + HgX_2 \longrightarrow RHgX + MX \qquad (8)$$

$$R' - M + RHgX \longrightarrow RHgR' + MX \qquad (9)$$
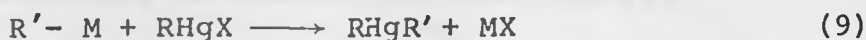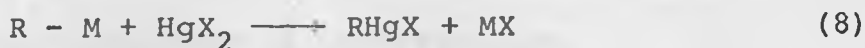
The transfer of an organic group from another
metal, to mercury (II) atom has been and is still used
in the synthesis of a number of organomercurials. A
variety of organometallic compounds have been employed,
including those of the electropositive alkali metals,
especially those of lithium, magnesium, zinc and
aluminium. Organometallic compounds of boron, the
Group IV B metals, arsenic, antimony and bismuth have
also been used. In addition, σ-bonded organotransition
metal compounds, such as, those of gold, silver,
chromium, manganese, iron, tungsten, and cobalt, can
transfer organic groups to mercury. Not all of these
reactions have synthetic value and the study of
transmetallations have often been made for other
reasons, for example, the biological importance of the
transfer of the metal group from primary alkyl cobaloximes
and vitamin B_{12} occurs readily and is relevant to
methyl-mercury pollution of the environment.[21]

Organolithium and organomagnesium compounds have extensive use in reactions with mercury salts, especially the halides, although this is limited by the range of available organolithium and magnesium species. The transfer from lithium and magnesium proceeds with retention of configuration.

The mechanism is bimolecular electrophilic substitution (S_E2) which involves a frontal attack of mercury salt on the alkyl-metal bond and hence leads to retention of configuration, unless steric hindrance prevents this.

It is important to point that symmetrization of alkylmercury salts can be regarded as a special case of transmetallation, where the organometallic reagent and the mercury derivative happen to be the same thus:-

$$2RHgX \longrightarrow R_2Hg + HgX_2 \qquad (10)$$

The reaction usually requires a catalyst such as zinc and Lewis acid.[22]

1.3.2 MERCURATION

This is replacement of hydrogen by mercury in aliphatic aromatic and heterocyclic compounds and in general, may be represented by equation (11), but obtaining R_2Hg requires rather forcing conditions.

$$RH + HgX_2 \xrightarrow{\quad -HX \quad} RHgX \xrightarrow[\quad -HX \quad]{\quad +RH \quad} R_2Hg \qquad (11)$$

For aliphatic compounds this reaction is generally limited to hydrocarbons, that contain acidic hydrogens activated by groups such as, ethyne, cyano, diazo, carbonyl, sulphonyl, phosphonyl and halide.

Cyclopentadiene can be both mercurated and polymercurated i.e.

$$(12)$$

$$(13)$$
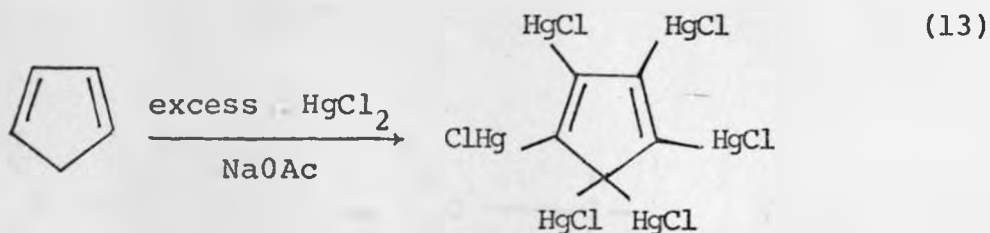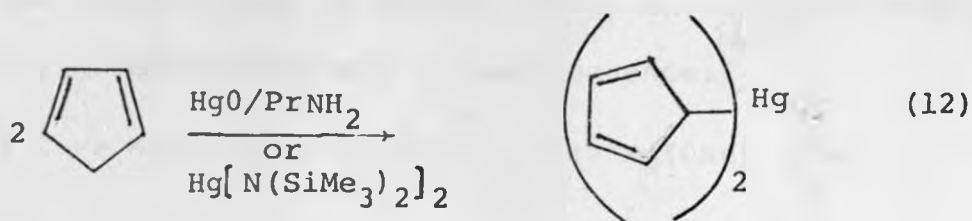
Substitution by halogens, particularly poly-halogens, enhances the activity of the remaining hydrogens and indeed mercuration of polyhalohydrocarbons such as C_5Cl_5H or HCX_3 proceeds particularly readily under basic conditions.

Mercuration of alkenes takes place but in general, reaction of alkenes with mercury salts frequently leads to solvomercuration. A few examples of vinylmercuration are known, for example, the use of ionic mercury salts containing weakly nucleophilic anions (BF_4^- or NO_3^-) in methylcyanide or benzene solution, resulted in vinylmercuration of 1,1-diarylethenes (see scheme 1). Some dimercuration to give $ArAr'C = C(HgX)_2$ also occurred.[23]

The reactivities of mercury salts in vinylmercuration of diarylethenes decreased in the sequence:[149]

$Hg(BF_4)_2 \gg Hg(NO_3)_2 > Hg(OCOCF_3)2 \gg Hg(OAc)_2$, $HgCl_2$, $HgBr_2$.

<u>Scheme 1</u>

ArAr'CYCH$_2$HgX

Solvomercuration

ArAr'C = CHHgX

Z and E
isomers
Vinylmercuration
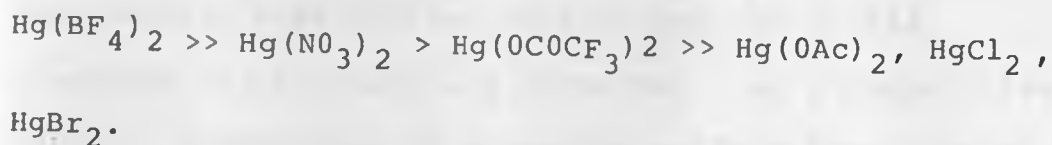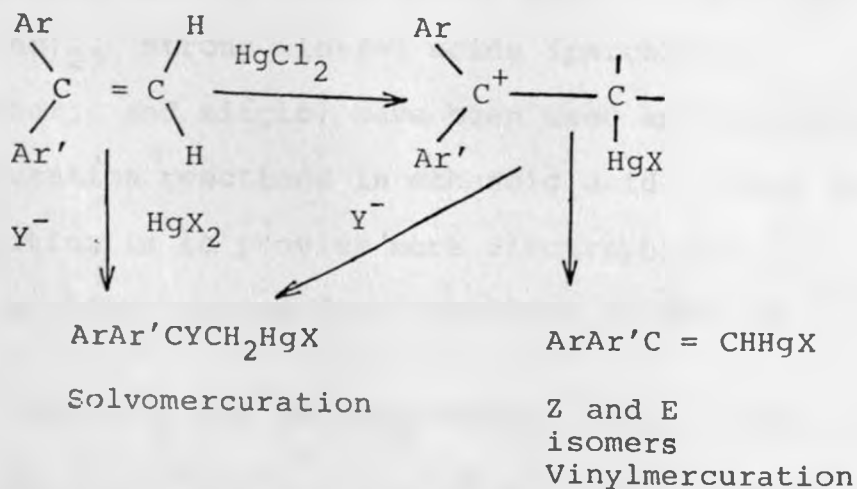
Apparently vinylmercuration does not proceed for alkenes containing three substituents at the alkene centre, for example, for $Ph_2C = CHBr$ or $Ph_2C = CHPh$. Again whether solvomercuration or vinylmercuration occurs depends on nucleophilicity of the medium and in some cases, both may occur.[149]

Mercuration proceeds for most aromatic compounds whether they are polycyclic aromatic or hetero-aromatic species or transition metal complexes, such as ferrocene and cyclobutadiene iron. This has become increasingly important as a synthetic method due to the general ease of the reaction and the facile cleavage of the resulting mercurial. As a preparative method, mercuration of aromatics suffers from lack of selectivity and frequently all possible ring substitution products occur. Extensive studies[24,25] have been made of reactions in ethanoic acid using $Hg(OAc)_2$. Strong mineral acids (perchloric, sulphuric and nitric) have been used as catalysts in mercuration reactions in ethanoic acid. Their mode of action is to provide more electrophilic mercurating species (see equations 14 and 15).

$$Hg(OAc)_2 + H^+ClO_4^- \rightleftharpoons [HgOAc]^+ ClO_4^- + HOAc \qquad (14)$$

$$[Hg(OAc)]^+ ClO_4^- + H^+ClO_4^- \rightleftharpoons Hg^{++} 2ClO_4^- + HOAc \qquad (15)$$
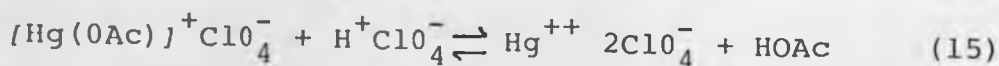
1.3.3.   BY DECOMPOSITION OF MERCURY CARBOXYLATES,
          SULPHONATES AND SULPHINATES

Synthesis of alkylmercuric salts using these
derivatives results from decomposition of the compounds
by ultraviolet radiation or by thermal or by peroxide
initiated reactions. In general the reactions may be
represented as follows:-

$$RCO_2HgX \xrightarrow[\substack{u.v. \ or \\ peroxide}]{\Delta} RHgX + CO_2 \qquad (16)$$

$$RSO_3HgX \longrightarrow RHgX + SO_3 \qquad (17)$$

$$RSO_2HgX \longrightarrow RHgX + SO_2 \qquad (18)$$

The mechanism for these decompositions is one
involving free radicals.

1.3.4   ELECTROCHEMICAL SYNTHESIS

Organomercurials may result from both
cathodic and anodic reactions. At mercury anodes,
reactions have involved other metallorganics such as
Grignard reagents and complex organometallic anions
such as $Na^+[MeAlCl_3]^-$ and $NaBEt_4$ i.e.

$$NaMeAlCl_3 \xrightarrow[1.2V, \ 216h]{Hg \ anode} Me_2Hg \qquad (19)$$

The cathodic processes have involved organic halides and unsaturated compounds such as alkenes and ketones. Organic bromides and iodides, for example decyl, allylic, benzylic and cyclopropyl halides, C_6F_5I and $BrCH_2CH_2CN$, lead to organomercurials as shown by equations (20) and (21).

$$2 \; n - C_{10}H_{21}I \xrightarrow[\text{DMF, Hg cathode}]{0.1N \; Me_4N^+ClO_4^-} (n\text{-}C_{10}H_{21})_2Hg \qquad (20)$$

$$\qquad (21)$$
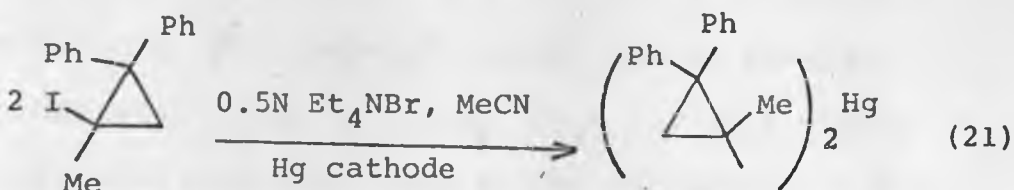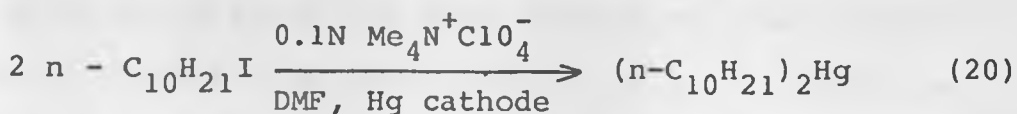
Possible mechanism would be[26]

Scheme 2

$$RI + e^- \longrightarrow R^\cdot + I^-$$

$$R^\cdot \longrightarrow R^\cdot \; \text{(adsorbed)}$$

$$R^\cdot \text{ (adsorbed)} \longrightarrow RHg^\cdot \text{ (adsorbed)} \longrightarrow R_2Hg + Hg$$
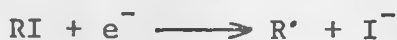
This works with alkenes and ketones but does not work very well with aldehydes.

1.3.5   BY DIAZONIUM SALTS

Either arylmercurychlorides or diarylmercury compounds may be prepared from aromatic primary amines (or arylhydrazines) (scheme 3). The reaction is regio-specific, from the amine and is reasonably high yielding and hence has some advantages over aromatic mercuration if the amine is available. In addition, most functional groups are stable to the reaction conditions, for compounds having strong electron withdrawing groups e.g. NO_2, CO_2H or SO_3H milder conditions should be used in the decomposition step[27] (step (iii) scheme 3).

Scheme 3

$$ArNH_2 \xrightarrow{\text{(i)}} ArN_2^+Cl^- \xrightarrow{\text{(ii)}} ArN_2^+HgCl_3^-$$

$$\text{(iii)} \swarrow \qquad \searrow \text{(iv)}$$

$$ArHgCl \qquad Ar_2Hg$$
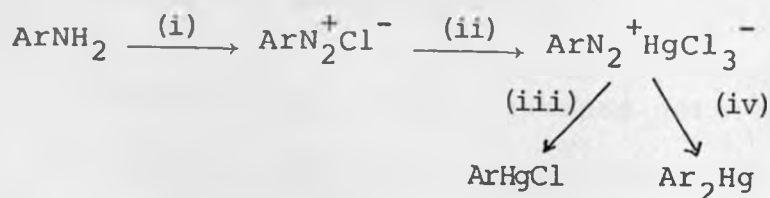
(i) $NaNO_2$, HCl

(ii) $HgCl_2$, HCl

(iii)   Cu, Cu(ll) or Cu(ll) and $HPO(OEt)_2$ in Me_2CO, $MeCO_2Et$, EtOH, or H_2O

(iv)   Cu in aqueous ammonia

1.3.6   <u>FROM AROMATIZATIONAL MERCURATION</u> [150]

This reaction is exemplified by equation (22). The driving force, to generate an aromatic system is great and even $Ph\bar{C}H_2HgCl$ unreactive in alkene reactions, reacts.

$$R = Et \text{ or } MeOCH_2, \tag{22}$$
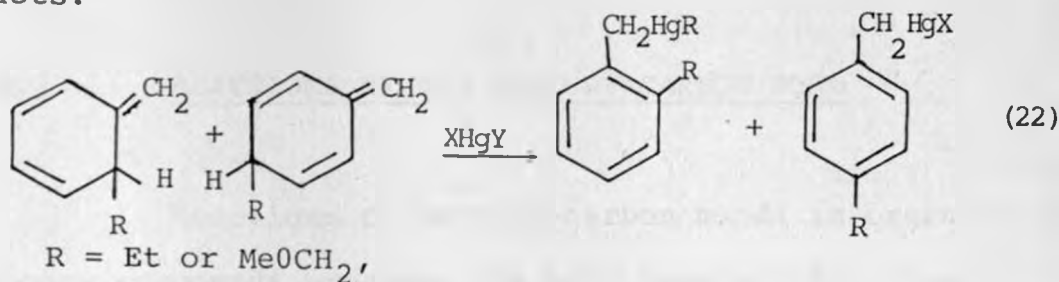
$$X, Y = Cl, Cl\text{-}; OCOCF_3, OCOCF_3; Ph, OCOCF_3;$$

$$Ph_2CH_2, Cl.$$

1.3.7   <u>FROM INSERTION OF CARBENES CR_2, INTO MERCURY - HALOGEN BONDS</u> [151]

Methylene and other carbenes generated from diazo compounds insert into a mercury-halogen bond to give α- haloalkylmercury compounds, also some unsymmetrical products such as $R^1HgCXR^2R^3$ may be produced. In addition some symmetrization may also result e.g.

$$R^1HgCl + R^2R^3C = \bar{C} \longrightarrow \overset{+}{N} \equiv N \xrightarrow[\substack{-5 \text{ to} \\ 10^{\circ}C}]{Et_2O} R^1HgCCClR^2R^3$$

$$\overset{+}{N_2} \qquad (23$$
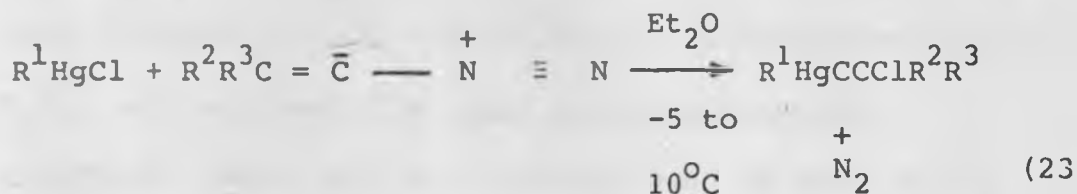
1.4   REACTIONS OF THE MERCURY-CARBON BOND

Reactions of mercury-carbon bonds in organo-
mercury compounds proceeds via both heterolytic, usually
by S_E2 mechanisms, and homolytic routes, including
reactions with halogens, alkylhalides, and other
electrophilic reagents. The simultaneous operation of
homolytic and heterolytic pathways e.g. in halogenations,
has obviously added to the problem of studying the
mechanisms of organomercury reactions. In comparison
with the alkali and alkali earth organometallics,
organomercury compounds are not very reactive towards
oxygen but oxidation of organomercurials does occur
and precautions need to be taken.

Organomercurials, in general are not good sources
of carbanions and are usually unreactive towards water,
alcohols, carbonyl compounds and simple alkylhalides

in heterolytic reactions. In electrophilic
substitutions e.g. by proton acids, diorganomercurials
R_2Hg, are more reactive than monoorganomercury
compounds, RHgX, and aryl-mercury bond is more easily
cleaved than an alkyl-mercury bond.

Compared to other organometallic compounds,
organomercurials are stable and have a relatively
simple linear structure. This accounts for their
popularity in mechanistic studies.

Various mercury-mercury exchange processes have
been investigated e.g. equations 24 - 27 which are
successively termed as the one-, two-, three- and
four-alkyl exchange reactions. These are usually
bimolecular (S_E2 open or cyclic) and proceed with three-
and four centred transition states respectively
(Scheme 4), and are reported to occur with
retention of configuration.[152]

$$R^*HgX + HgX_2 \rightleftharpoons RHgX + {}^*HgX_2 \qquad (24)$$

$$R_2Hg + HgX_2 \rightleftharpoons 2RHgX \qquad (25)$$

$$R_2Hg + R'{}^*HgX \rightleftharpoons R'{}^*HgR + RHgX \qquad (26)$$

$$R_2Hg + R'_2{}^*Hg \rightleftharpoons R_2{}^*Hg + R'_2Hg \qquad (27)$$

Scheme 4

$$\left[\begin{array}{c} {}^{*}HgX \\ R \\ HgX_2 \end{array} \right]^{\ddagger}$$

$S_E 2$ open

$$HgX_2 + {}^{*}RHgX \qquad\qquad RHgX + {}^{*}HgX_2$$

$$\left[\begin{array}{c} X \\ {}^{*}Hg \\ R \qquad X \\ Hg \\ X \end{array} \right]^{\#}$$

$S_E 2$ closed
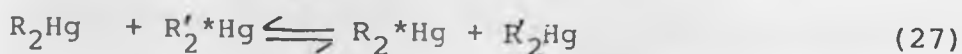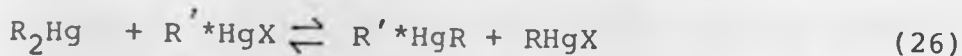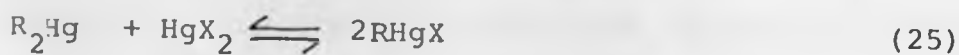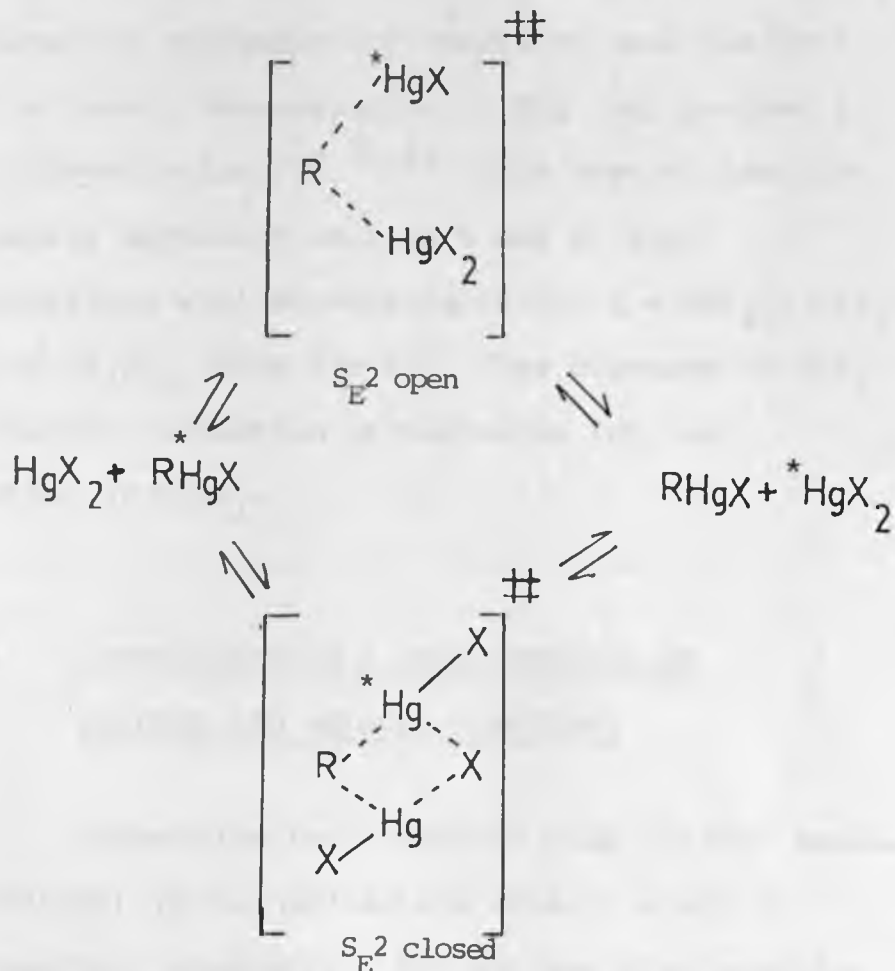
The disproportionation reactions and symmetrization reactions follow a similar scheme to that above.

In electrophilic cleavage of organomercurials generally, nucleophilic catalysis, by anion, a neutral ligand or solvent (or even by nucleophilic residue of the electrophilic reagent) as in the $S_E 2$ cyclic mechanism has often been cited.[152]

Carbonium ion intermediates have also been indicated in organomercury reactions when the Hg-X bond is ionic, demercuration of RHg^+ may proceed to give carbonium ion, R^+.[28,29] This type of reaction is clearly dependent on both R and X, e.g. demercuration will be more rapid for X = HSO_4^-, ClO_4^- NO_3^- or $CF_3CO_2^-$ than for Br^-. The presence of HgX_2 may help the formation of carbonium ion, on formation of Hg_2X_2.

1.4.1 OXYMERCURATION - DEMERCURATION OF ALKENES AND RELATED REACTIONS

Oxymercuration (together with related amino-mercuration) is the most active area of study in Organomercury chemistry. It involves electrophilic attack of a mercury salt upon an alkene with consumption of the resultant mercury-containing cation by an appropriate nucleophile HY or Y^- resulting in the formation of a β-substituted organomercury compound, as in equation (28). Since the compound HY is sometimes used as the solvent in these reactions the process has been called 'solvomercuration' or 'oxymercuration' if HY is water, an alcohol, or

carboxylic acid.

$$RCH = CH_2 + HgX_2 + HY \rightleftharpoons \overset{\overset{\displaystyle Y}{\displaystyle |}}{RCH} - CH_2HgX + HX \qquad (28)$$

where $Y = OH$, OR', $OCOR'$, $NR'R^2$ etc.

In this reaction various mercury (II) salts have been used but mercuric ethanoate and trifluoroethanoate have been found the most effective. Mercury (II) ethanoate reactions go practically to completion; in contrast to the more electrophilic, and hence more reactive salts, $Hg(NO_3)_2$ and $Hg(ClO_4)_2$, where bases have to be present to remove the liberated acids, HX, and thus drive the reaction completely to the right. The ease of protonolysis of solvomercuration by HCl generally limits the use of mercury (II) chloride. Aminomercuration can be achieved with this mercury (II) chloride, however, if sufficient amine is added to act both as the base and the nucleophile.[30]

An important feature of these reactions is that they show very high regioselectivity for Markownikov-type additions. They are believed to proceed by rate-determining attack of the nucleophile on a bridged mercurinium ion.[31] Oxymercuration has been demonstrated to be reversible and the reverse reaction is called deoxymercuration.

1.4.1.1   THE MECHANISM OF OXYMERCURATION

Lucas and Winstein [32] were the first to suggest an ionic mechanism for oxymercuration. They obtained evidence for the existence, in solution of co-ordination complexes 1 and 2.

1   2
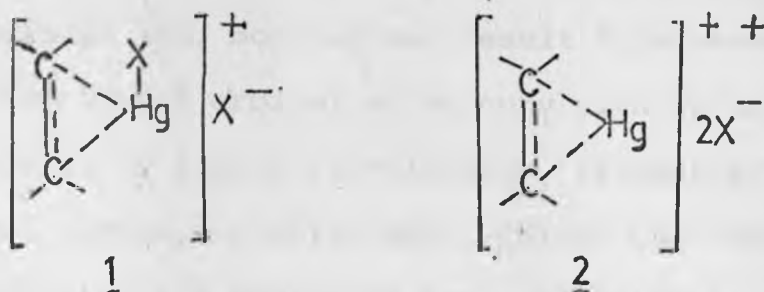
Thus they predicted the oxymercuration reaction to be represented as follows:

(29)
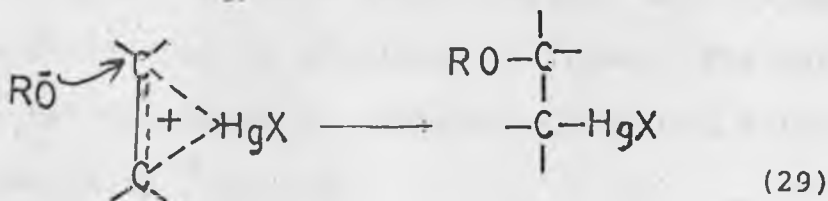
This intermediacy of mercurinium ions in the oxymercuration reaction was based on analogy with (d^{10}) Ag^+ - olefin complexes [33] and bromonium ions, [34] and their ease of explaining trans addition.

This mechanism has further been supported by Kreevoy et al, [35-38] studying the deoxymercuration reaction. He showed that the same mercurinium ion 1 was involved in the deoxymercuration reaction.

Such π- complexes were considered as intermediates
in oxymercuration. The actual structure of the
mercurinium ion was considered initially in terms of
resonance theory,[39] but approaches based on molecular
orbital theory have been used in discussions of the
bonding in olefin-metal complexes. In the case of
mercurinium ion, bonding may result from interaction
of a 6sp hybrid orbital of mercury with 2p orbitals of
the olefin to form a two-electron, triangular, three
orbital system, in which each orbital has considerable
overlap with the remaining two. Additional
stabilization resulting from 5d $-\pi*$ interaction may be
considered, but such "back-bonding" would appear less
important than in platinum (II) case. The system
may be considered to conform to Hückels's criterion for
aromaticity[40] $(n = 0)$.

In solvents usually employed for oxymercuration
e.g. alcohols or water, any such mercurinium ion
intermediate would not normally be expected to
survive long enough for spectral detection. In reaction
equation (30) the ion (3) is detected, however, since
intramolecular coordination of Cyano group to mercury
leads to sufficient stability for detection by n.m.r.[41]

$$(30)$$

$$(3)$$
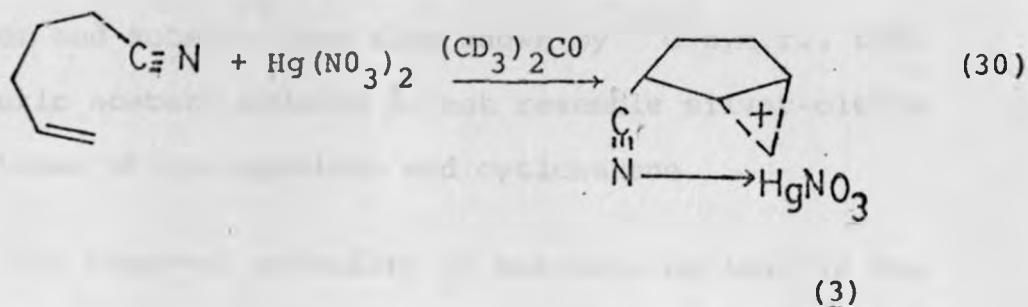
Using the poorly nucleophilic magic-acid medium $FSO_3H - SbF_5 - SO_2$, alkylmercurinium ions have been found to have sufficient stability to be studied by ^{13}C n.m.r. and i.r. spectroscopy. The ^{13}C n.m.r. data suggests dorminant σ-donation from the alkene to the Hg^{2+} with significant decrease in the electron density at the alkenic centre.

Olah and Clifford [42-45] have verified the existence of the ethylene mercurinium ion in $FSO_3H - SbF_5 - SO_2$ by observing its proton n.m.r. spectrum.

$$MeOCH_2CH_2HgCl \xrightarrow[- 30^{o}C]{FSO_3H - SbF_5 - SO_2}$$

$$(31)$$
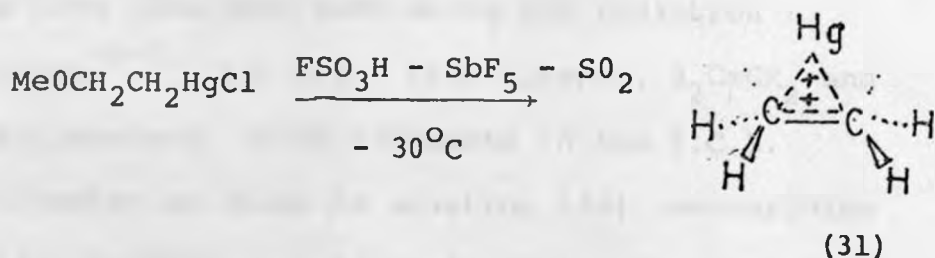
Brown, Rei and Liu [46] have shown using n.m.r. spectra that adducts from mercuric trifluoroethanoate

and norbornene or related olefins in benzene are covalent $Hg - C - C - O_2CCF_3$ structures and do not resemble the stable silver-olefin π-complexes.

Parker and Roberts[47] have also shown by ^{13}C n.m.r., that mercuric acetate adducts do not resemble silver-olefin complexes of cyclopentene and cyclohexene.

The observed stability of mercurinium ions in the absence of nucleophiles is consistent with extended Hückel calculations carried out by Bach and Heinneike.[48] The bonding of ethylene with mercury (II) was calculated to be intermediate between that with Cl^+ and that with Ag^+. The mercury (II) withdraws a considerable amount of electron density from the carbon atom in accord with the high reactivity of these complexes. The ethylene - Ag^+ complex was calculated to have little positive charge on carbon atoms, in accord with its lack of chemical reactivity.

Observations of mercurinium ions in the gas phase have also been made using ion cyclotron resonance[49-51] (I.C.R.). From alkenes, $R_2C=CR_2$ and dimethylmercury, which fragments in the I.C.R. spectrometer as shown in equation (33), mercurinium ion (4) and (5) were observed. The lifetimes of (4) and (5) are at least $3 \times 10^{-3}s$.

$$Me_2Hg \xrightarrow[22eV]{ICR} Me_2Hg^+ + MeHg^+ + Hg^+ \qquad (32)$$

$$\qquad\qquad\qquad 28\% \qquad\quad 41\% \qquad 31\%$$

$$Me_2Hg + R_2C = CR_2 \xrightarrow[22eV]{ICR} R_2C\!\!\overset{+}{\underset{Hg-Me}{\diagdown\diagup}}\!\!CR_2 + R_2C\!\!\underset{Hg^+}{\diagdown\diagup}\!\!CR_2 \qquad (33)$$

$$\qquad\qquad\qquad\qquad\qquad\qquad (4) \qquad\qquad\qquad (5)$$
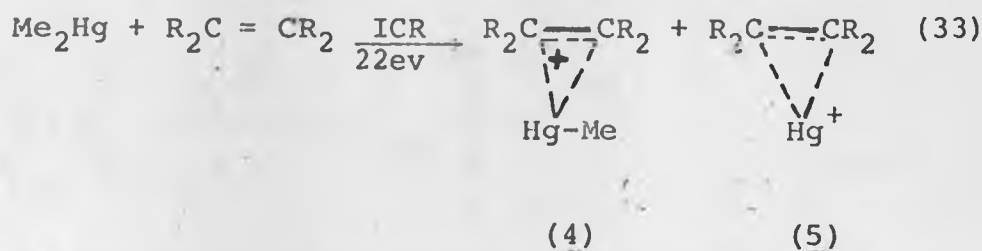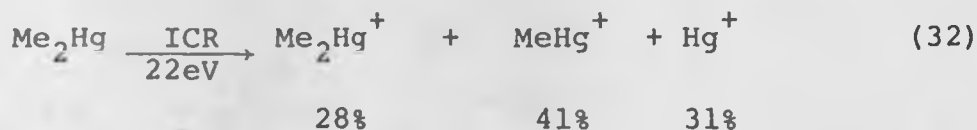
Bach and Richter[52] have presented support which
implies that neither the rate of oxymercuration nor
the degree of π- complex formation with silver ion is
related to the ground-state energies of olefins. These
workers concluded that the rate-determining step in
oxymercuration involves attack by solvent on a
mercurinium ion intermediate.

1.4.1.2   THE KINETICS OF OXYMERCURATION

Halpern and Tinker[53] have measured the
kinetics of hydroxymercuration of 20 olefins in aqueous
perchloric acid. Several cases of the expected trans
addition were confirmed, including the reactions of Z
and E-but-2-ene (6) and (7).

$$CH_3 \quad CH_3 \qquad \qquad HgX \quad CH_3$$

(chemical structure)

$$\overset{\cdot\cdot}{C} = C \xrightarrow[\quad H_2O \quad]{Hg^{2+}} CH_3 \overset{\cdot\cdot}{C} - C \overset{H}{<}_{OH} \qquad (34)$$

$$H \quad (6) \quad H \qquad \qquad \cdot H$$

$$CH_3 \qquad H \qquad \qquad HgX \quad H$$

(chemical structure)

$$C = C \xrightarrow[\quad H_2O \quad]{Hg^{2+}} CH_3 \overset{\cdot\cdot}{C} - C \overset{CH_3}{\diagup} \qquad (35)$$

$$H \diagup \quad (7) \quad \diagdown CH_3 \qquad \qquad H \quad OH$$
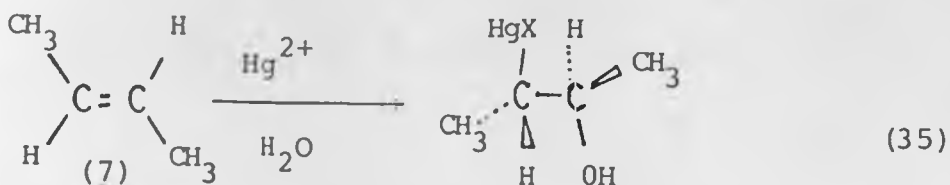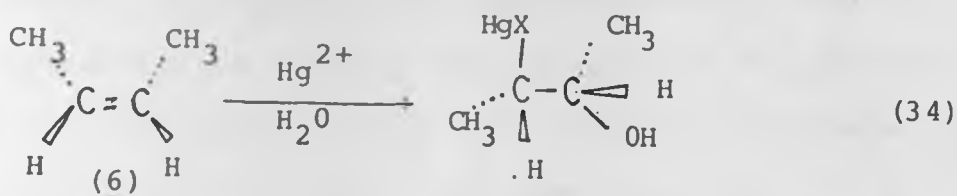
These reactions are quite fast and the rate law in each case was first order in Hg^{2+} and first order in olefin.

Catalysis by hydrogen peroxide and oxygen was not observed[54] (contrary to an earlier claim); this removed, what some authors considered to be a troublesome feature of the ionic addition mechanism.

The rate law is insensitive to acid and mercurous ion does not yield an oxymercuration rate equal to that expected from the amount of Hg^{2+} in equilibrium with Hg_2^{2+} and Hg^{0}.

Halpern and Byrd[55] formulated a rate equation of deoxymercuration and through measurements verified the mechanism of oxymercuration.

Other kinetic data on methoxymercuration by $Hg(OAc)_2$ in methanol have been discussed[56] and interpreted in terms of the mercurinium ion mechanism, which can explain the solvent effects, stereochemistry and other evidence of ionic participation.

$$Hg(OCOCH_3)_2 \rightleftharpoons {}^+HgOCOCH_3 + CH_3COO^- \qquad (36)$$
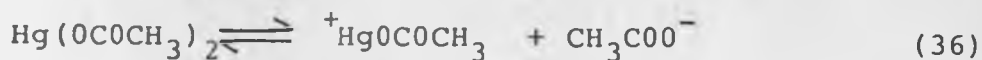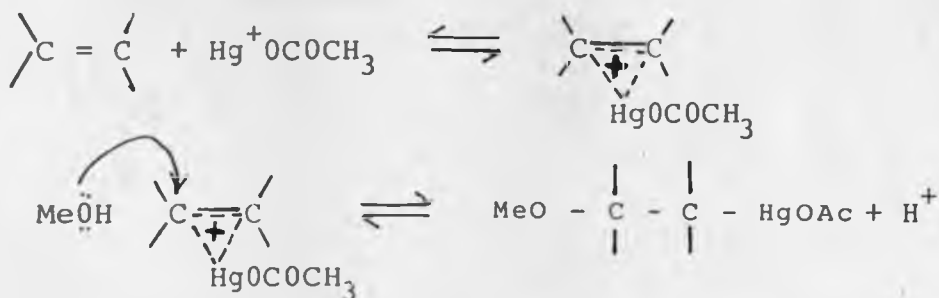
Scheme 5

From data of stereochemistry, kinetics and the intermediate mercurinium ions, it is now accepted that the mechanism of oxymercuration of unstrained olefins may in general be represented as follows:

Scheme 6
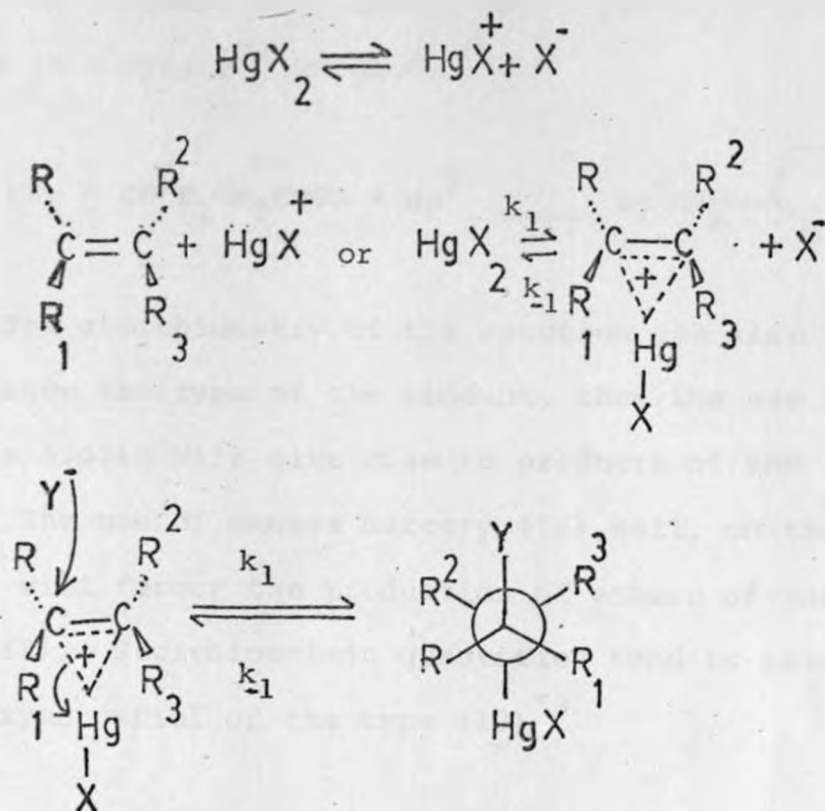
$$HgX_2 \rightleftharpoons Hg\overset{+}{X} + \overset{-}{X}$$

$$\underset{R_1}{\overset{R}{}} \underset{R_3}{\overset{R^2}{}} C = C + Hg\overset{+}{X} \quad \text{or} \quad HgX_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{R_1}{\overset{R}{}} C \overset{R^2}{\underset{R_3}{\equiv}} C \cdot + \overset{-}{X}$$

$$\underset{R_1 \overset{|}{\underset{Hg}{}}}{\overset{R}{}} \overset{Y}{\underset{\overset{|}{X}}{\downarrow}} \underset{R_3}{\overset{R^2}{C \equiv C}} \underset{\overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}}}{} \quad R^2 \underset{R}{\overset{Y}{\underset{\overset{|}{HgX}}{\bigotimes}}} \overset{R^3}{\underset{R_1}{}}$$

The type of the reaction product is influenced by two factors. The first is dependent upon the other functional groups present in the molecule; for example, o-allylphenol, ring closes to give a dihydrobenzofuran derivative.[57]

$$\text{[o-allylphenol]} \xrightarrow{Hg(OAc)_2} \text{[dihydrobenzofuran]} - CH_2HgOAc + HOAc \qquad (37)$$

Scheme 6

$$HgX_2 \rightleftharpoons Hg\overset{+}{X} + \overset{-}{X}$$
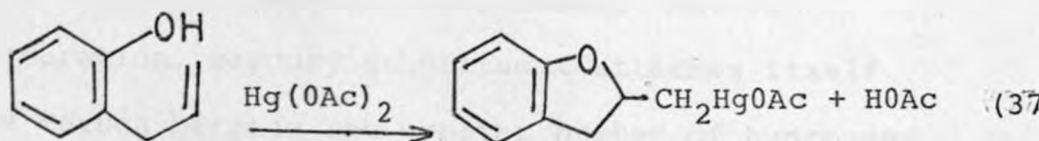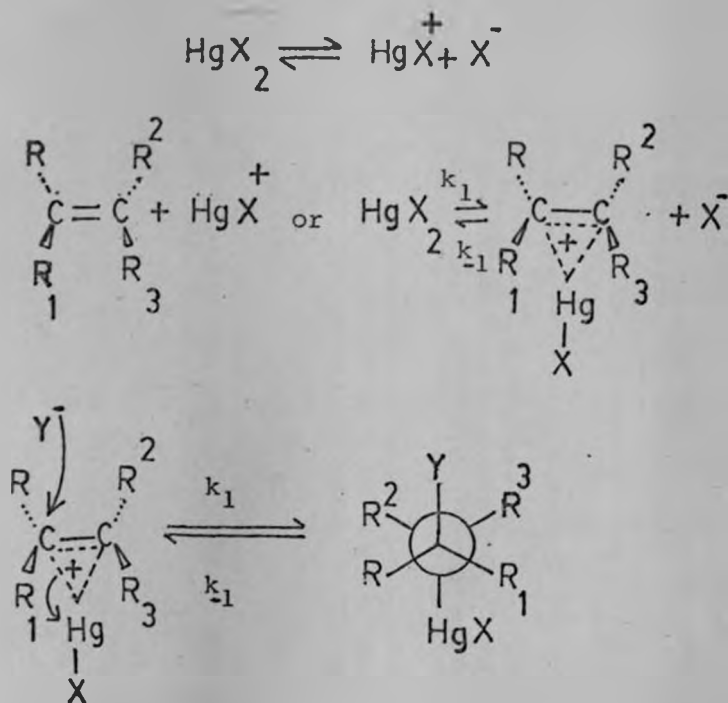
The type of the reaction product is influenced by two factors. The first is dependent upon the other functional groups present in the molecule; for example, o-allylphenol, ring closes to give a dihydrobenzofuran derivative.[57]

$$-CH_2HgOAc + HOAc \qquad (37)$$
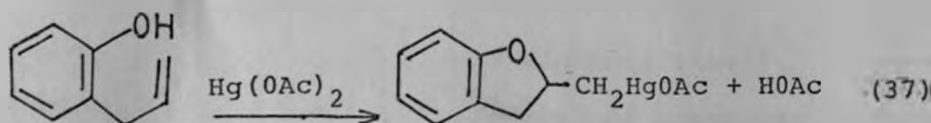
The reaction of $CH_2 = CHCH_2CH_2CH_2OH$ is exceptionally rapid as a result of hydroxyl group participation and leads to a cyclic[53] product.

$$CH_2 = CHCH_2CH_2CHOH + Hg^{2+} \longrightarrow Hg^+CH_2- \underset{O}{\bigcirc} \qquad (38)$$
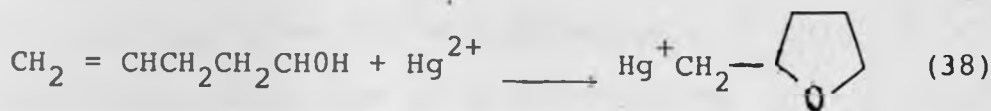
The stoichiometry of the reaction can also influence the type of the product, thus the use of excess olefin will give rise to products of the type (8). The use of excess mercury (II) salt, on the other hand, will favour the production of ethers of the type (9). Stoichiometric quantities tend to favour the oxymercurial of the type (10).[58]

$$\underset{\underset{OMe}{|}}{CH_2}-CH_2Hg-CH_2-\underset{\underset{OMe}{|}}{CH_2} \qquad\qquad XHg-CH_2CH_2-O-CH_2CH_2-HgX$$

$$(8) \qquad\qquad\qquad\qquad\qquad (9)$$

$$\begin{array}{c} OMe \quad H \\ | \qquad | \\ H - C - C - H \\ | \qquad | \\ H \quad HgOAc \end{array} \qquad (10)$$
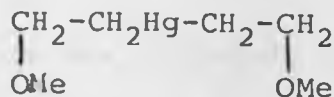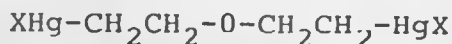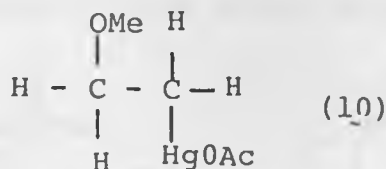
It is also a general rule, infact that in oxymercuration, mercury substituent attaches itself to the carbon bearing the greater number of hydrogens unless other electronic influences are operative.[59]

The discussion has, so far, been restricted to
relatively simple olefins, and it would be useful
to consider oxymercuration of the more complicated
bicyclic systems, since the stereochemistry of this
reaction differs from that of simple olefins.

The mechanisms proposed by Winstein[32] and Kreevoy[35-38]
for oxymercuration and deoxymercuration reactions are
seen to be self-consistent and explain the result
for simple unstrained olefins. Norbornene, however,
oxymercurates to give cis - exo - products. How the
general mechanism may be modified has been discussed
by Traylor[60,61] and was critically reviewed by
Ormand.[62]

In his proposal, Traylor, considered the
mercurinium ion as a key tenet in the overall scheme,
but his explanation for exo approach of the electrophile
to give (11) as shown below was not convincingly done.

$$(39)$$
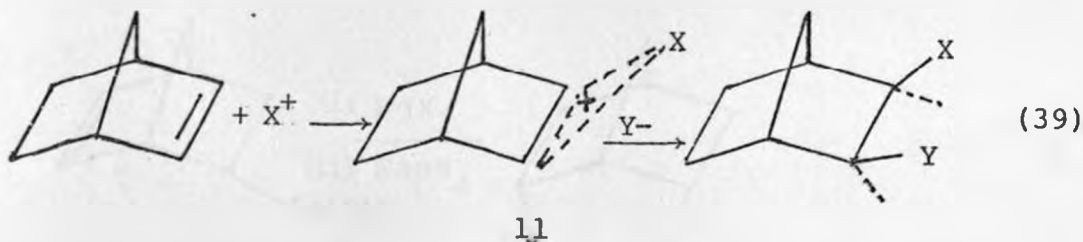
Another important feature was that cis or front side
opening of the mercurinium ion was favoured, since the
nucleophile may be considered to be already located

on that side by its attachment to mercury.

Neighbouring groups manifest themselves rather dramatically in oxymercuration of certain substituted norbornenes, and even poor neighbouring groups such as hydroxyl and carboxyl override the features that normally lead to cis-, exo - oxymercuration. Some examples are shown and stereochemistry is based largely on p.m.r. spectra and reduction experiments producing compounds of known configurations.[63,64]

(40)

(41)
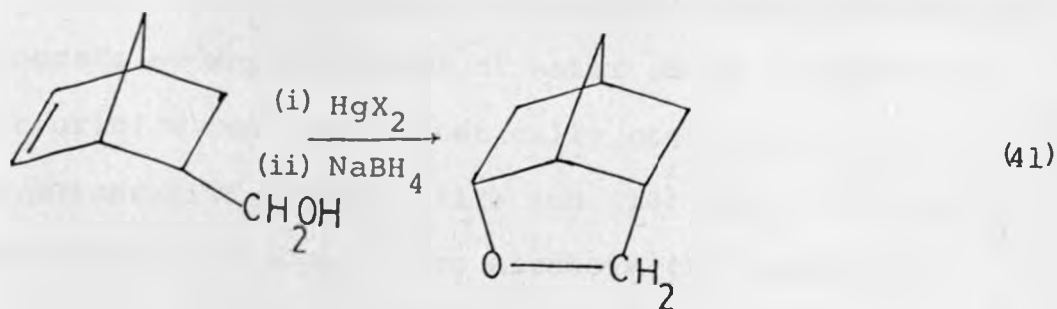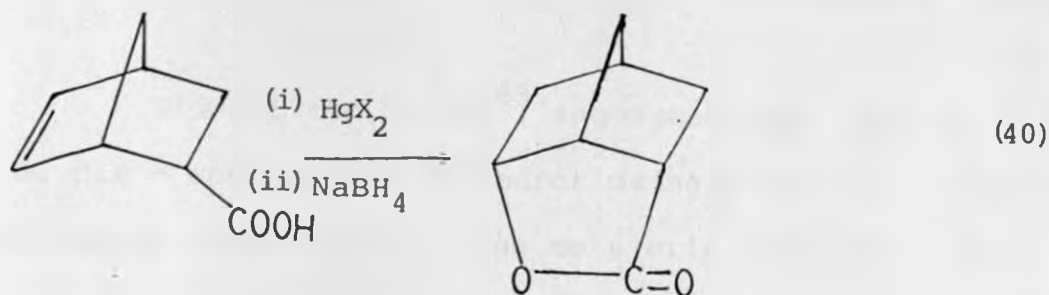
The most peculiar aspect of the oxymercuration of norbornenes is that syn substituents in the 7-position do not alter the preference for cis, exo addition.[65] 1,4,7,7-Tetramethylnorbornene, for example, yields the cis, exo product.

(42)
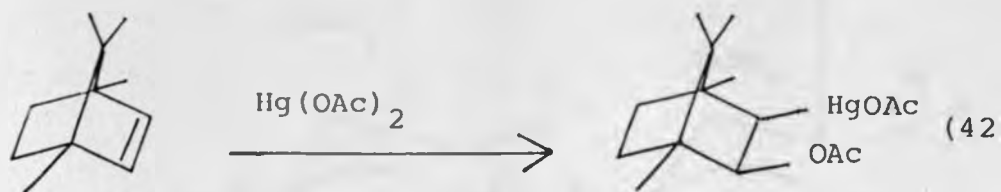
Brown and co-workers[66] have also observed cis, exo oxymercuration with 7,7-dimethylnorbornene.

Tidwell and Taylor[65] suggested that lack of the cis - endo addition product using a syn - 7 - methyl or -bromo substituent is due to steric reasons.

Unstrained cyclic systems have been shown to undergo the normal trans addition by Pasto and Gontarz[67] who reported that oxymercuration of 4-t-butylcyclohexene proceeds by way of attack of water on an intermediate mercurinium ion. The kinetically controlled oxymercuration products (12) and (13) were characterized with sodium borohydride to alcohols (14) and (15).

Scheme 7
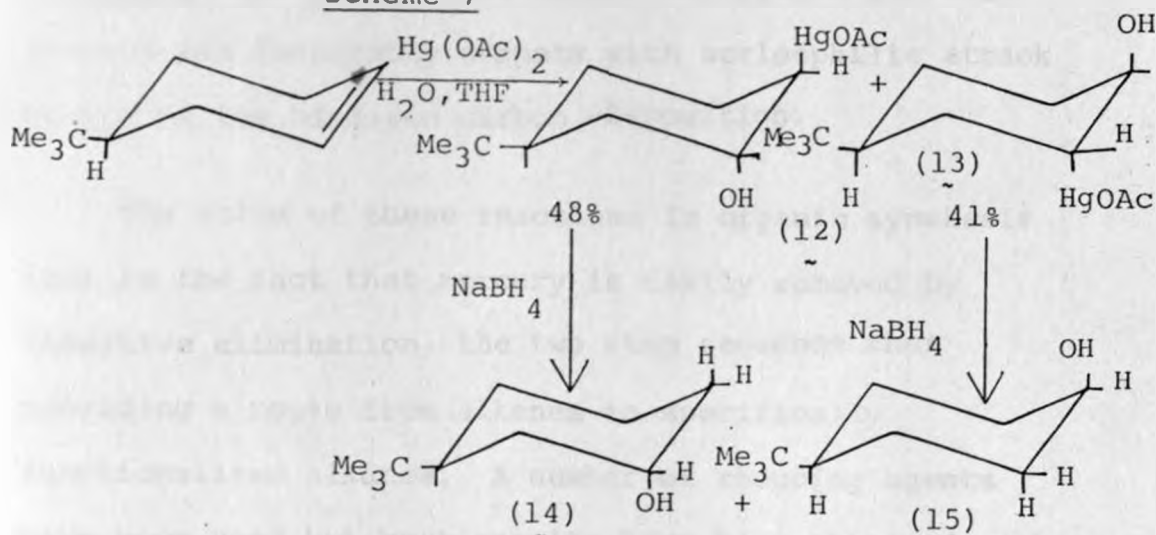
For some hindered olefins vinylmercurials are
formed. This is possibly because the acetoxymercurinium
ion formed loses a proton more rapidly than it is
attacked by a nucleophile.[68]

Scheme 8
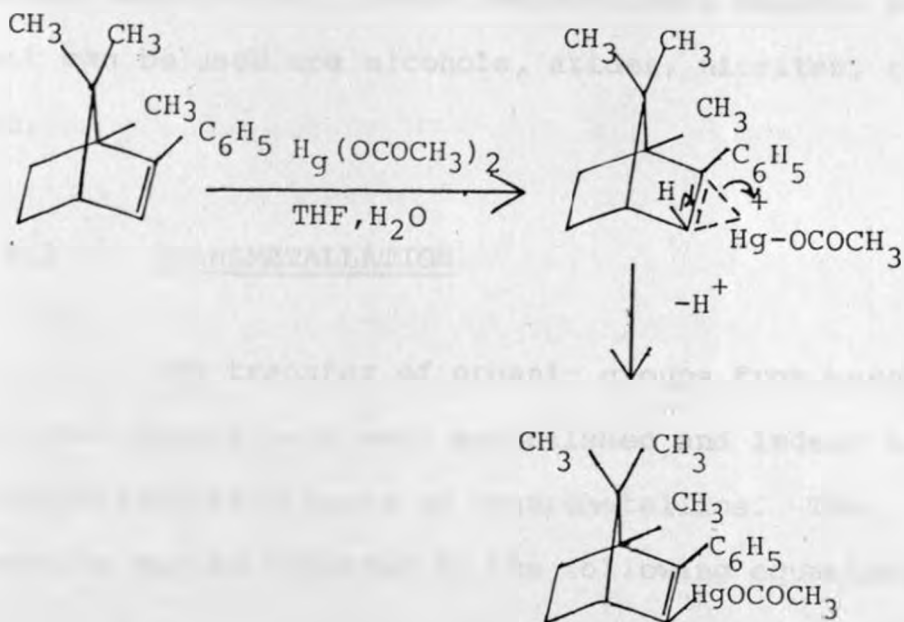
The vinylmercury acetate is considered to arise
by loss of the proton from carbon-3-position and this
process can favourably compete with nucleophilic attack
by H_2O at the hindered carbon -2-position.

The value of these reactions in organic synthesis
lies in the fact that mercury is easily removed by
reductive elimination, the two step sequence thus
providing a route from alkenes to specifically
functionalized alkanes. A number of reducing agents
have been used but best results have been obtained with
an alkaline solution of sodium borohydride.

Probably the most widely used application of this
procedure is in the hydration of alkenes to alcohols,
which is effected by mercuration in the presence of
water followed by reductive demercuration with
sodium borohydride. Other nucleophiles, besides water,
that can be used are alcohols, azides, nitrites, nitrides
etc.

1.4.3   TRANSMETALLATION

The transfer of organic groups from mercury
to other metals is a well established and indeed a
classic synthetic route to organometallics. The
reaction may be depicted by the following equations:

$$R_2Hg + R'-M \longrightarrow RHgR' + R-M \qquad (43)$$

$$R_2Hg + 2M \longrightarrow Hg + 2 R-M \qquad (44)$$
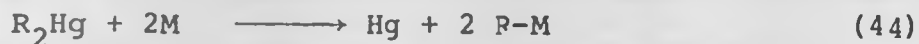
e.g. M = metal of group IA, IIA, or IIIA

M/Hg alloy e.g. M = Sn or Bi or

transition metal zero valent complex

e.g. $Pt(PPh_3)_n$.

$$R_2Hg + MX \longrightarrow R - M + R-HgX \text{ or } (Hg + RX) \qquad (45)$$

X = halide, hydride or acetate

M = Group III, IV or V metal or

transition group metal.

Advantage of reaction (43) is that the new organometallic compound is obtained salt-free and, for example, it has found use in the synthesis of organolithiums. Reaction (44) is similar to the Grignard and organolithium routes but the disadvantage of this reaction is the poor nucleophilicity of carbon-mercury bonds, however, there is an advantage in that functional groups are tolerated.

The mercury exchange mechanism has been a subject of discussion and Abraham[69] has given a valuable treatment of the principle of microscopic reversibility as pertaining to symmetrical isotopic exchanges.

1.4.4   CARBENE-TRANSFER REACTIONS OF HALOMETHYLMERCURY COMPOUNDS

Recently, α-halomethylmercury compounds have come into prominence in organic synthesis, as a source of 'carbenes', particularly of dihalogeno carbenes, which are generated from trihalogenoalkylmercurials. These have been widely employed in the synthesis of gem-dihalogenocyclopropanes. Generally the phenyl-mercurials, PhHgCXYZ with at least X,Y and Z being halogen are used as carbene transfer agents in thermal α-eliminations, e.g.

$$\text{PhHgCXYZ} + \begin{array}{c}\diagdown \\ \diagup\end{array}\!\!C = C\!\!\begin{array}{c}\diagup \\ \diagdown\end{array} \xrightarrow{\Delta} \text{PhHgX} + \begin{array}{c}Z \diagup\!\!\diagdown\!\!\diagup Y \\ \triangle\end{array} \qquad (46.)$$
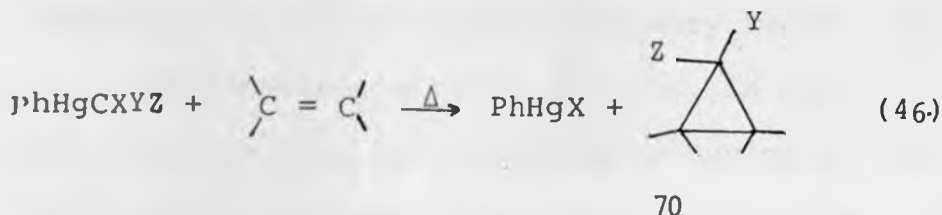
The scheme below has been proposed,[70] from kinetic experiments, as the mechanism for alkene – PhHgCCl$_2$Br reactions; similar mechanisms should apply for other phenyltrihalomethylmercury reactions. In these reactions the ease of transfer of the α-halide

on carbon to mercury is in order I > Br > Cl > F thus: CCl_2 is generated from $PhHgCCl_3$, $PhHgCCl_2Br$ and $PhHgCCl_2I$.

Scheme 9

$$PhHgCCl_2Br \underset{\text{k-1 fast}}{\overset{k_1 \text{ slow}}{\rightleftharpoons}} PhHgBr + :CCl_2$$
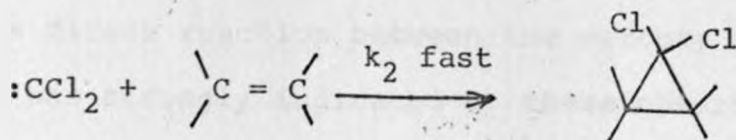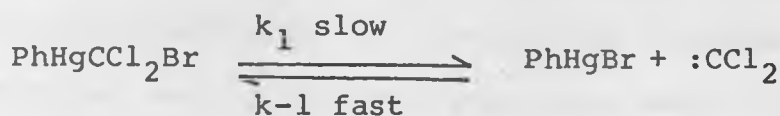
Other mechanisms are possible, Seyferth et al.[71] report that methylenation of alkenes using bis(bromomethyl)-mercury does not involve free carbenes but rather a direct reaction of the mercurial itself. In their study, they reported that bis(bromomethyl)mercury reacts with olefins at temperatures of $80^{\circ}C$ or above, in inert solvents, resulting in the formation of cyclopropanes via CH_2 transfer from the mercurial to the olefin.

They pointed out that, in the reactions they investigated, addition of CH_2 to C = C bonds, was the only process observed; no evidence of CH_2 insertion

into C-H bonds was obtained. Other observations made were: reactions of bis(bromomethyl)mercury with E- and Z-3-heptene were stereospecific; and bis(bromomethyl)-mercury is stable in refluxing benzene. In addition heating bis(bromomethyl)mercury for up to 20 days was examined and was observed that the initial concentration of the olefin affected the rate of the transfer. These observations were different from those made with $:CCl_2$ transfer from phenyl(bromodichloromethyl)mercury as such, a direct reaction between the mercury and the olefin was strongly indicated by these observations.

Advantages of using Organomercury carbenoids are:-

(i)   The reaction proceeds at reasonable temperatures and under neutral conditions.

(ii)   The usual insolubility of the organomercuryhalide allows it to be readily removed and without intervention of the carbanions, $\bar{C}Hal_3$.

(iii)   They transfer the carbene $:CX_2$ successfully to alkenes which are poorly reactive towards "conventional reagents; for example trans-stilbene and tetrachloroethene are readily converted into corresponding cyclopropane derivatives on reaction with phenyl(bromodichloromethyl)mercury."

into C-H bonds was obtained. Other observations made were: reactions of bis(bromomethyl)mercury with E- and Z-3-heptene were stereospecific; and bis(bromomethyl)-mercury is stable in refluxing benzene. In addition heating bis(bromomethyl)mercury for up to 20 days was examined and was observed that the initial concentration of the olefin affected the rate of the transfer. These observations were different from those made with $:CCl_2$ transfer from phenyl(bromodichloromethyl)mercury as such, a direct reaction between the mercury and the olefin was strongly indicated by these observations.

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(iv) They are highly stereoselective.

Many functional groups can be tolerated but carboxylic acids, hydroxyl, amines, and any group with an atom carrying lone pair of electrons undergo Michael addition of the intermediate anion $\bar{C}Hal_3$ leading to unrequired products. gem-Dihalogenocyclopropanes can be prepared from such molecules by using trihalogenomethylmercurials.

Trihalomethylcarbanions can be involved in those reactions in which the carbene is not readily released thermally by the mercurial; iodide can be employed to displace the trihalomethylanion, which then decomposes to the dihalocarbene[72] (Scheme 10). This method nicely supplements the older methods.

Scheme 10

$$PhHgCF_3 + I^- \xrightarrow{80^{o}C} PhHgI + CF_3^-$$

$$CF_3^- \longrightarrow F^- + :CF_2$$
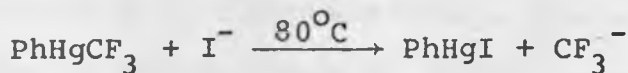
1.4.5.   THERMOLYSIS AND PHOTOLYSIS OF
          ORGANOMERCURIALS[152]

      The mercury-carbon bond is not energetically
weak but is relatively non-polar and readily undergoes
homolysis. The thermolysis of simple diorganomercurials
and organomercurials has been shown to be a homolytic
process and a possible mechanism is:

$$R_2Hg \xrightarrow{\Delta \text{ or } h\nu} RHg^{\cdot} + R^{\cdot} \qquad (47)$$

$$RHg^{\cdot} \xrightarrow{\Delta \text{ or } h\nu} R^{\cdot} + Hg \qquad (48)$$

$$R_2Hg \xrightarrow{\Delta \text{ or } h\nu} 2R^{\cdot} + Hg \qquad (49)$$
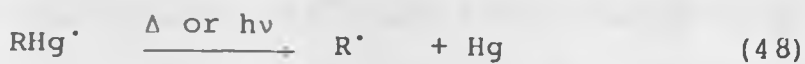
    Photolysis may occur as single-step, or two-step
reaction or both reactions may occur together.   The
products, depend upon the substrates and the solvent.
The reactions of diphenylmercury, for example, in
alcohols in sealed tubes at 200°C, gave mercury, benzene,
some aldehydes, and esters, while the irradiation of
diphenylmercury in methanol in u.v. light, gave a
quantitative yield of mercury, benzene and methanal after
35 hours.

Donor solvents such as THF, dioxane, pyridine or HMPT, accelerate the reaction of R_2Hg with trichloromethane.

Secondary or tertiary alkylmercurials are particularly thermally unstable, for example, butylmercury decomposes at $40^{\circ}C$, on the other hand, organomercurials containing electron withdrawing groups are thermally stable to at least their melting points. Di(pentabromobenzene)mercury, and di(pentachlorobenzene)mercury, for example, are stable to their melting point at $406^{\circ}C$ and $386^{\circ}C$ respectively.

Transition metals such as Ni, Pd, Pt, Cu, Au, and Ag catalyse the decomposition of diarylmercury, and dibenzylmercury compounds to form biaryl and bibenzyl species. These dimerisation processes can be either head to head or head to tail.

The mechanism of these reactions involves free radicals and the reaction is stereoselective.

Synthetic use has been made of the thermolysis of vinylmercurials ($CH_2 = CHHgX$) where $X = O_2CR$, OAr, SAr, SR, OSO_2, $OSO_2C_6H_4Me$-p, SCO(OR) and SCN. The reaction is as follows:

$$CH_2 = CHHgX \xrightarrow{\Delta} CH_2 = CHX + Hg \qquad (50)$$
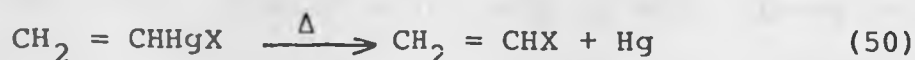
1.4.6   <u>PHOTOLYSIS OF α-DIAZOALKYLMERCURIALS</u>

Photolysis of the diazoalkylmercury compounds,
for example, $Hg(CN_2CO_2Et)_2$ at wavelengths shorter
than 290 nm, provide methyne derivatives (equation 51).
Photolysis of $Hg(CN_2CO_2Et)_2$ using a medium pressure
lamp, at room temperature, using trichloromethane,
pyrrolidine and THF as solvents, provides solvent
derived products.

$$Hg(CN_2CO_2Et)_2 \longrightarrow 2N_2 + Hg + 2:\overset{\cdot}{C}CO_2Et \qquad (51)$$
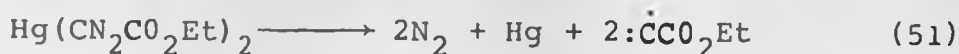
Compounds of the type $RHgNC_2CO_2Me$ have also been
studied. The two competing routes of photolytic
decomposition are given in equations (52) and (53).

$$RHgCN_2CO_2Me \xrightarrow{\text{hv}} RHg\overset{..}{C}CO_2Me + N_2 \qquad (52)$$

$$RHgCN_2CO_2Me \xrightarrow{\text{hv}} R^{\cdot} + Hg + N_2 + :\overset{\cdot}{C}CO_2Et \qquad (53)$$
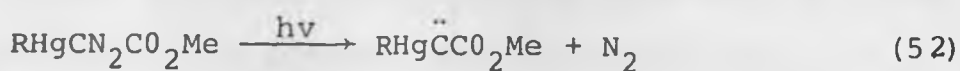
1.4.7   <u>REACTION WITH PROTON ACIDS</u>

Substitution of hydrogen, by the action of
acids is a heterolytic reaction, resulting in cleavage
of C-Hg bond. Mineral acids such as HCl, cleave both

the C- Hg bonds in diorganomercurials, whereas,
carboxylic acids such as ethanoic acid only cleave one
bond, for example tertiarybutylmercury ethanote in
ethanoic acid solution at 37.5°C does provide some
propene, tertiary butylethanoate and metallic mercury.[73]

The reaction proceeds by the following two steps:

$$R_2Hg + HX \longrightarrow RH + RHgX \qquad (54)$$

$$RHgX + HX \longrightarrow RH + HgX_2 \qquad (55)$$
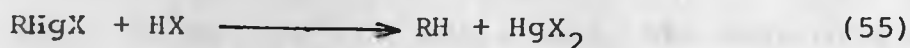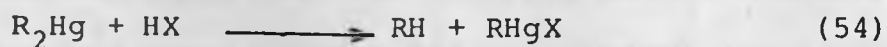
At moderate temperature, the reaction stops at the
first stage, provided strong concentrated mineral acids
are not used. The second stage of the reaction occurs
under more vigorous conditions.

Protonolysis of the aryl-mercury bond occurs
more readily, than that of alkyl-mercury bond.
Mineral acids, react with R_2Hg and RHgX with second
order kinetics (S_E2 mechanism) while with excess or
carboxylic acids, the kinetics are pseudo first order
(S_E1 mechanism).[153]

According to Nugent and Kochi,[73] evidence for nucleophilic participation by the conjugate base during protonolysis, as reported by Dessy[74] was limited and ambiguous.

Nugent and Kochi[73] studying the acidolysis of C-Hg bond in reactions of ethanoic acid with the unsymmetric dialkylmercurials, RHgR' (equation (56)) which proceed via rate limiting proton transfer, both leaving group effects HgR and cleaved group effects were detected. Leaving group abilities vary as $RHg = Bu^t Hg > Pr^i Hg > EtHg > MeHg$; the ease of cleavage of R' is in the sequence $R' = Me < Et > Pr^i > Bu^t$.

The logarithms of pseudo-first-order rate constants for RHg-Me cleavage correlate with the vertical ionization potentials determined by He(I). photoelecton spectroscopy. Thus, the effect of the leaving group RHg^+, on the rate of cleavage of RHgMe provides a good indication of the ability of R to delocalize positive charge in the transition state under conditions in which, the RH group remains intact. Large kinetic isotope effects (9-11) were found.

To account for their findings and the previously reported retention of stereochemistry at carbon,

Nugent and Kochi suggested that the reaction proceeds
via the three-centre transition state (16).

$$R - Hg - R' + HOAc \longrightarrow \begin{cases} \longrightarrow RHgOAc + R'H \\ \\ \longrightarrow RHgOAc + RH \end{cases} \qquad (56)$$

$$\left[\begin{array}{c} R \\ \vdots \\ Hg \\ \mid \\ R \end{array} \quad H \; ----OAc \right]$$

16
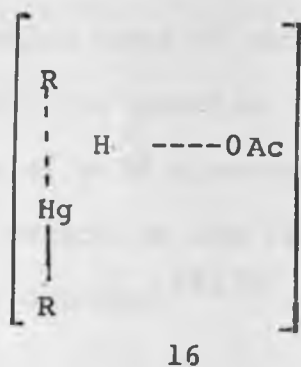
Earlier Dessay[74] had proposed a four-centre
transition state (17)

$$R - Hg - R \atop HCl \quad \rightleftharpoons \quad \begin{array}{c} R \longrightarrow Hg - R \\ \vdots \qquad \vdots \\ H \longrightarrow Cl \end{array} \longrightarrow RH + RHgCl \quad (57)$$

(17)
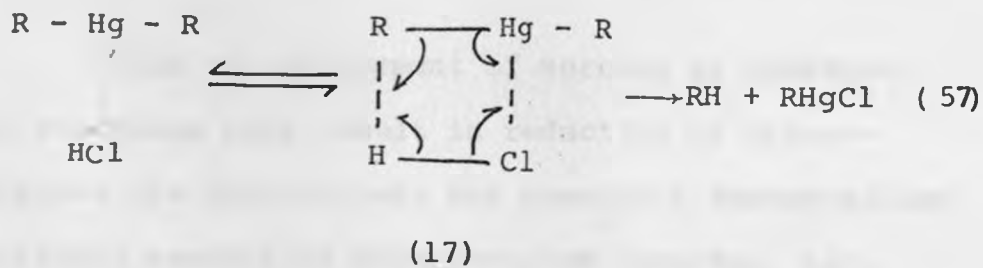
Protodemercuration[75] of exo-2-methylmercury-
norbornane is faster than that of endo isomer and was
considered further evidence for σ-participation in the
transition state.

Reaction of proton acids with solvomercurated
products leads to retro-formation of alkene and hence
alternative ways of reduction of organomercurials
are used, for example, $NaBH_4$ in demercuration. Another
problem of acid cleavage, especially using strong acids,
can be carbonium ion formation from the ionic organo-
mercury species.[28,76] e.g.

$$RHgX \rightleftharpoons RHg^+ + X^- \qquad\qquad (58)$$

$$RHg^+ \longrightarrow R^+ + Hg \qquad\qquad (59)$$
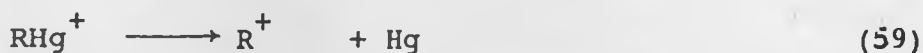
1.4.8   REDUCTION

This is replacement of mercury by hydrogen.
Other reactions that result in reduction of organo-
mercurials are protonolysis and homolytic decomposition
in solvents capable of hydrogen atom transfer, e.g.
alcohols or THF. The latter is not a good synthetic
method while protonolysis suffers from retro formation
to the alkene. Reduction of organomercurials can be

done, using lithium borohydride, sodium amalgam, the
alkali and alkali earths, lithium aluminium hydride,
hydrazine and sodium borohydride. Electrolytic methods
may also be used.

The mechanism often involves a free radical
chain mechanism.[77-79] In keeping with this mechanism:
the reactions are not stereospecific, free radical
rearrangements occur, and intermediate radicals may be
trapped by oxygen, to give oxygen drived products e.g.
(equation 60.).

$$\text{HgBr} \xrightarrow[\text{THF,H}_2\text{O}]{\text{NaBH}_4} \text{OH} + \text{OH} + \text{OH} + \quad (60)$$
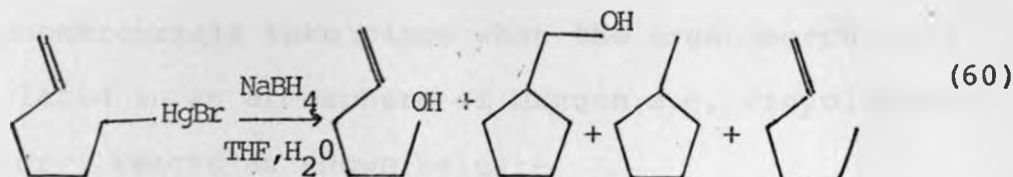
The possibility of the participation of ionic
intermediates was rejected after consideration of the
following reactions:-

(i) No rearrangements occured using Me_3CCH_2HgBr
implying the ion $Me_3CC^+H_2$ was not involved

(ii) When $NaBD_4$ was used to reduce Me_3CCH_2HgBr
in THF/H_2O a high incorporation of deuterium
was observed.

Sodium amalgam reductions do not proceed via free-
radical pathways. The reduction is stereospecific and
therefore could be of use in structure determination studies.

1.4.9   OXIDATION BY OXYGEN

Organomercury compounds have been described as being stable to oxygen and that they can be handled without special precautions, however, it is becoming increasingly apparent, that care must be exercised especially with secondary-alkyl, tertiary-alkyl, allyl, and benzyl mercury derivatives. The oxidation products are probably derived from free radical reactions.

Reactions involving secondary and tertiary organomercurials take place when the organomercurial is placed in an atmosphere of oxygen e.g. dicyclohexyl-mercury, reacts as shown below:-

$$(C_6H_{11})_2 \; Hg \; \xrightarrow{\; O_2 \;} \; [(C_6H_{11})_2Hg.O_2] \longrightarrow C_6H_{11}OH + C_6H_{10}O + Hg^O \qquad (61)$$
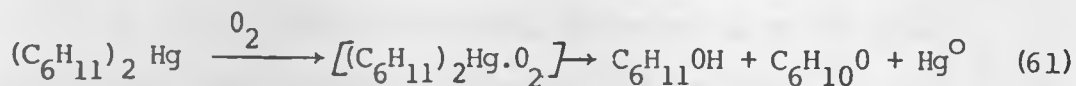
Primary, secondary and tertiary organomercurials will react with oxygen when in solution. In these reactions additional oxidation products are observed which are clearly derived from participation of the solvent. Dicyclohexylmercury in benzene at $60^O C$ produced the following oxidation products[80]:-

$$(C_6H_{11})_2Hg \xrightarrow{\quad O_2 \quad} C_6H_{11}OH + C_6H_{10}O + Hg^o + \text{small amounts of} \quad (62)$$

$$\phantom{(C_6H_{11})_2Hg \xrightarrow{\quad O_2 \quad}} 57\% \quad\quad 45\%$$

cyclohexene,
cyclohexane,
biphenyl and other
mercury containing
compounds.
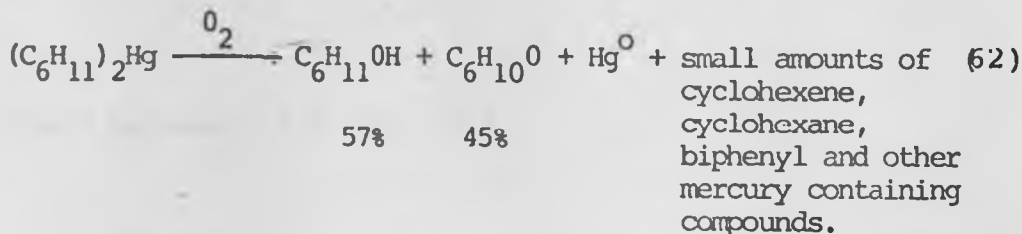
Similarly, in the oxidation of diisopropylmercury in benzene, solvent derived products (diphenylmercury, diphenyl, etc) are also produced but account for only a small proportion of the yield. The major products are isopropylmercuryisopropylate, isopropylmercury-hydroxide, isopropylalcohol, acetone, mercury, propylene and traces of propane.

The primary alkylmercurial, dibenzylmercury gives benzaldehyde when oxidized by oxygen in benzene. The mechanism of these oxidations have been studied by Razuvaev et al,[80] and Jensen and Heyman.[81]

Razuvaev's mechanism may be depicted as follows:

Scheme 11

$$R - Hg \quad R \longrightarrow [RHg-O-O-R] \qquad (i)$$
$$O = O \qquad\qquad\qquad A$$
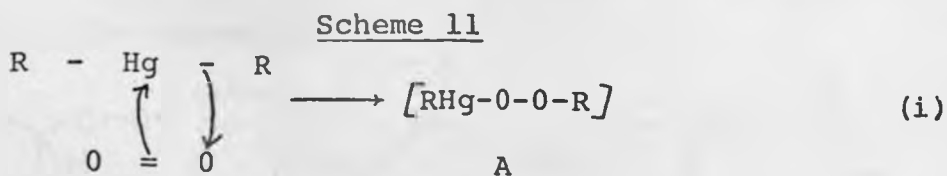
This is an oxygen attack on the metal, accompanied by subsequent migration of the alkyl group from the metal to oxygen, thus producing a peroxide A which may react

in a variety of ways to produce the observed products
e.g.

(a) The cleavage of 0 - 0 bond

R - 0 - 0 - Hg - R ⟶ RO· + ·O - Hg - R

R - Hg - R

2R - 0 ·· Hg - R

(alkoxy compound)

(b) The cleavage of oxygen-mercury bond which is a
partial decomposition to peroxy and alkyl mercury
radicals.

R - 0 - 0 - Hg - R ⟶ RO$_2^·$ + RHg·

The peroxyalkyl radical may then react with the
original organomercurial producing alcohols, ketones
and alkylmercury radicals.. In the dicyclohexylmercury
reaction for example,

(ii)

The formation of the RHg· in the reaction is proved by formation of substantial amounts of RHgCl when the reaction proceeds in halide containing solvents.

The RHg. radical can be further oxidized with formation of the alkylmercury peroxide radical. It may also decompose into mercury and an alkyl radical.

$$RHg^{\cdot} \quad + \quad 0 \ = \ 0 \ \longrightarrow \ RHgO_2^{\cdot} \quad \text{oxidation}$$

(iii)

$$R \ - \ Hg^{\cdot} \ \longrightarrow \ R^{\cdot} + Hg^O \quad \text{decomposition}$$
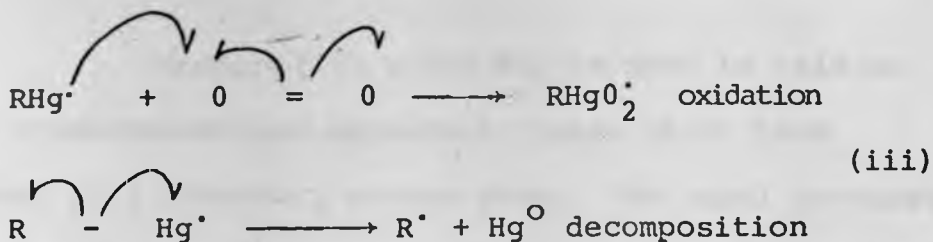
Alkylradicals $R^{\cdot}$ may be produced directly from the organomercurial thus:

$$R \ - \ Hg - R \ \longrightarrow \ R^{\cdot} + \ ^{\cdot}Hg - R \qquad \text{(iv)}$$
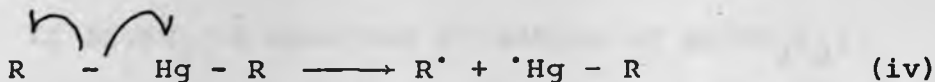
Thermal decomposition may also occur with R-Hg-0-R as follows:

$$R \ - \ Hg \ - \ 0 - R \ \longrightarrow \ RHg^{\cdot} + \ ^{\cdot}OR \qquad \text{(v)}$$
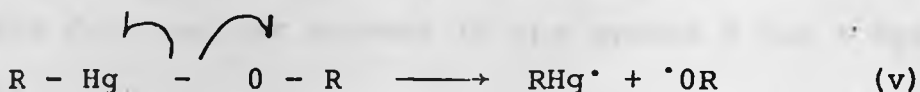
The alkyl and alkoxy radicals produced may react with the solvent and produce solvent derived oxidation products.

In addition to oxidation with oxygen organomercurials may also be oxidized by ozone, peroxides and peracids. These reactions also involve a free radical mechanism.

1.4.10   OXIDATION BY MERCURY(II) SALTS

Mercury(II) salts may be used to oxidize some organomercurials especially those which have mercury at a secondary carbon atom. The usual products are alcohols, (and products of their further oxidation) ethers, and metallic mercury.

The oxidant, Hg(II) salt, reduces to Hg(I) or Hg^o. If $RHgNO_3$ is oxidized by action of $Hg(NO_3)_2$, esters of nitric acid are produced, the formation of which is unusual under the experimental conditions.

Robson and Wright[82] proposed the following scheme for the free radical process in the system $R'HgX + HgX_2 + ROH$:

Scheme 12

$$HgX_2 \rightleftharpoons X^. + {}^.HgX \qquad (i)$$

$$XHg^. + R - O - H + X \rightleftharpoons ROHgX + HX \qquad (ii)$$

$$RO - HgX \rightleftharpoons RO^. + {}^.HgX \qquad (iii)$$
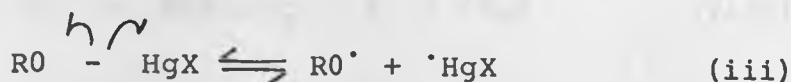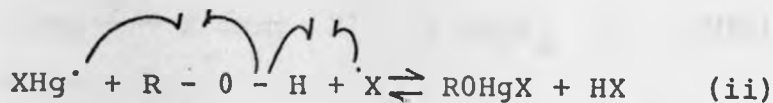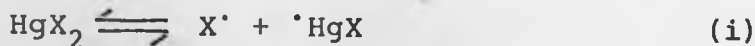
It is suggested that mercuric salt in alconol very slowly undergoes a homopolar fission into anionomercury

radicals and a radical (acetato, nitrato, methoxy, or hydroxy) derived from the salt or its solvolysis product. The behaviour is described in equations (i) (ii) and (iii). The reactions are slow especially at room temperature, as the chains are broken by oxygen. The radical population generated is also low.

$$R' - HgX \rightleftharpoons R: + \cdot HgX \qquad \text{(iv)}$$

(This is decomposition of some organomercuric salts into radicals and is able to neutralize the action of O_2).

$$XHg\cdot + XHg - OR \rightleftharpoons RO\cdot + Hg_2X_2 \qquad \text{(v)}$$

$$RO\cdot + R - HgX \rightleftharpoons ROR + \cdot HgX \qquad \text{(vi)}$$

$$XHg\cdot + XHg - X \rightleftharpoons X\cdot + Hg_2X_2 \qquad \text{(VII)}$$

$$X\cdot + R - HgX \rightleftharpoons R'X + \cdot HgX \qquad \text{(Viii)}$$
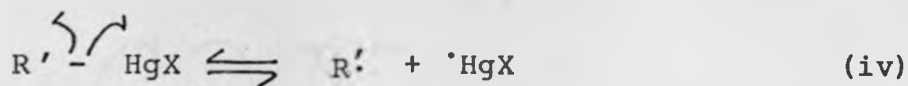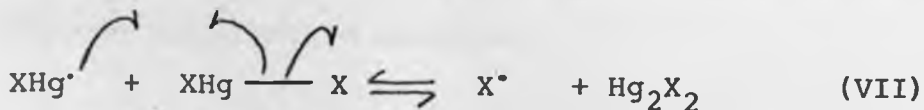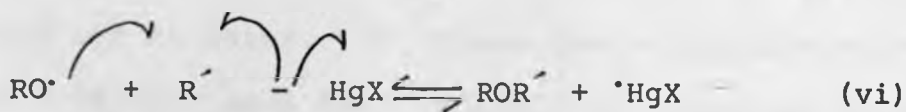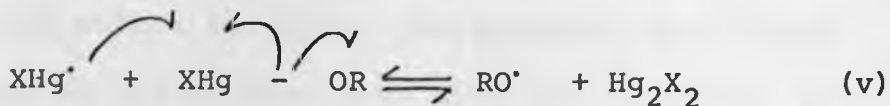
The following reactions terminate the radical chain

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$$RO \cdot + R - HgX \rightleftharpoons ROR + \cdot HgX \qquad \text{(vi)}$$

$$XHg \cdot + XHg - X \rightleftharpoons X \cdot + Hg_2X_2 \qquad \text{(VII)}$$

$$X \cdot + R - HgX \rightleftharpoons R X + \cdot HgX \qquad \text{(Viii)}$$

The following reactions terminate the radical chain

$$RO^. \longrightarrow H^. + (R - H) \quad 0 \qquad (ix)$$

$$H^. + RO - HgX \longrightarrow ROH + \ ^.HgX \qquad (x)$$

$$RO^. + \ ^.H \longrightarrow ROH \qquad (xi)$$

$$XHg^. + \ ^.HgX \rightleftharpoons Hg_2X_2 \qquad (Xii)$$

$$XHg^. + 0 = 0 + \ ^.HgX \rightleftharpoons XHgOOHgX \qquad (Xiii)$$

Oxidation of organomercuric salts by inorganic mercuric salts is inhibited by oxygen, but is accelerated to some extent by acids. The products from these reactions are esters, even when the reactions are carried out in water. All these facts together with kinetic studies show that radicals are involved in a self-regenerating chain reaction.

1.4.11   AUTOOXIDATION OF ORGANOMERCURY SALTS

Organomercury compounds, having a mercury atom at the secondary carbon atom, alkylmercuryethanoate (alkyl = cyclohexyl, isopropyl and ethylpropyl) in presence of $BF_3.0(C_2H_5)_2$, undergo auto-oxidation.

$$RO^{\bullet} \longrightarrow H^{\bullet} + (R - H) \; O \qquad (ix)$$

$$H^{\bullet} + RO - HgX \longrightarrow ROH + {}^{\bullet}HgX \qquad (x)$$

$$RO^{\bullet} + {}^{\bullet}H \longrightarrow ROH \qquad (xi)$$

$$XHg^{\bullet} + {}^{\bullet}HgX \rightleftharpoons Hg_2X_2 \qquad (Xii)$$

$$XHg^{\bullet} + O = O + {}^{\bullet}HgX \rightleftharpoons XHgOOHgX \qquad (Xiii)$$

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Cyclohexylmercury trifluoromethylethanoate and
cyclohexylmercury trifluoromethylnitrate, undergo
monomolecular auto-oxidation even in the absence of the
catalyst. It is thought the reaction involves a
heteropolar mechanism.[83] In this case, mercury and
olefins are produced. The reaction takes place at $50^{\circ}C$
in methanol, in presence of $HgCl_2$, which combines with
the olefinic double bond (methoxymercuration reaction).
It is proposed, that catalysts, such as Lewis acids
increase the polarity of the C-HgX bond. Phenylmercury-
ethanoate and the primary organomercury salts such as
butylmercuryethanoate do not undergo this type of
oxidation.

A scheme for the heteropolar process(R = cyclohexyl)
is as follws:-

Scheme 13

$$RHgOCOCH_3 + BF_3 \rightleftharpoons RHg^+ + [BF_3OCOCH_3]^-$$

$$RHg^+ \longrightarrow Hg^0 + R^+$$

$$R^+ \longrightarrow H^+ + C_6H_{10}$$
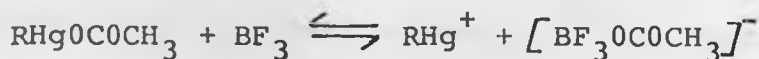
A reaction which goes through a cyclic, six-membered transition is also possible:
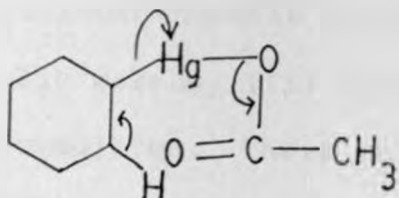
1.4.12   ALLYLIC OXIDATION

Cyclohexene may be oxidized at the allylic position by mercury (II) ethanoate in ethanoic acid, to give cyclohexylethanoate.[84]

(63)
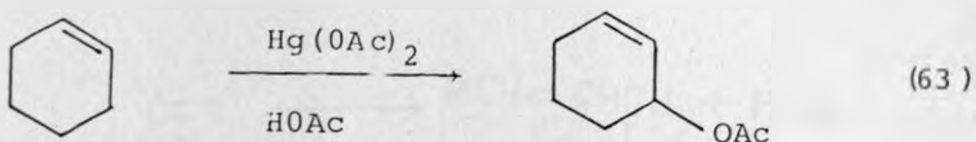
Considerable discussion has taken place, as to whether an organomercury adduct is involved,[85] but from studies of α-pinene oxidation,[84] it appeared that an allylic mercurial was involved as an intermediate. Strong evidence that allylic mercurials were involved in this reaction was provided by Winstein et al[86] and Wolfe et al.[87] in their thorough studies of the chemistry of allylic mercurials.

Rappoport et al [88,89] have reviewed the allylic

oxidation reaction of olefins by mercury (II) ethanoate

and through kinetic studies have demonstrated that

allylic mercury (II) ethanoates are the most plausible

intermediates. These workers proposed that allylic

oxidation involves a rate-determining formation of

allylic mercury (II) ethanoate by an SE' reaction and is

followed by product determining solvolysis of the

mercurial.

The mechanism below was proposed

Scheme 14
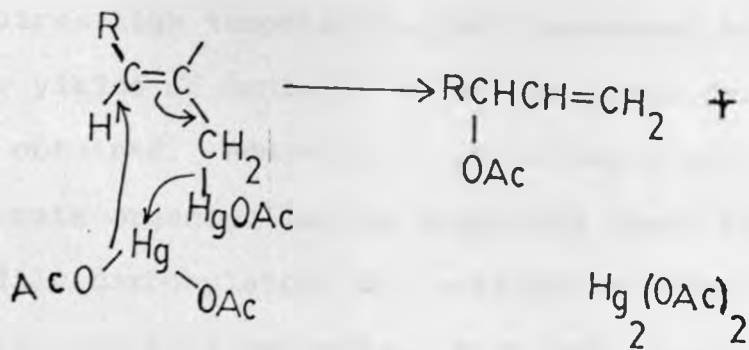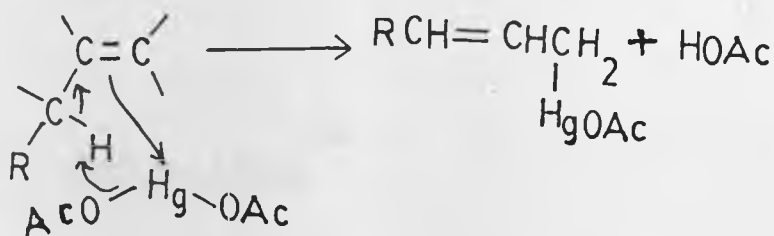
Allylic oxidation is also suggested to be a Diels-Alder reaction. Hoye and Rother,[90] for example reports that, oxidation of 1-vinylcycloalkenes is a Diels-Alder reaction which results to allylic diene ethanoates i.e.

Scheme 15
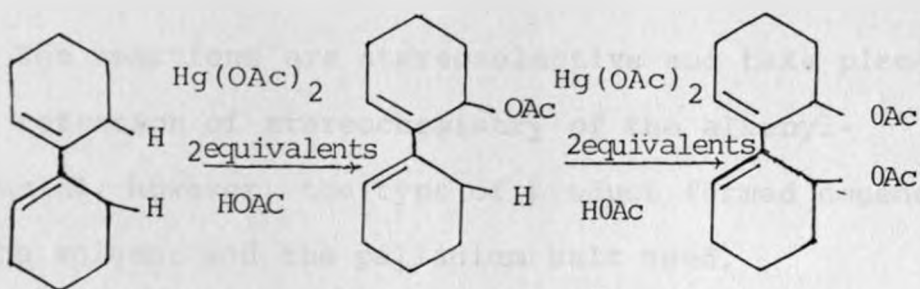
1.4.13   CARBONYLATION[154]

Uncatalysed carbonylation of organomercurials requires high temperatures and pressures and then only poor yields of carboxylic acids and their derivatives are obtained. Addition of palladium salts, usually generate organopalladium compounds which are much more readily carbonylated, but even under these conditions alkyl- and aryl-mercurials give only poor yields of carbonylated products. These reactions have little

synthetic value; on the other hand, 1-alkenylmercuric halides which are readily available from alkynes, react with carbon monoxide at atmospheric pressure in an alcoholic solvent in the presence of palladium chloride or lithium chloride, to give α, β - unsaturated esters in high yield. α, β - Unsaturated carboxylic acids can also be obtained but less readily, by conducting the reaction in THF.

The reactions are stereoselective and take place with retention of stereochemistry of the alkenyl-mercurial, however, the type of product formed depends on the solvent and the palladium salt used.

The reactions may be effected using stoichiometric or catalytic amounts of palladium chloride, in the latter case, copper (II) chloride is added to reoxidize Pd^O back to Pd(II).

An example for this reaction is:-

$$\text{(structure)} \xrightarrow[\text{PdCl}_2, \text{LiCl}]{\overset{\text{HgCl}_2}{\underset{\text{CO,EtOH}}{}}} \text{(structure)} \quad \text{COEt} \qquad (64)$$

93%
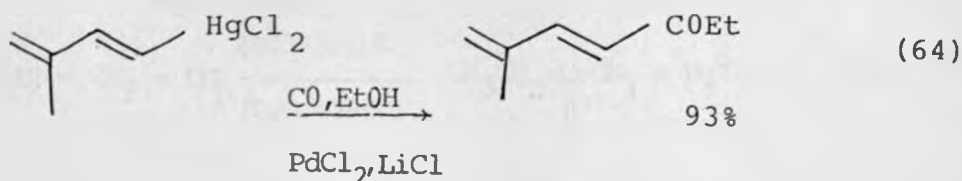
The mechanism of oxypalladation by palladium (II) salts have been investigated but is not well understood.

Scheme 16

$$>C = C< \quad + PdCl_2 + H_3O^+ \longrightarrow [PdCl_2(H_2O)olefin] + Cl^- + H^+$$

$$\downarrow$$

$$CH_3-CH$$
$$\parallel$$
$$O$$
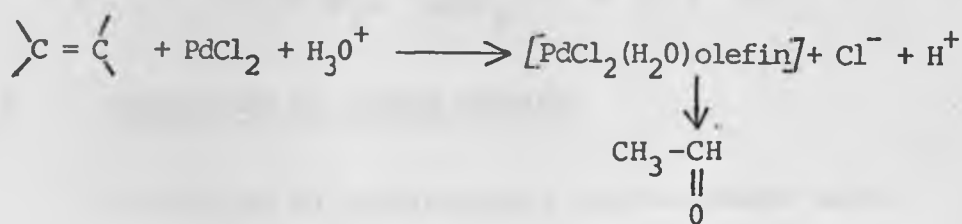
Mercury (II) has also been reported to catalyze carbonylation reactions.[91-93] Arai et al and Macho et al. for example, pointed out that mercury (II) chloride on activated carbon would catalyze the reaction described below by Saito[94] in 1973. Mercury (II) chloride has also been reported to catalyze aminomercuration.[95]

Saito described the oxidation of alkenes to produce aldehydes and ketones using mercury (II) salts in aqueous solution. Typical reactions are shown below:-

$$CH_3CH = CH_2 \xrightarrow[H_2O, \ HgCl_2]{(320-31)K} CH_3-C-CH_3 + Hg^O \qquad (65)$$
$$\parallel$$
$$O$$

$$CH_3CH = CH_2 - CH_3 \xrightarrow[H_2O, \ HgCl_2]{(303-311)K} CH_3CH_2-C-CH_3 + Hg^O \qquad (66)$$
$$\parallel$$
$$O$$

$$CH_3CH = CHCH_3 \xrightarrow[\text{H}_2\text{O, HgCl}_2]{(270 - 301)\text{K}} CH_3CH_2\overset{\overset{\text{O}}{\|}}{C} - CH_3 + Hg^O \qquad (67)$$

$$CH_3CH = CH-CH_2CH_3 \xrightarrow[\text{H}_2\text{O, HgCl}_2]{(270 - 282)\text{K}} CH_3CH_2CH_2\overset{\overset{\text{O}}{\|}}{C} CH_3 + Hg^O \qquad (68)$$
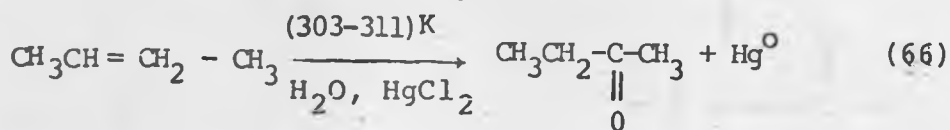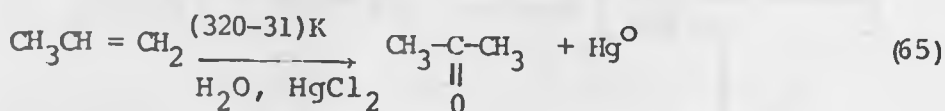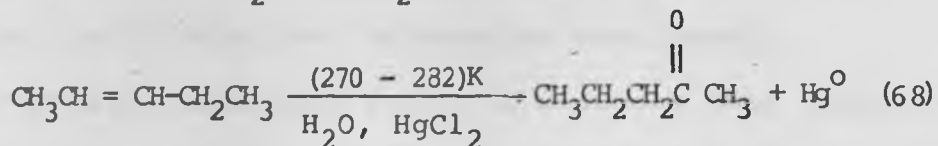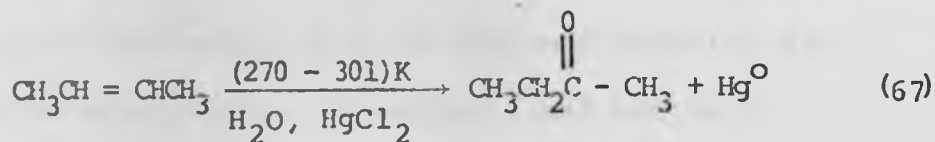
1.4.14   OXIDATION BY OTHER METALS

Oxidation of unsaturated hydrocarbons with mercury(II), thallium(III) or lead(IV) can afford a variety of products depending on the nature of the anion, the cation, the solvent and the structure of the unsaturate. Unfortunately, oxidation of unsaturated hydrocarbons by toxic thallium (III) compounds has not been an exploited area of research as compared to that of mercury.[96] Oxidation of unsaturated hydrocarbons by thallium (III) nitrate in methanol, however, is a reaction of synthetic importance in preparation of aldehydes and ketones from olefins.

Scheme 17

$$\overset{\diagdown}{\diagup}C = C\overset{\diagup}{\diagdown} + Tl(NO_3)_3 \xrightarrow{CH_3OH} \begin{bmatrix} \text{Oxythallation} \\ \text{adduct} \end{bmatrix}$$

$$\downarrow$$

$$-\overset{|}{\underset{|}{C}} - \overset{\overset{\text{O}}{\|}}{C} -$$
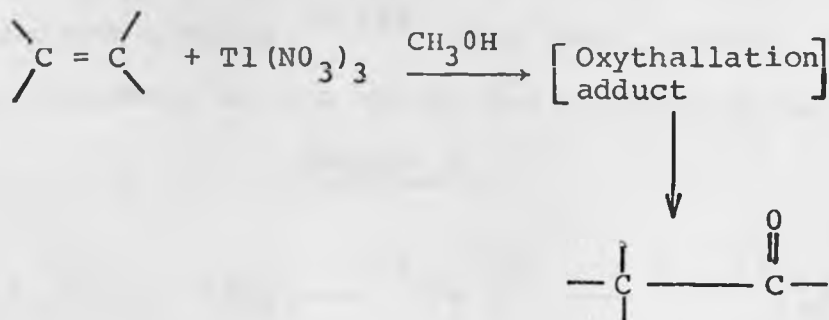
The final products of oxidation depend on the nature of the media; e.g. in aqueous solution the products are glycols, aldehydes, and ketones. In ethanoic acid solution, ethanoates are formed. Structurally rearranged products suggests that product-determining intermediates with some positive charge (thallium ions) are involved.[97,98]

(69)
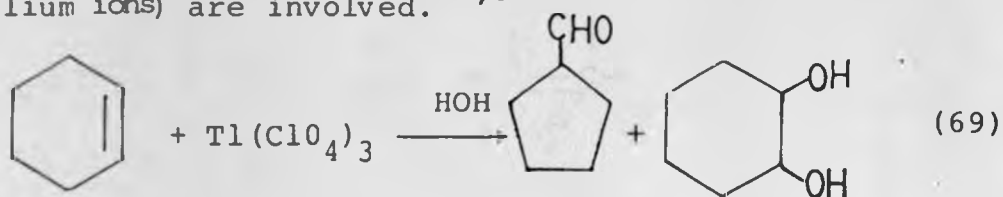
Kinetic studies are sometimes difficult because thallic ethanoate forms a double salt with the thallous ethanoate which arises from the rapid solvolysis of oxythallium adduct. Studies on the reaction of ethene and thallium ethanoates, suggest that an activated oxythallation complex is formed. This complex has a high degree of order in which considerable carbon-thallium bond formation has occurred. Rearrangement of a π-complex (19) to a σ-organothallium species is consistent with stereochemical studies in the cyclohexene systems.[99,100] This data, though limited is in agreement with a cyclic activated complex (20)

Scheme 18
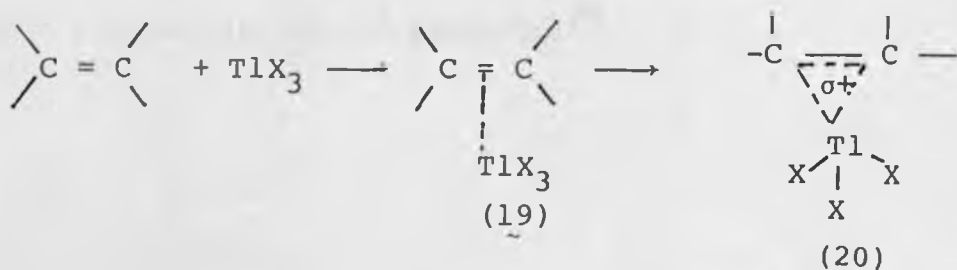
It is also possible, that the reaction involves
the fast reversible formation of a bridged ion (22).
The rate limiting step is thought to be the attack of
the solvent on the ion (22).

Scheme 19
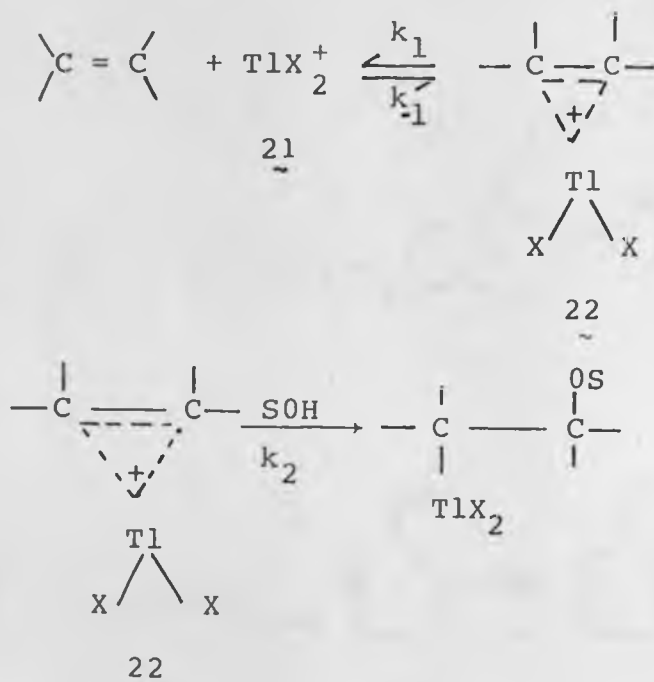
The most common reactions of lead (IV) salts with
unsaturated compounds involves the use of lead ethanoate.
Lead ethanoate reacts with carbon-carbon double bonds
to give a wide variety of products:[96]

$$\text{C} = \text{C} \quad + \quad Pb(OAc)_4 \longrightarrow -\overset{|}{\underset{|}{\text{C}}} - \overset{|}{\underset{|}{\text{C}}} - \quad + \quad Pb(OAc)_2 \qquad (70)$$
$$\overset{|}{\underset{OAc}{}} \quad \overset{|}{\underset{OAc}{}}$$

$$-\overset{|}{\underset{|}{\text{C}}} - \overset{|}{\text{C}} = \text{C} + Pb(OAc)_4 \longrightarrow \overset{OAc}{-\overset{|}{\underset{|}{\text{C}}}} - \overset{|}{\text{C}} = \text{C} + HOAc + Pb(OAc)_2 \quad (71)$$

 $+ Pb(OAc)_4 \longrightarrow$ $+ Pb(OAc)_2 \qquad (72)$

(73)

 $+ Pb(OAc)_4 \longrightarrow$
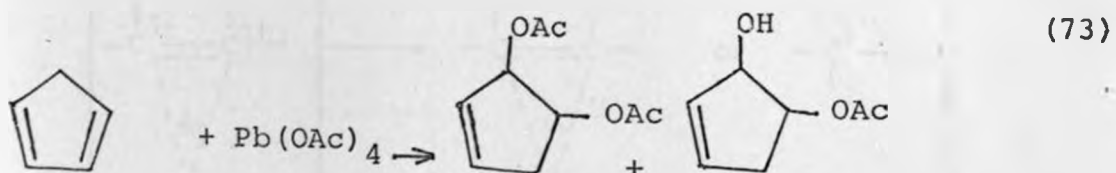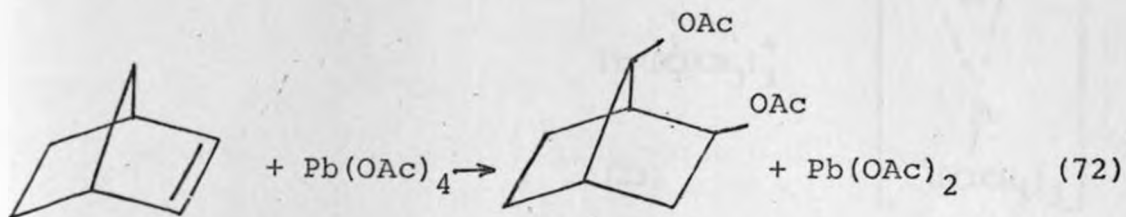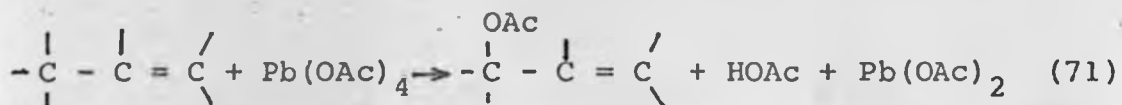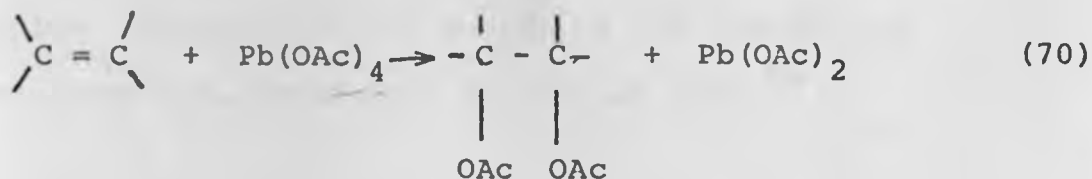
Lead ethanoate is capable of reacting by a free-radical pathway, but it is not unreasonable to expect lead ethanoate to be an electrophilic oxidant which can reversibly add to carbon-carbon double bond to give a $\overset{\pm}{\pi}$ - complex (23) which could resemble (24). This

complex, depending on the degree of the carbon-lead
bond formation, could lead to (25) or (26).[96]

Scheme 20

(23)

(24)
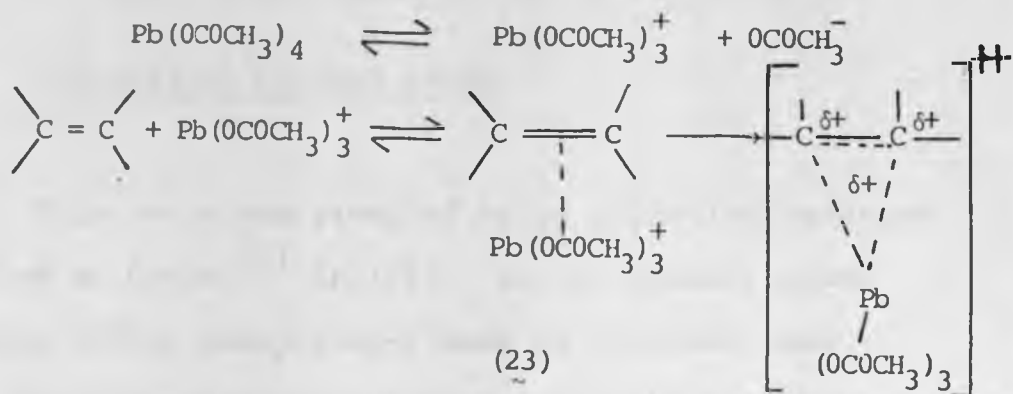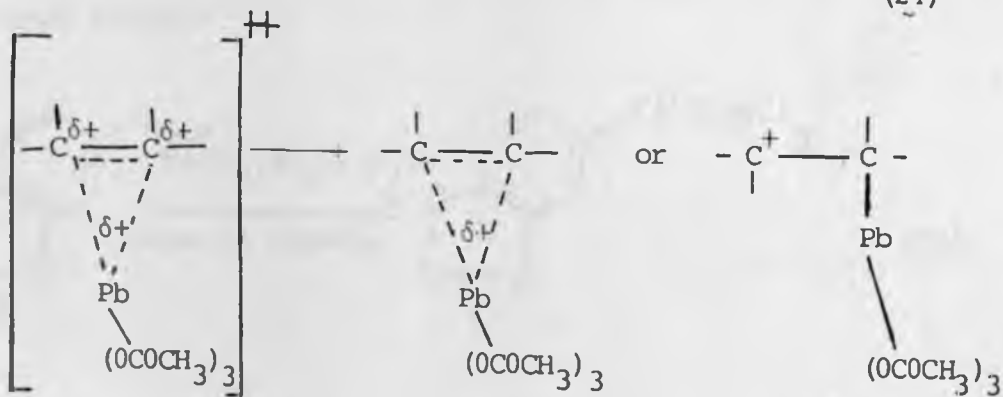
(24)   (25)   or   (26)

Products

This mechanism is analogous to that proposed for oxymercuration and oxythallation, however, in contrast to mercury (II) and thallium (III) salts no acyclic or monocyclic intermediate of organolead compounds have been isolated.

1.5 OBJECTIVES OF THIS STUDY

This study was prompted by an oxidation reaction reported by Ormand[101] in 1967. In his general study of oxidation of phenylprop-1-enes he reported that, 3, 4- methylenedioxyphenylprop-1-ene could be oxidized, as shown below:-

(74)
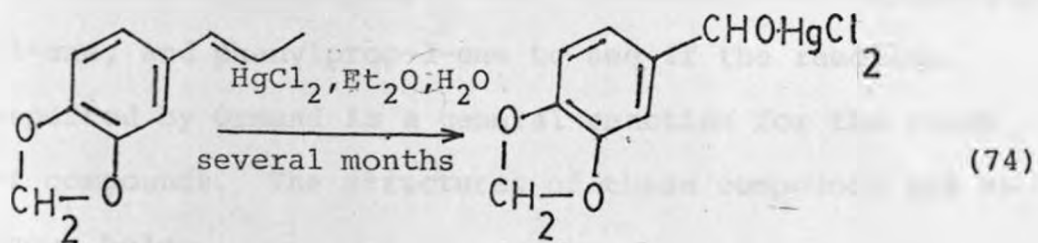
The reported yield was 45%.

The oxidation of alkenes by mercury (II) salts is a well known reaction, but the reaction type described by Ormand, has not previously been reported. This reaction is extremely slow and attempts will be made in this study to increase the reaction rate in order to make the reaction more synthetically useful. The

reaction has considerable industrial potential, especially as the mercury (II) chloride can be recovered unchanged on completion of the reaction. A useful oxidation would be the oxidation of isoeugenol (4-hydroxy-3-methoxyphenylprop-1-ene), which may be readily obtained from cinnamon leaf by isomerisation of eugenol. Oxidation of the double bond would produce vanillin, a compound of commerical importance in the flavouring and cosmetic industry.

It is proposed to examine the oxidation of isoeugenol and other phenylprop-1-enes such as anethole (4-methoxyphenylprop-1-ene), 3,4-dimethoxyphenylprop-1-ene, 3,4-methylenedioxyphenylprop--1-ene, and phenylprop-1-ene to see if the reaction reported by Ormand is a general reaction for the class of compounds. The structures of these compounds are as shown below.
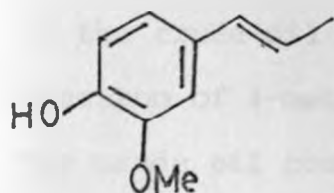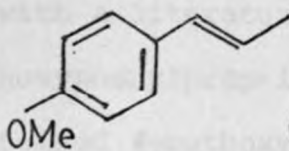
Isoeugenol   anethole   3,4-dimethoxy-
                                   phenylprop-1-ene
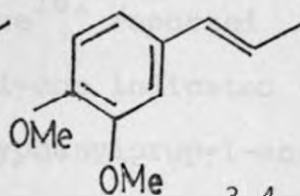
Phenyl-   3,4-methylenedioxy-
prop-1-ene   phenylprop-1-ene
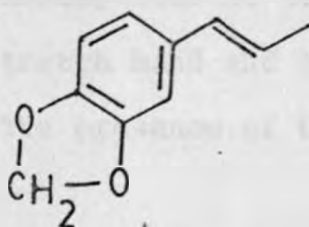
2.1   RESULTS AND DISCUSSION (SYNTHESIS)

The main objective of this project was to
study the oxidation of phenylprop-1-enes using mercury(II)
salts, however, some of the phenylprop-1-enes
such as 4-methoxyphenylprop-1-ene (anethole),
phenylprop-1-ene, 3,4-dimethoxyphenylprop-1-ene and
3,4-methylenedioxyphenylprop-1-ene (isosafrole) were not
locally available at the beginning of the project
and were therefore synthesized from available compounds.

4-Methoxyphenylprop-1-ene was obtained as a
crude oil by steam distillation of star anise seeds
(Illicium verum). An attempt to purify the crude oil
by distillation resulted in decomposition.

Comparison of the infrared and n.m.r. spectra
of the crude oil with a literature[102] reported
spectrum of 4-methoxyphenylprop-1-ene indicated that
the crude oil contained 4-methoxyphenylprop-1-ene
as the major product. In addition, the infrared
spectrum showed absorptions at νmax 2770 cm^{-1},
moderate, H-CO stretch band and 1715 cm^{-1}, strong,
C = 0 stretch. The presence of these absorptions

indicates presence of both aldehyde and ketone. This
was not a surprise because the crude oil (essential
oil) from star anise seeds contains, among other
compounds, 4-methoxyphenylprop-1-ene (80- 89%),
4-methoxyphenylpropanone and 3,4-methylenedioxyphenyl-
prop-2-ene. In addition the oil may be decomposed
by light and the 4-methoxyphenylprop-1-ene be oxidized
to 4-methoxybenzaldehyde and its corresponding acid
by atmospheric oxygen.[103]

Steam distillation was thought to be a good method
for extracting 4-methoxyphenylprop-1-ene, because
the components of the volatile oil were distilled at
temperatures below their boiling points and charring
and undesirable products, were avoided.

Further purification of 4-methoxyphenylprop-1-ene
was not necessary because the previously ordered
sample from Britain arrived.

Phenylpropan-1-ol was readily available and
dehydration using phosphoric acid (85%) as a catalyst,
produced a compound which distilled at 175°C. This
compound was produced in 60% yield and its i.r.
spectrum showed the absence of an absorption band at
νmax 3300 cm^{-1}, O-H stretch but showed an absorption

band at νmax 1630 cm^{-1}, C=C stretch. Absence of the 0-H stetch band at νmax 3300 cm^{-1} and appearance of the C = C stretch band at νmax 1630 cm^{-1} indicated that the dehydration had occurred. The i.r. spectrum of this compound compared well with a literature[104] reported spectrum of phenylprop-1-ene. Furthermore, presence of olefinic protons at δ, 6.3 - 5.8, multiplet, 2H, ArCH = CH and the total number of protons as deduced from integrated area of the n.m.r. signals confirmed the compound to be phenylprop-1-ene.

A yield of 60% is not unexpected because the phenylprop-1-ene produced is conjugated and would therefore be the favoured thermodynamic product. However, purification of the phenylprop-1-ene by a second distillation may have lowered the yield by losing some of the compound in the apparatus.

3,4-dimethoxyphenylprop-1-ene was prepared from a reaction of 4-hydroxy-3-methoxyphenylprop-1-ene with iodomethane in presence of potassium carbonate as the base and propan-2-one as the solvent medium. On running i.r. spectrum of the reaction mixture there was a strong absorption band centred at νmax 3450 cm^{-1}, 0-H stretch, but the T.L.C. showed the

mixture to have a fast running and a slow running compounds. The separation of these components was done using a wet column of aluminium oxide and petroleum ether b.p. (40-60°C) as an eluent.

The i.r. spectrum of the reaction mixture obtained after evaporating the solvent showed absorption band at νmax 3450 cm^{-1}. Presence of this band at νmax 3450, 0-H stretch in the reaction mixture indicated that the reaction had not gone to completion, however, its absence in the separated compound indicated that methoxylation had taken place. Comparison of the i.r. spectrum with that reported in literature[105] and the n.m.r. spectrum of the compound confirmed it to be 3,4-dimethoxyphenylprop-1-ene.

Although 3,4-dimethoxyphenylprop-1-ene could be prepared by this method, chromatographic separation was very time consuming. However, the reaction could have gone to completion if the conditions had been modified; for example, since 4-hydroxy-3-methoxyphenylprop-1-ene is electron rich, a stronger base, such as sodium hydroxide could have been used. Furthermore, carrying out the reaction at higher temperatures and use of phase transfer catalysts could

result in greater solubility of the base and
consequently more base would be available for the
reaction.

2.1.1   SYNTHESIS OF 3,4-METHYLENEDIOXYPHENYLPROP-1-ENE
        (ISOSAFROLE)

Because 3,4-methylenedioxybenzaldehyde
(piperonal) was available it was chosen as the starting
material for this synthesis. It was reacted with
ethyl magnesium bromide to produce
3,4-methylenedioxyphenylpropan-1-Ol in
good yield. Care was taken to hydrolyse the product
of the Grignard reaction with an aqueous solution of
ammonium chloride, because addition of strong mineral
acids such as hydrochloric acid and sulphuric acid
may have resulted in dehydration of the secondary
alcohol and consequently polymerisation may have
resulted.

The infrared spectrum of the unpurified
3,4-methylenedioxyphenylpropan-1-ol showed an
absorption at νmax 1700 cm^{-1}, strong C = O stretch,
which indicated presence of unreacted 3,4-methylene-
dioxybenzaldehyde, which on addition of sodium

hydrogen sulphite formed a complex which was removed by filtration.

The i.r. spectrum of the pure alcohol showed absorptions at νmax 3360 cm^{-1}, for a broad intermolecular hydrogen bonded, O-H stretch, and at νmax 1235 cm^{-1}, a strong O-C stretch, however, absorption at νmax 1700 cm^{-1}, strong, C = O stretch, was conspicuousily missing. Presence of O-H stretch at νmax 3360 cm^{-1} and absence of C = O stretch at νmax 1700 cm^{-1} indicates alkylation of the aldehyde had taken place and the alcohol (3,4-methylenedioxyphenyl-propan-1-ol) had been formed.

A possible mechanism for the alkylation reaction may be represented as follows:-

Scheme 21

$$C \!=\! O \qquad R \;-\; MgX \longrightarrow R - \overset{|}{\underset{|}{C}} - \overset{-}{O} \; \overset{+}{M}gX$$

$$\Big\downarrow \; H_2O, \; H^+$$

$$R - \overset{|}{\underset{|}{C}} - OH + Mg^{2+} + X^-$$

$$+ \; H_2O$$
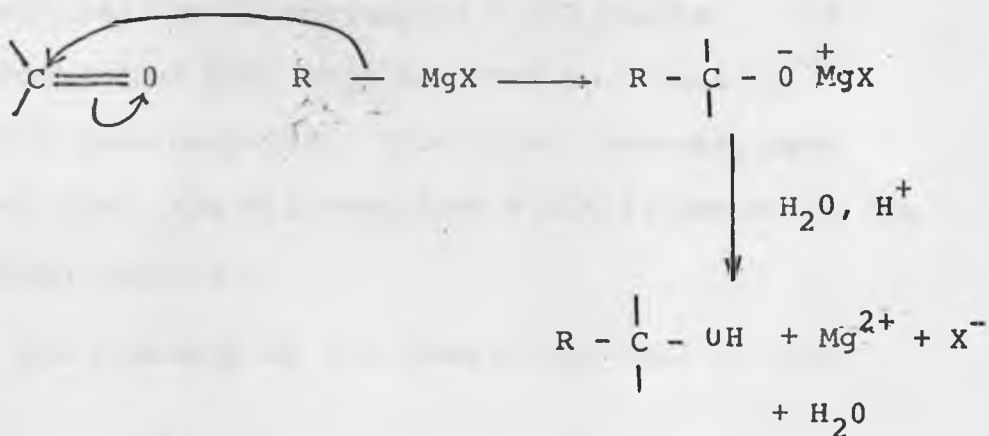
Dehydration of 3,4-methylenedioxyphenylpropan-1-ol using concentrated phosphoric acid as the catalyst was attempted several times but each attempt resulted in polymerization and decomposition. An attempt to carry out this reaction in Dean and Stark apparatus showed that, water was eliminated, but an attempt to separate any 3,4-methylenedioxyphenylprop-1-ene produced resulted in polymerization and decomposition.

Dehydration of this alcohol was, however, achieved by reacting the alcohol with potassium hydroxide dissolved in ethanol and water, stirring for 32 hours, and heating under reflux for a further 1 hr. After cooling and acidifying, the mixture was extracted with chloroform. On drying and concentrating the chloroform extract, a yellow oil was obtained.

The i.r. spectrum of the crude oil showed a band at νmax 1635 cm^{-1}, conjugated C = C stretch. This was consistent with that reported by Grasselli,[106] for the same compound. Thin layer chromatography showed that, the oil contained a little amount of the starting material.

The presence of i.r. absorption band at νmax

1635 cm^{-1}, C = C stretch and the absence of the absorption band at νmax 3360 cm^{-1}, O-H stretch indicates that dehydration and formation of another compound (3,4-methylenedioxyphenylprop-1-ene) had resulted.

The failure of the dehydration reaction under acidic conditions was rationalized in the following way: The dehydration reaction involves El mechanism where the acid protonates the O-H group and converts it into a good leaving group $(OH_2)^+$. The protonated alcohol undergoes heterolysis to form water and carbocation. Once formed the carbocation may: combine with a nucleophile, rearrange to more stable carbocation or eliminate a proton to form an alkene. The mechanism may be presented as shown below:

Scheme 22

(i) $-\overset{|}{\underset{\overset{|}{O}H}{C}} - \overset{|}{\underset{|}{C}} - + \text{ H:B} \overset{\text{fast}}{\rightleftharpoons} -\overset{|}{\underset{H}{C}} - \overset{|}{\underset{(OH_2)^+}{C}} - \quad + \text{ B:}$

       alcohol   acid   protonated conjugate
                                 alcohol   base

(ii) $\quad$ $-\overset{\mid}{\underset{H}{C}} - \overset{\mid}{\underset{(OH_2)^+}{C}} \rightleftharpoons -\overset{\mid}{\underset{H}{C}} - \overset{\mid}{\underset{+}{C}} - \quad + H_2O$

(iii) $-\overset{\mid}{\underset{\substack{\mid \\ B:}}{C}} \overset{H}{\diagdown} \overset{\mid}{\underset{+}{C}} - \rightleftharpoons \overset{\diagdown}{\underset{\diagup}{C}} = \overset{\diagup}{\underset{\diagdown}{C}} \quad + H:B$
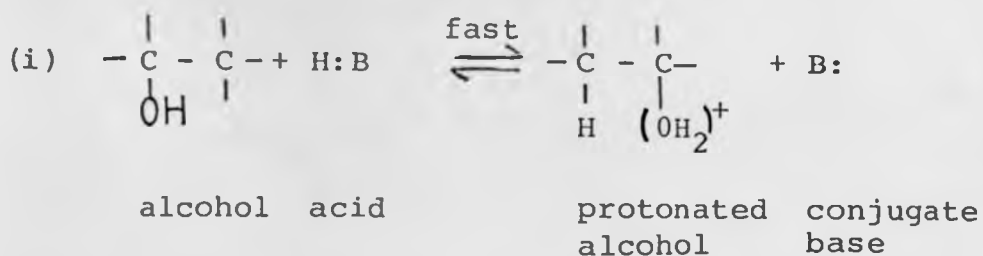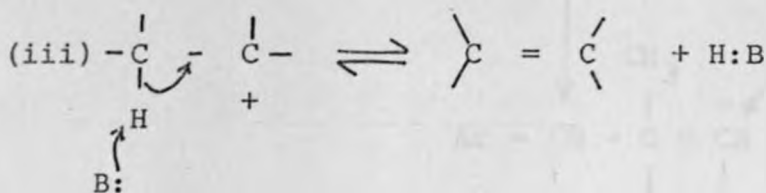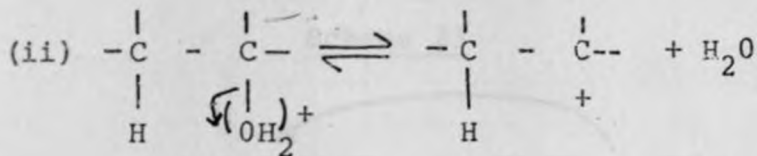
Dehydration is reversible, but under the conditions
of the experiment, the alkene being volatile is
generally driven from the reaction mixture and the
equilibrium is shifted to the right. However,
3,4-methylenedioxyphenylprop-1-ene has a relatively
high b.p. 248°C [107] and therefore the equilibrium was
mainly to the left. This therefore called for strong
heating and as a result decomposition or polymerization
occurred. The polymerization was thought to proceed
by the following mechanism:

Scheme 23

$$·Ar - CHCH_2CH_3 \quad + \quad CH_3CH \; = \; CHAr$$

$$Ar - \underset{\underset{\underset{CH_3}{|}}{CH_2}}{\overset{\overset{CH_3}{|}}{CH}} - \underset{H}{\overset{}{C}} - \underset{Ar}{\overset{}{CH}} \quad \underset{Ar}{\overset{+}{CH}} = \underset{}{\overset{CH_3}{CH}} \quad \rightarrow etc$$
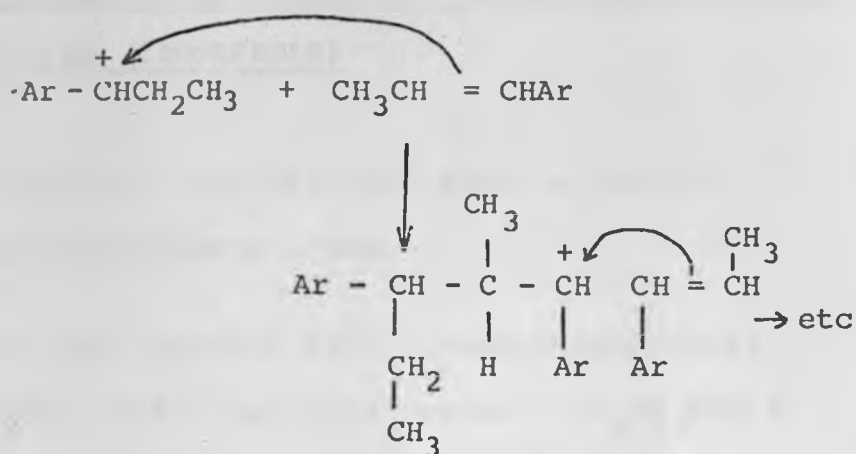
Base catalysed dehydration which gave good results did not involve strong heating conditions and did not result in polymerization. However, the presence of unreacted alcohol as indicated by TLC, showed that the reaction had not gone to completion, but stirring or heating under reflux for a longer period could have yielded better results.

Possible mechanism would be bimolecular elimination (E2).

(75)
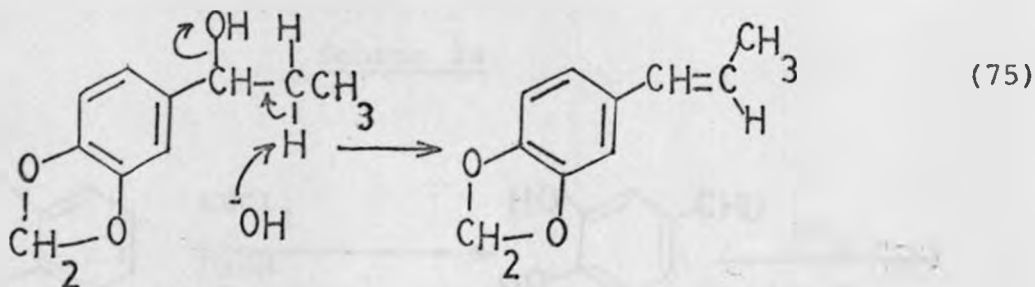
2.1.2   OTHER ATTEMPTS TO OBTAIN 3,4-METHYLENEDIOXYPHENYL-
         PROP-1-ENE (ISOSAFROLE)

The following attempts were made to obtain
3,4-methylenedioxyphenylprop-1-ene:-

(1) Synthesising the compound from 3,4-methylenedioxy-
    benzaldehyde and the Grignard reagent (CH_3CH_2MgBr);
    and dehydration of the resulting alcohol.
(2) Isomerisation of 3,4-methylenedioxyphenylprop-2-ene
     (safrole).
(3) Hydrochlorination of 3,4-methylenedioxyphenyl-
     prop-2-ene followed by dehydrohalogenation.

2.1.3   ATTEMPTED SYNTHESIS OF 3,4-METHYLENE-
         DIOXYPHENYLPROP-1-ENE

The following scheme had been proposed for
the synthesis of 3,4-methylenedioxyphenylprop-1-ene:[103]

Scheme 24
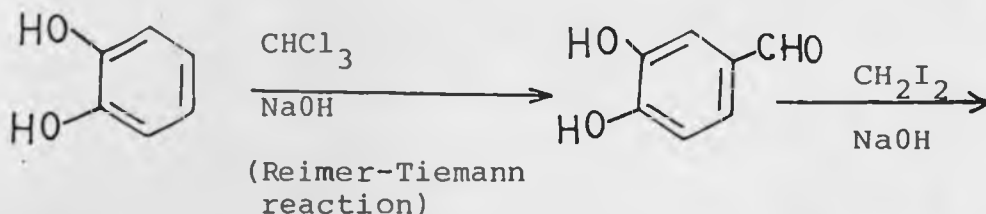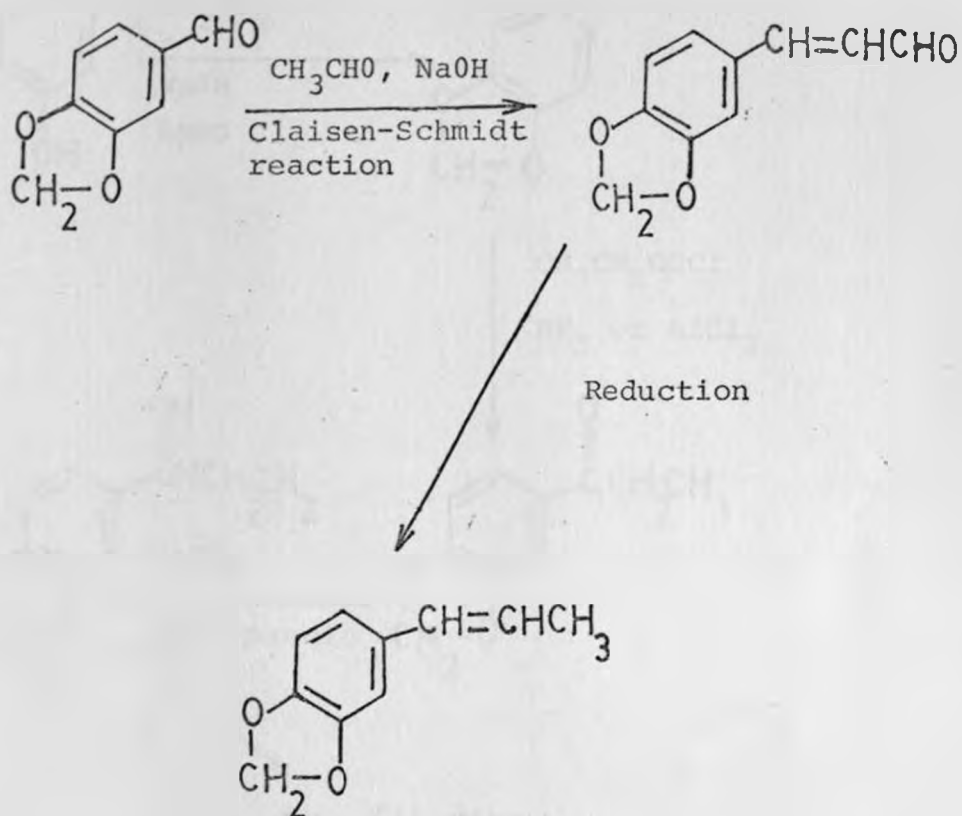
However, due to possibilities of difficulties in reduction of the carbonyl group in presence of the conjugated carbon-carbon double bond, the scheme shown below was thought to have greater potential.

Scheme 25
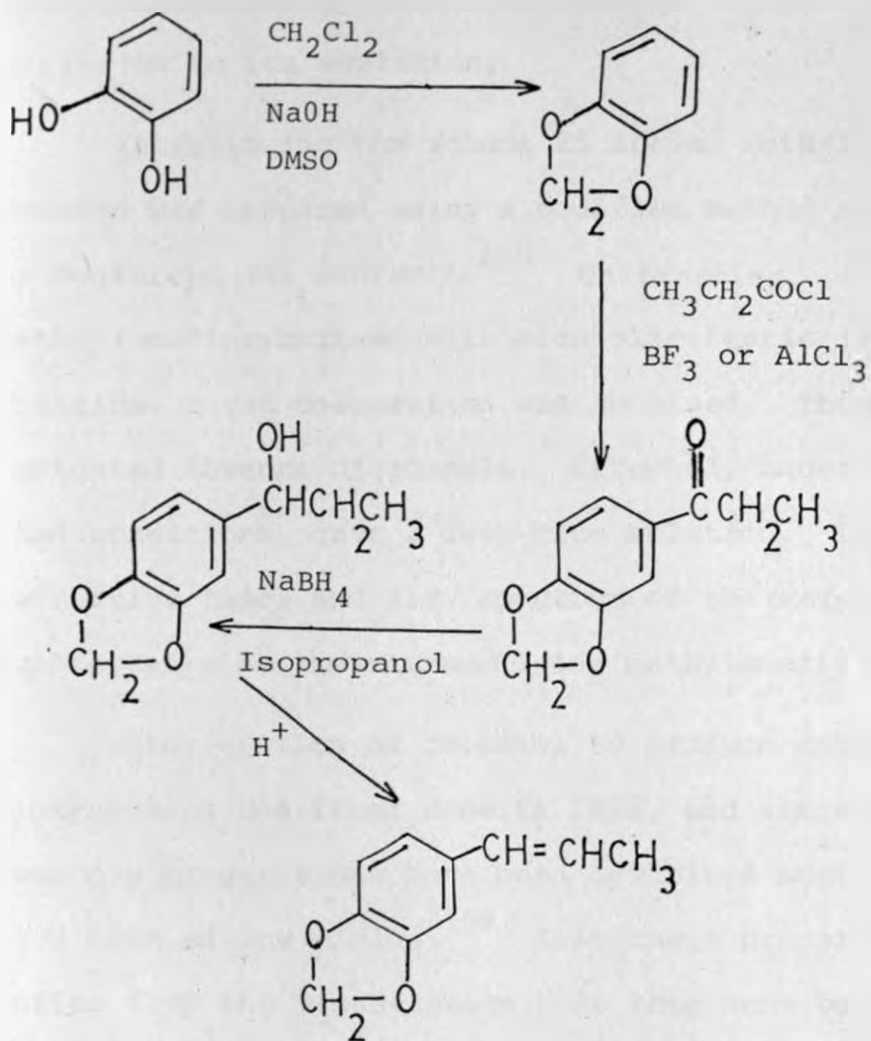
Aryl ethers and phenols contains ring activating and ortho-para-directing groups and consequently Friedel-Crafts acylation would be expected to be carried out easily on these type of compounds. However, for phenols 0-acylation may be in

competition with Friedel-Crafts acylation and as such, methylenation of 1,2-dihydroxybenzene (catechol) was preferred to its acylation.

In following the scheme 25 above, methylenedioxy-benzene was prepared using a modified method reported by Bonthrone and Conforth.[109] On treating methlylenedioxybenzene with alcoholic Ferric (III) chloride, a red colouration was obtained. This indicated absence of phenols. Catechol, under the same conditions, gave a deep blue solution. The refractive index and i.r. spectrum of the compound were consistent with the compound being methylenedioxybenzene.

Methylenation of catechol to produce methlene-dioxybenzene was first done in 1896, and since then numerous preparations have been described most of which have been of low yields.[109] Also these preparations suffer from the disadvantage that they must be effected in aprotic solvents under anhydrous conditions, but these drawbacks have been overcome by use of phase transfer catalysts. Methylenation of catechol using phase transfer catalysts for example, have been effected with a yield of 76%.[110]

In our experiment, the percentage yield was 43% (literature 53%), however, we had not used catalysts. Low yields were obtained because catechol was easily oxidized by air in alkaline media.

Several attempts were made to acylate methylenedioxybenzene by Fridel-Crafts acylation but none was successful. An attempt to acylate this compound using propionyl chloride as the acyl halide and alcoholic boron triflouride as catalyst produced an oil. The i.r. spectrum of this oil showed an absorption at vmax 1745 cm^{-1}, strong C = 0 stretch band (literature for conjugated ArCOR 1685 - 1666 cm^{-1})[111] This oil was reduced using sodium borohydride, dehydrated and distilled. The i.r. spectrum of the distillate showed it was not the required alcohol. The n.m.r. spectrum of the residue analysed for methylenedioxybenzene implying that acylation of the compound had not occurred. Presence of i.r. absorption band at vmax 1745 cm^{-1}, C= 0 stretch was a bit too high for a conjugated aromatic ketone, however, this could have been from traces of propionyl chloride in the oil. Further, this bottle containing boron triflouride had been lying on the bench for

a long time and possibly most of the boron triflouride
had decomposed.

Attempted acylation of methylenedioxybenzene
using propionyl chloride and anhydrous aluminium chloride
as the catalyst produced a resinous intractable gum.

Acylation of methylenedioxybenzene was expected
to be carried out with ease since, methylenedioxy is
a ring activating and ortho-para-directing. In
addition, no polyacylation would be expected since the
conjugated carbonyl group is ring deactivating.
It is difficult to explain, why acylation did not
occur under these conditions, although methylenedioxy
group have been reported as being easily cleaved by
Friedel-Crafts type reagents.[112] However, many
successful acylation reactions using aryl ethers have
been achieved using borontriflouride and aluminium
chloride and in some cases without the Friedel-Crafts
catalysts.[113]

2.1.4   ATTEMPTED ISOMERISATION OF SAFROLE

Safrole (3,4-methylenedioxyphenylprop-2-ene)
which is a fragrant compound derived from sassafras

(Sassafras officinalis) and camphor (Cinnamomum camphora)
oils, has been reported as being successfully
isomerised to isosafrole (3,4-methylenedioxyphenylprop-1-
ene) in presence of potassium hydroxide at 9 mm Hg.[114]
It has also been successfully isomerised by heating it
under reflux in alcoholic potassium hydroxide.[115,116]

In our experiments, the reaction was followed by
using refractometer, infrared spectrophotometer or
thin layer chromatography. Changes in refractive index
indicate production of a new compound, while in i.r.
appearance of an enhanced absorption vmax around 1625 cm^{-1},
C = C - Ar stretch, olefinic bond conjugated with
aromatic ring indicated presence of a new compound.
The unconjugated olefins usually show C = C stretch
band around vmax 1667 - 1640 cm^{-1}.[117]

Safrole was therefore heated under reflux in
presence of potassium hydroxide and at atmospheric
pressure. The reaction was followed using changes
in refractive index. In this reaction it was observed
that, there was only very little change in refractive
index for experiments where heating under reflux was
done for 2 and 5.5 hours, but for the experiment where
heating under reflux was done for 30 hours changes in

refractive index accompanied by a substantial decomposition was observed.

In another attempted isomerisation, safrole was heated under reflux in alcoholic potassium hydroxide for 21 hours. The reaction was followed using TLC and i.r. The TLC showed development of fast and slow running spots. The fast running spot was identified as safrole. The i.r. and n.m.r. spectra of the final mixture showed that little isosafrole had been produced.

Heating safrole under reflux in alcoholic hydrochloric acid and following the reaction using i.r and TLC failed to produce any isomerisation. An attempt to isomerise the same compound using sunlight again did not produce any isomerisation.

The fact that no evidence of isosafrole was observed in experiments carried out in presence of potassium hydroxide, but was observed in the experiment carried out in presence of alcoholic potassium hydroxide suggests that a solvent (ethanol) was a requirement under the reaction conditions. However, absence of isosafrole from the experiment carried out in presence of alcoholic hydrochloric acid suggests

that the acid may not catalyze the reaction or
stoichiometric quantities of the acid may have been
required.

Double bond migration in alkenes may be
catalysed by acids or bases, metals, metal complexes
and boron compounds. The mechanism involves a slow
rate-determining stage of deprotonation by the base to
form a reactive anion, and it is the relative
stabilities of the isomers of the anion which determine
the overall stereochemical course of the reaction. In
general the cis-allylic anion is more stable than the
trans-isomer. Furthermore, reprotonation of a
conjugated carbanion may occur at a site other than
that from which the proton was abstracted and the
result is that, the migration of the double bond will
favour the most stable product. The carbanion in
this reaction is an intermediate and the rearrangement
is not a concerted reaction.[118]

The mechanism may be depicted as follows:-

Scheme 26
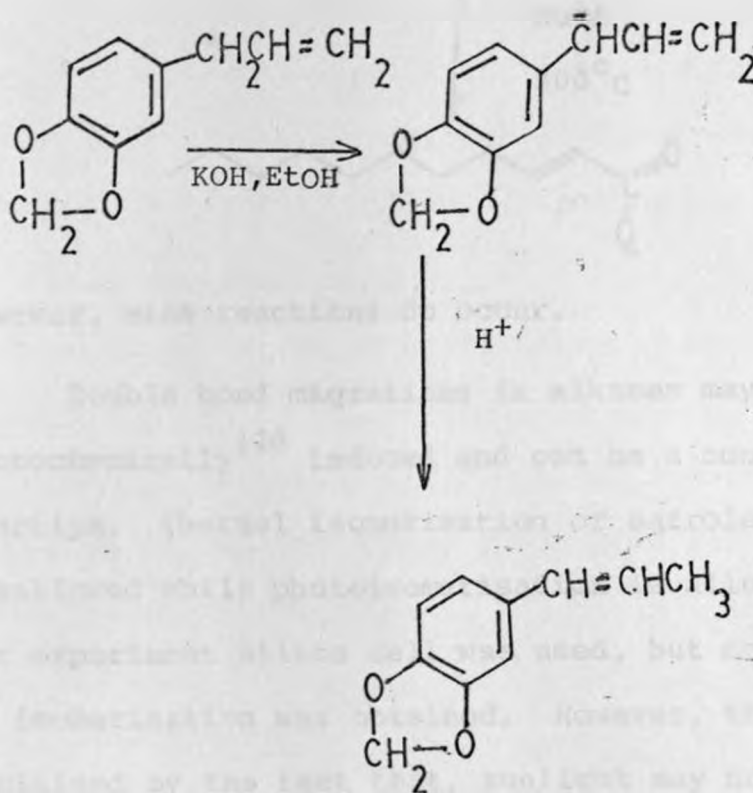
Base catalysed isomerisation can be a useful
synthetic procedure and one remarkable example is the
Varrentrapp[119] reaction which has been known since
1840. i.e.

$$NaOH$$
$$300^{\circ}C \qquad (76)$$
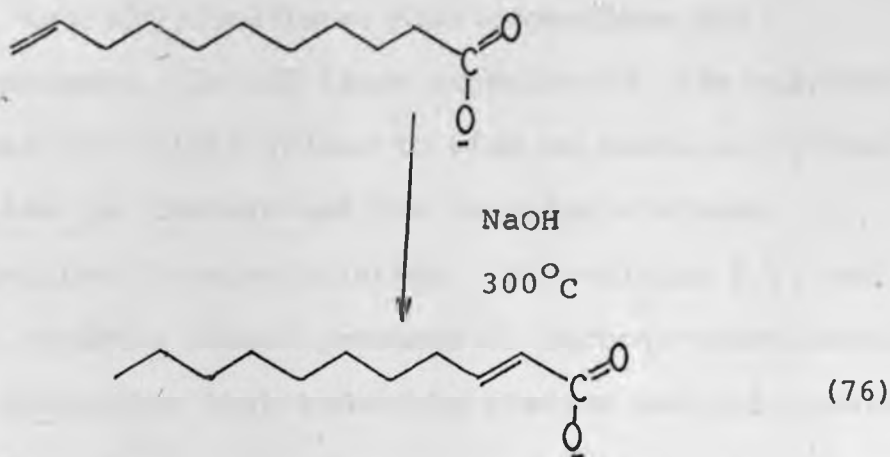
However, side reactions do occur.

Double bond migrations in alkenes may also be photochemically[120] induced and can be a concerted reaction. Thermal isomerisation of safrole is disallowed while photoisomerisation is allowed. In our experiment silica cell was used, but no evidence of isomerisation was obtained. However, this may be explained by the fact that, sunlight may not have contained enough light of the right energy to effect the isomerisation. Possibly if u.v. lamp was available this isomerisation could have been effected.

2.1.5   HYDROCHLORINATION

A modified method reported by Brown and Rei[121]

was used in these attempted preparations. In our preparations, dry hydrogen chloride gas was bubbled through safrole in the following solvent conditions:- neat, tetrachloromethane, dichloromethane and nitromethane. In all these experiments, the mixtures changed from light yellow to blue on bubbling hydrogen chloride gas through and the reaction mixtures decolourised bromine solution. In addition i.r. and n.m.r. spectra showed presence of carbon-carbon double bond indicating that hydrochlorination had not occurred.

However, the change of colour from light yellow to blue could be due to protonation of methylenedioxy group resulting to the cleavage of $ArO-CH_2$ bond and consequently further reactions could result to compounds containing highly resonating structures which could be coloured.

2.2. OXIDATION

2.2.0 4-METHOXYPHENYLPROP-1-ENE

The oxidation of 4-methoxyphenylprop-1-ene using mercury (II) chloride was investigated under the following experimental conditions:-

(1) Mixture of diethyl ether and water as solvent mixture.

(2) Mixture of dimethyl sulphoxide and water

(3) Absolute ethanol

(4) Oxygen gas bubbled through absolute ethanol

(5) Mixture of ethanol and water

(6) Mixture of ethanol and water with suspended mercury (II) chloride.

In the first four experiments, 4-methoxybenzalde-hyde was produced as confirmed by i.r. and n.m.r. spectra and also the m.p. of the hydrazone derivatives. The percentage yield in these experiments were 3.7, 20.5, 15 and 12.9 consecutively. In addition, investigations done on head space vapours in experiment (4), indicated that ethanal was the second product of oxidation.

The relatively high yields obtained in experiments (2) to (4) suggest that dimethyl sulphoxide and absolute ethanol could be better solvents than diethyl ether in this type of reaction. A very low yield was observed in experiment (1) because an attempt to separate the 4-methoxybenzaldehyde by steam distillation resulted in loss of the product, however, the observation of a relatively high yield

in experiment (4) suggests that oxygen could be
facilitating or participating in the oxidation reaction.

Experiments set in ethanol and water as solvent
mixture such as in condition (5), produced
4-methoxyphenylpropan-2-ol as confirmed by i.r. spectrum.
In one of these experiments, a hydrazone, prepared
using 2,4-dinitrophenylhydrazine solution, produced
a hydrazone m.p. $176^{\circ}C$. Since 4-methoxybenzaldehyde
2,4-dinitrophenylhydrazone has a m.p. of $234^{\circ}C$, this
hydrazone prepared from this experiment could not be
from 4-methoxybenzaldehyde.

Formation of a secondary alcohol indicates that
under the experimental conditions, oxymercuration
occurred, but formation of hydrazones under the
conditions is not a surprise because 2,4-dinitrophenyl-
hydrazine is known to oxidize some allyl alcohols to
aldehydes or ketones which give positive test with
the reagent.[122]

This may be depicted as follows:

Scheme 27

2,4-dinitrophenylhydrazine
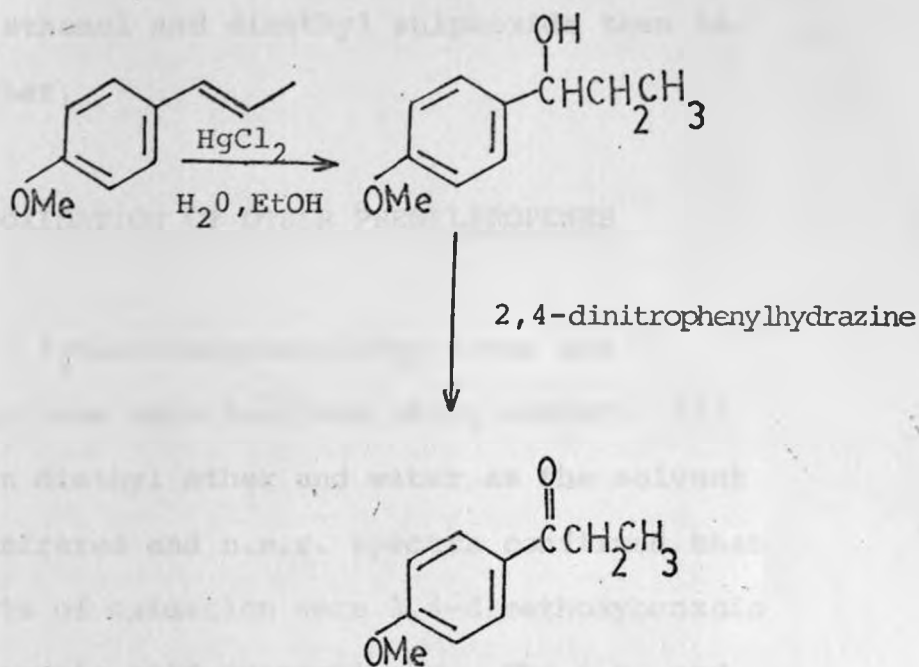
In the experiment carried out in the solvent
mixture of ethanol and water with suspended mercury (II)
chloride, the i.r. and n.m.r. spectra showed
that the product was mainly unreacted 4-methoxyphenyl-
prop-1-ene. This suggested that dissolving of
mercury(II) chloride in a solvent medium was a
necessary condition for either oxidation or
oxymercuration of the phenylpropene to occur.

An attempt to follow the oxidation reaction by
testing aliquots of the reaction mixture with

2,4-dinitrophenylhydrazine solution in a consecutive
number of days, showed that, the reaction was generally
faster in ethanol and dimethyl sulphoxide than in
diethyl ether.

2.2.1   OXIDATION OF OTHER PHENYLPROPENES

3,4-Dimethoxyphenylprop-1-ene and
phenylprop-1-ene were oxidized using mercury (II)
chloride in diethyl ether and water as the solvent
medium.   Infrared and n.m.r. spectra confirmed that
the products of oxidation were 3,4-dimethoxybenzoic
acid and benzoic acid respectively. The i.r. and
n.m.r. spectra of these acids corresponded well with
those of their respective authentic compounds, but
their n.m.r. spectra in d_6 dimethyl sulphoxide did
not show the low field absorptions associated with
hydrogen bonded hydroxyl groups. However, benzoic
acid in tetrachloromethane showed this peak at δ,
11.45, singlet, 1H, (CO_2-H) but the peak disappeared
on addition of a drop of d_6 dimethyl sulphoxide.

Hydrogen bonding is known to shift the hydroxyl
proton to low field absorptions and therefore absence

of this proton in these spectra may be explained by the fact that this hydroxyl proton formed very strong hydrogen bonds with dimethyl sulphoxide which shifted the hydroxyl proton absorption to very low fields that were not investigated.

Oxidation of crude 3,4-methylenedioxyphenylprop-1-ene using mercury (II) chloride in ethanol produced a solid which on separation from the liquid reaction mixture and recrystallization from diethyl ether, a crystalline colourless compound m.p. 160°C (with decomp) (Literature 158°C) was obtained. The n.m.r. spectrum of this compound was consistent with the compound being 3,4-methylenedioxybenzaldehyde mercury (II) chloride complex and compared well with the spectrum of the same compound reported by Ormand.[101] Formation of this compound indicates that 3,4-methylenedioxyphenylprop-1-ene was oxidized to 3,4-methylenedioxybenzaldehyde.

An attempt to analyse this compound with 2,4-dinitrophenylhydrazine produced a hydrazone of m.p. 219-223°C while an authentic sample 3,4-methylene-dioxybenzaldehyde 2,4-dinitrophenylhydrazone melted at 264°C.

This implies that the hydrazone could have been impure. However, the authentic hydrazone had been crystallized from ethanol while the hydrazone from the reaction mixture was recrystallized from glacial ethanoic acid and as a result this hydrazone may have been protonated and hence the observed difference of m.p. between the synthetic and authetic samples.

4-Hydroxy-3-methoxyphenylprop-1-ene was oxidized using mercury (II) chloride in diethyl ether and water as the solvent mixture. A test of the reaction mixture with 2,4-dinitrophenylhydrazine solution produced red-orange precipitate. After a week the reaction mixture started producing a sweet smelling substance but separation of this substance by steam distillation was not successful. Extracting the reaction mixture with diethyl ether and carrying out column chromatography on the diethyl ether soluble residue a colourless crystalline material m.p. 167-168°C was obtained.

The i.r. spectrum of the compound was determined as a deposited film from a solution of diethyl ether and the spectrum gave the following absorptions at

νmax, 3450, (OH stretch); νmax, 2980-2840, (C-H stretch), νmax, 1600(C=C stretch or C≡C stretch). But the absorption centred at 3000cm^{-1}, C = C - H stretch present in isoeugenol was conspicuousily missing. The n.m.r. in tetrachloromethane gave the following absorptions at δ, 6.8 - 6.45, multiplet, 3H, (aromatic protons); δ, 5.6 - 5.4, singlet, 1H, (OH which disappears on addition of D_2O); δ, 4.0 - 3.8, two signals, 3H, (OC$\underline{H}_3$); δ, 2.9 - 2.3, multiplet, 1H, (PhC$\underline{H}$-Cl); δ, 1.8 - 1.5 multiplet, 1H, (Cl$\underline{H}$C - CH$_3$); δ, 1.15 - 0.90, doublet, 3H, (C$\underline{H}_3$). But the absorptions at δ, 5.9 - 5.3, multiplet, 2H, CH = CH present in isoeugenol were absent while absorptions at δ, 1.60 - 1.25, doublet, 3H, (C$\underline{H}_3$) in isoeugenol appears shifted towards high fields in this compound.

Ultraviolet (u.v.) spectra for both the unknown compound and isoeugenol in 95% ethanol showed λmax 300 nm., but on adding a drop of aqueous sodium hydroxide the unknown had λmax at 297 nm while isoeugenol had λmax at 294 nm. This hypsochromic shift was also accompanied by a substantial increase in $E_{1cm}^{1\%}$ for both compounds.

An alcoholic solution of the same compound gave a white precipitate with silver nitrate, which on standing turned brown. When the same solution was acidified and tested with iodine and with hydrogen sulphide in propan-2-one, the respective precipitates of mercuric iodide and mercuric sulphide were not observed.

A positive test of 2,4-dinitrophenylhydrazine solution with the iseugenol reaction mixture indicates that an aldehyde or ketone had been formed as one of the products of oxidation.

The fact that the compound separated by column chromatography was shown to form a white precipitate with silver nitrate solution indicated that this compound contains chlorine.

The i.r. spectrum of this compound did not show absorption at νmax $3000cm^{-1}$ C = C - H stretch, while the n.m.r. spectrum did not show absorptions at δ, 5.9 - 5.3, C$\underline{H}$ = C$\underline{H}$ which were present in isoeugenol. It is known that aliphatic methyl protons appear at high nuclear magnetic resonance fields while the vinylic methyl protons appear in a relatively low field. Our compound showed absorptions at δ,

1.15-0.90, doublet, 3H, CH-C$\underline{H}_3$ while isoeugenol for the same, showed absorptions at δ, 1.60-1.25 doublet, 3H, (=C - C$\underline{H}_3$).

Presence of chlorine in the compound and this information derived from i.r. and n.m.r. spectra indicated an addition reaction on the double bond had occurred. This reaction would be oxymercuration but failure of the compound to give mercuric sulphide and mercuric iodide precipitate with hydrogen sulphide and iodine seems to suggest absence of mercury adduct on the product.

Oxymercuration reaction does not go to completion when strong nucleophilic salts such as mercury (II) chloride are used. These salts under the reaction conditions liberate their respective mineral acids which then protodemercurate the oxymercuration product resulting to retro-formation of the alkene. However, presence of chlorine in the compound, absence of C = C - H stretch band at νmax 3000 cm^{-1} in i.r. spectrum and absence of alkenic protons at δ, 5.9-5.3 in n.m.r. spectrum indicates absence of alkene. But, presence of HCl formed from mercury(II) chloride in the reaction mixture may have resulted in reduction of the organomercurials formed from oxymercuration reaction.

This reaction may now be depicted as follows:-

Scheme 28
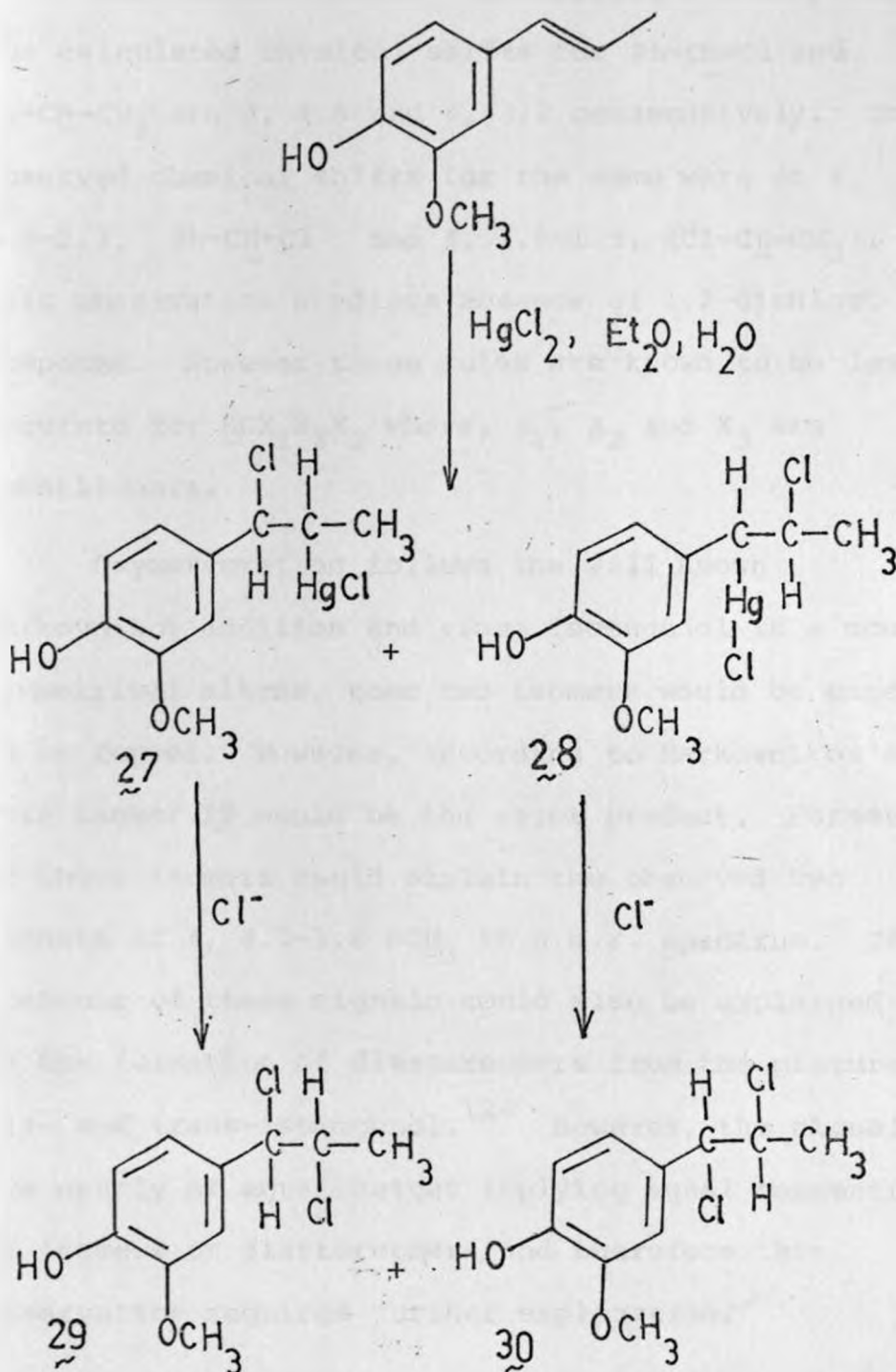
Furthermore, using the modified Shoolery rules[123]
the calculated chemical shifts for Ph-CH-Cl and
Cl-CH-CH$_3$ are δ, 4.5 and δ, 3.2 consecutively. The
observed chemical shifts for the same were at δ,
2.9-2.3, Ph-CH-Cl and δ, 1.8-1.5, (Cl-CH-CH$_3$).
This observation predicts absence of 1,2-dichloro
compound. However,these rules are known to be less
accurate for HCX$_1$X$_2$X$_3$ where, X$_1$, X$_2$ and X$_3$ are
substituents.

Oxymercuration follows the well known
Markovnikov addition and since isoeugenol is a non-
symmetrical alkene, then two isomers would be expected
to be formed. However, according to Markovnikov's
rule isomer 29 would be the major product. Formation
of these isomers could explain the observed two
signals at δ, 4.0-3.8 OCH$_3$ in n.m.r. spectrum. The
presence of these signals could also be explained
by the formation of diastereomers from the mixture of
cis- and trans-isoeugenol.[124] However, the signals
are nearly of equal height implying equal concentrations
of isomers or diastereomers and therefore this
observation requires further explanation.

Generally absorption due to conjugation of
multiple bonds occurs at relatively longer wavelengths
and stronger intensities in u.v. spectroscopy.
Isoeugenol would be expected to give u.v.
absorption at shorter wavelength than its phenoxide
ion, but was observed to give a λmax at 300 nm, while
its phenoxide ion gave a λmax at 294 nm. This was
conflicting data and was discarded.

Oxidation of 3,4-methylenedioxyphenylprop-2-ene
(safrole) was attempted using mercury(II) chloride
in presence of diethyl ether and water as the solvent
mixture but the phenylpropene was recovered unchanged
as indicated by n.m.r. and i.r. spectra and T.L.C.
However, the absorptions observed in i.r. spectrum at
νmax 3600 - 3200 cm^{-1}, 0-H stretch and νmax 1350 cm^{-1},
0-H in-plane bending must have been due to water.

In general, the conjugated phenylprop-1-enes:
4-methoxyphenylprop-1-ene (anethole), phenylprop-1-ene,
3,4-dimethoxyphenylprop-1-ene, 4-hydroxy-3-methoxy-
phenylprop-1-ene (isoeugenol) and 3,4-methylenedioxy-
phenylprop-1-ene (isosafrole) were oxidized using
mercury(II) chloride. The phenylprop-1-enes were
oxidized to their respective aldehydes and ethanal

with a carbon-carbon double bond cleavage. The
aldehydes were further oxidized to their respective
carboxylic acids and this resulted to low yields of the
aldehydes. Addition of oxygen gas was observed to
enhance the yield.

Olefins readily undergo autoxidation under
relatively mild conditions even in the absence of
catalysts. The most reactive olefins are generally
those containing conjugated unsaturation while
terminal olefins are least reactive.[125] This
explains the observation that 3,4-methylenedioxyphenyl-
prop-2-ene (safrole) did not undergo oxidation under
the experimental conditions. Further, it was observed
that phenylprop-1-ene took more days to give a positive
test with 2,4-dinitrophenylhydrazine solution as
compared to the other phenylprop-1-enes which
contained electron-donating groups. The activation
of these groups to the conjugated carbon-carbon double
bond must have been transmitted through the ring[126] and
consenquently these phenyiprop-1-enes were more
reactive.

2.3   ATTEMPTED STUDIES ON THE MECHANISM OF THE
OXIDATION REACTION OF PHENYLPROP-1-ENES USING
MERCURY (II) CHLORIDE

2.3.0   RISE OF MERCURY IN A CAPILLARY TUBING EXPERIMENT

In the oxidation reaction reported by Ormand in 1967,[101] mercury (II) chloride was reported to have been recovered unchanged. Furthermore, this oxidation reaction was shown in our laboratory to occur in presence of oxygen. These two facts prompted further investigations on the effect of oxygen gas from air on this reaction.

In our experiment, two equal portions of a reaction mixture were placed into two flasks of equal volume. One of them was set at room temperature while the other was set at 40°C. These flasks were sealed with an adaptor which narrowed down to a capillary tube, the end of which was placed in a reservoir of mercury. The mercury rise in each capillary was measured daily for five consecutive days and from the results a plot of mercury rise in a capillary, in cm., against time, in days was made. (Fig. (i)).

MERCURY RISE IN CAPILLARY

AGAINST TIME

Mercury
Rise
(cm.)

Set in water-
bath at 40°C

Set at room
temperature

Fig.(i) Time (Days)

MERCURY RISE IN CAPILLARY

AGAINST TIME

Mercury Rise (cm.)

Set in water-bath at 40 °C

Set at room temperature

Time (Days)
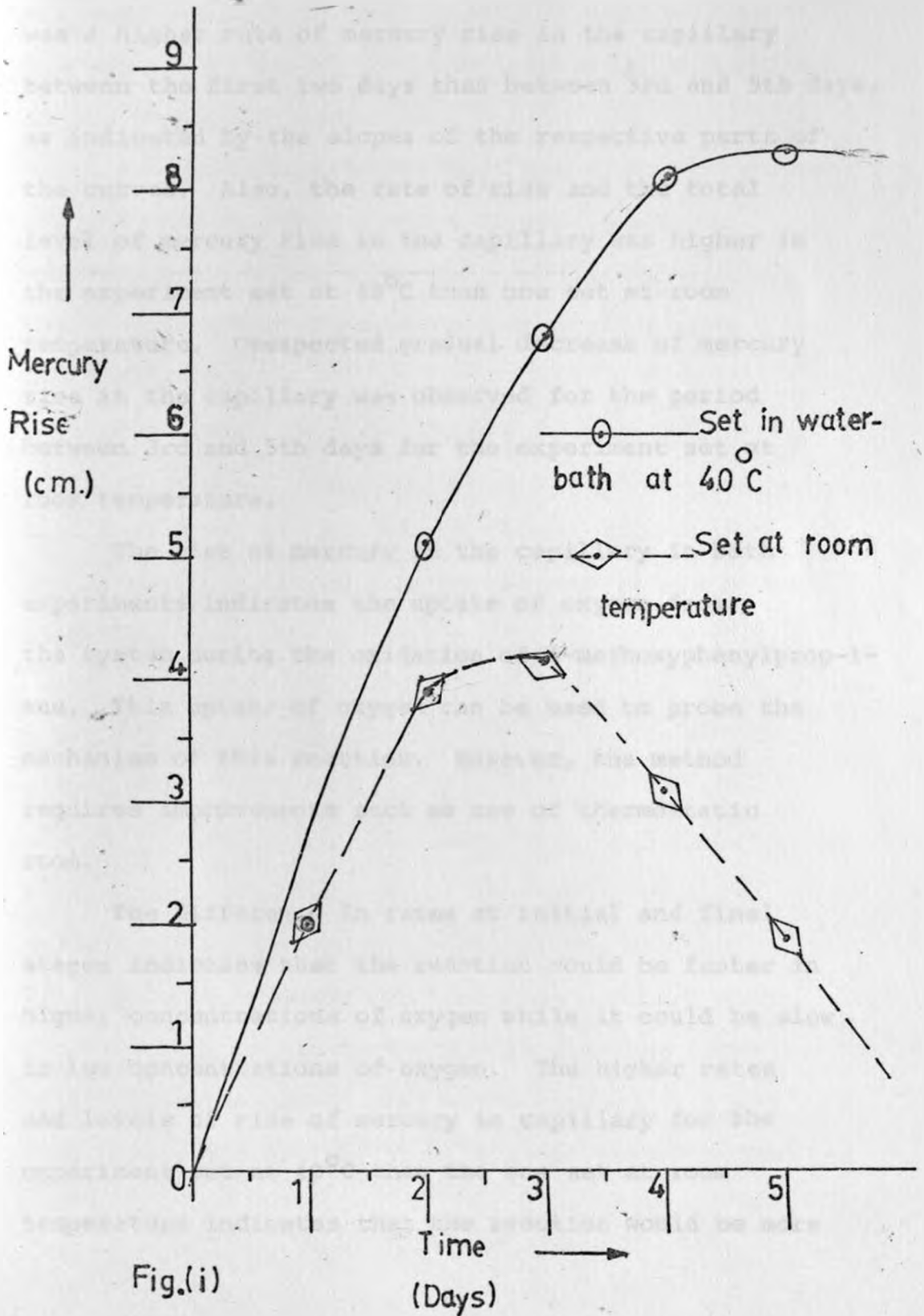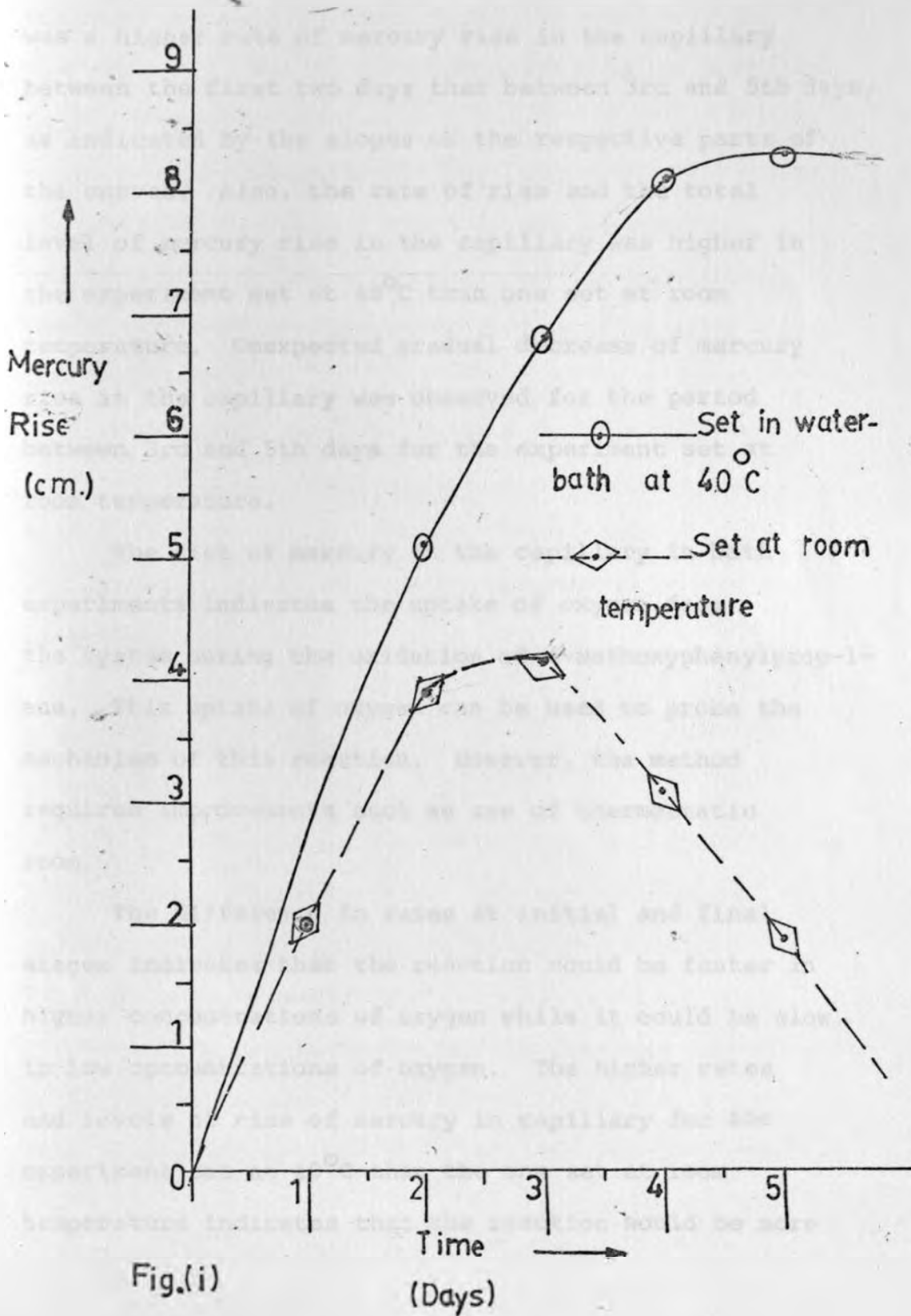
Fig.(i)

From this plot it can be observed that, there was a higher rate of mercury rise in the capillary between the first two days than between 3rd and 5th days, as indicated by the slopes of the respective parts of the curves. Also, the rate of rise and the total level of mercury rise in the capillary was higher in the experiment set at $40^{o}C$ than one set at room temperature. Unexpected gradual decrease of mercury rise in the capillary was observed for the period between 3rd and 5th days for the experiment set at room temperature.

The rise of mercury in the capillary in both experiments indicates the uptake of oxygen from the system during the oxidation of 4-methoxyphenylprop-1-ene. This uptake of oxygen can be used to probe the mechanism of this reaction. However, the method requires improvements such as use of thermostatic room.

The difference in rates at initial and final stages indicates that the reaction could be faster in higher concentrations of oxygen while it could be slow in low concentrations of oxygen. The higher rates and levels of rise of mercury in capillary for the experiment set at $40^{o}C$ than the one set at room temperature indicates that the reaction would be more

favoured at 40°C than at room temperature. However,
the observed drop of mercury rise in capillary in
the experiment set at room temperature could probably
be due to an air-leak.

When both experiments were opened to allow more
air into the reaction mixture it was in general
observed that, after a resetting of the experiments,
the reaction started again as indicated by rise in
the capillary.

The n.m.r. and i.r. spectra for the compound
obtained from the reaction set at 40°C confirmed
that 4-methoxybenzaldehyde was formed consequently
the oxidation occurred with carbon-carbon double bond
cleavage.

2.3.1   NMR STUDIES

This oxidation reaction has been investigated
using aqueous diethyl ether, dimethyl sulphoxide
and ethanol as the solvent media of the reaction.
In these solvent media, the reaction occurred with
carbon-carbon double bond cleavage with the formation
of benzaldehyde and ethanol which escaped as a gas
from the reaction mixture. Since the reaction involves

formation of aldehyde and disappearance of the olefin
bond, the n.m.r. as an analytical technique was
thought to have a great potential for following the
mechanism of this reaction.

Using this technique, the amount of the aldehyde
in the reaction mixture was determined by use of the
aldehydic proton which is a singlet and occurs at δ,
10.4-9.6. This region of the spectrum was free of other
resonance lines and integration of this peak was
performed without interference.

The remaining concentration of the phenylprop-1-ene
in the reaction was determined by use of the disappearance
of the methyl protons of the alkene. Methyl protons in
practical n.m.r. spectroscopy occur around δ, 1.0, are
easy to use because they are strong, show first order
splitting patterns and are therefore easily distinguished.
They are also influenced by only one group in the
α-position. Furthermore, because of the unique three-
fold axis of symmetry and very low rotational barriers,
the three protons of the methyl group are always
magnetically equivalent.[127]

Because the reaction reported by Ormand was
done in aqueous diethyl ether, it was necessary to

study this reaction using this solvent. An attempt
to prepare a calibration curve using this solvent did
not give good results. This could be due to the fact
that the solvent was in a relatively high concentration
as compared to that of the phenylproprop-1-ene. As
a result the CH_2O and CH_3 proton signals of diethyl
ether could not allow the use of the allylic methyl
protons of the phenylprop-1-ene. However, the olefinic
protons were used instead and since their absorptions
were close to those of the aromatic protons their
integration was interfered with and consequently
poor results were obtained. Furthermore, the ethers
are known to contain peroxides which could easily oxidize
the aldehyde to the corresponding carboxylic acid
and as a result would reduce the concentration of the
aldehyde.

In our study, this reaction was found to be
relatively faster in ethanol than in diethyl ether.
As a result a reaction mixture of 4-methoxyphenylprop-1-
ene, mercury (II) chloride and ethanol was prepared and
an aliquot of mixture was set in an n.m.r. tube and
after a week the n.m.r. spectrum of this aliquot did
not show any signal at δ, 10.4-9.6, CHO proton.

However, a test of the stock reaction mixture with 2,4-dinitrophenylhydrazine solution showed presence of a carbonyl which had been formed during this period.

The n.m.r. spectra for the aliquot and stock reaction mixtures of this compound in ethanol showed an absorption signal at δ, 5.35, singlet, (RO-CH-OR) proton. On addition of acid this signal disappeared and another one appeared at δ, 9.75, singlet, CHO proton. This indicates that an acetal is formed as an end product in the oxidation of the phenylprop-1-ene in ethanol, however, on addition of acid the acetal is hydrolyzed into its respective aldehyde.

Oxidation of phenylprop-1-ene using mercury(II) chloride was also found to occur in dimethyl sulphoxide as the solvent medium, as a result further studies on this reaction using this solvent were found to be necessary.

To carry out this study, it was again necessary to prepare a calibration curve using this solvent. After several attempts to prepare this calibration curve, a good one was obtained when d_6 dimethyl sulphoxide was used.

Absence of n.m.r. hydrogen methyl protons from the solvent made it possible for the use of methyl protons of the phenylprop-1-ene. Furthermore, this solvent contained no resonance lines in the region δ, 10.4-9.6 and consequently the concentrations of the alkene and the aldehyde obtained gave good calibration curves.

A plot of concentration of phenylprop-1-ene against both the peak areas and peak heights of the allylic methyl protons and a plot of concentration of the aldehyde against both peak areas and heights of the aldehydic proton gave straight lines (Figs ii and iii).

Even though calibrations using both peak areas and heights gave straight lines, the calibration using peak heights gave better results. This was unexpected, because it is known that peak heights are generally susceptible to nuclear relaxation processes and instrumental conditions, such as field homogeneity.[128] Furthermore, use of peak heights assumes that peak areas are proportional to the height but the width and the shape of the measured peaks are not always the same.

CONCENTRATION AGAINST NMR PEAK HEIGHTS
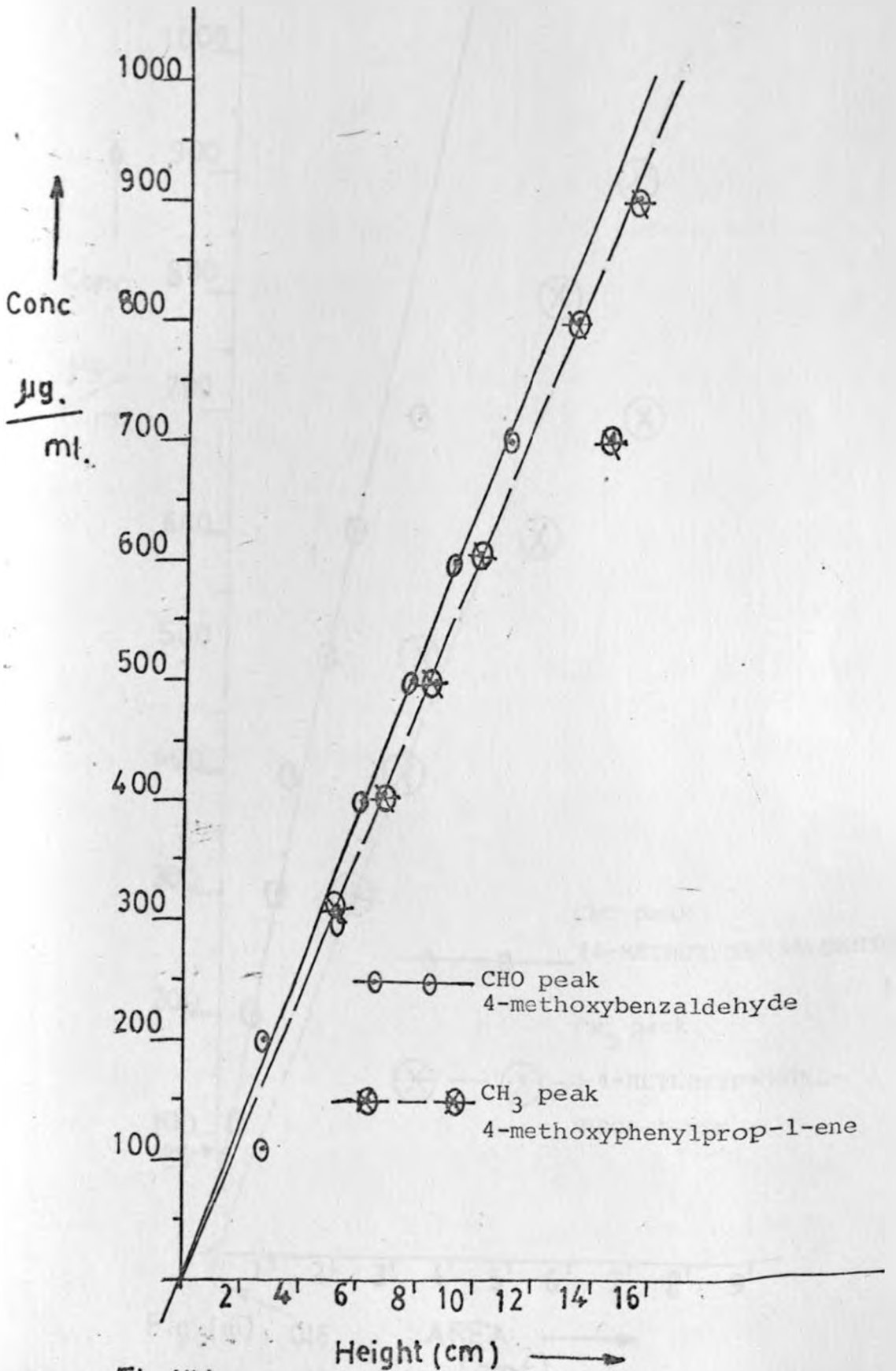
Fig.(ii)

CONCENTRATION AGAINST n.m.r. PEAK AREA

Fig. (iii)

CHO peak
(4-METHOXYBENZALDEHYDE)

CH$_3$ peak
(-4-METHOXYPHENYL-
PROP-1-ENE
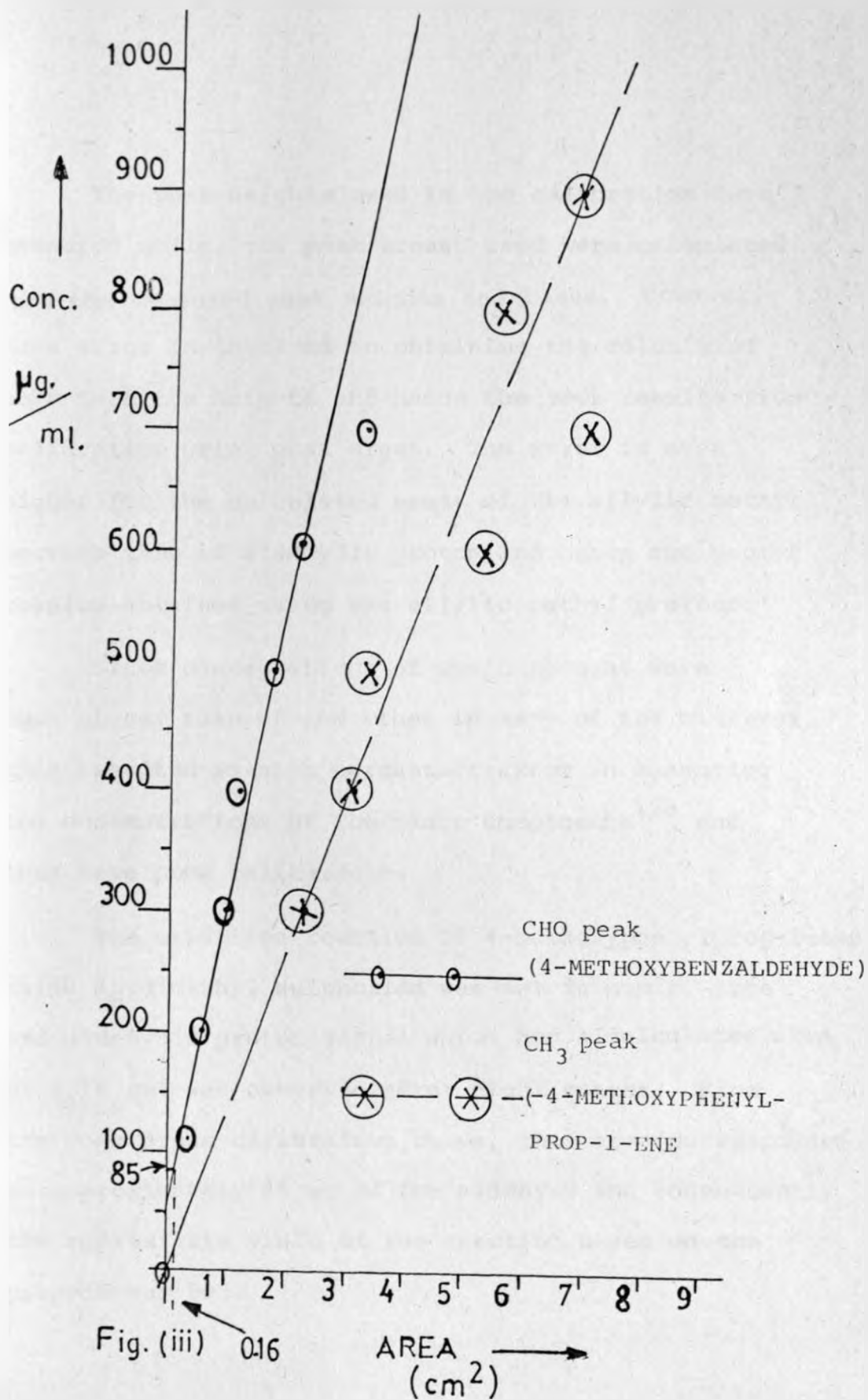
The peak heights used in the calibration were measured while, the peak areas, used were calculated from the measured peak heights and bases. However, more error is involved in obtaining the calculated areas than the heights and hence the poor results from calibration using peak areas. The error is even higher for the calculated areas of the allylic methyl protons than of aldehydic proton and hence the poorer results obtained using the allylic methyl protons.

Since concetrations of one component were much higher than of the other in many of the mixtures, this resulted in high percentage error in measuring the concentrations of the minor components[128] and thus gave poor calibration.

The oxidation reaction of 4-methoxyphenylprop-1-ene using d_6 dimethyl sulphoxide was set in n.m.r. tube and aldehydic proton signal which had a calculated area of 0.16 cm^2 was observed after eight months. From the peak areas calibration curve, this area corresponded to approximately 85 µg of the aldehyde and consequently the approximate yield of the reaction based on the propene was 80%.

The fact that an n.m.r. absorption at δ, 9.7, singlet, C$\underline{H}$O proton accompanied by a change of ratio of aromatic to allylic methyl protons for both 4-methoxyphenyl-prop-1-ene and 3,4-dimethoxyphenylprop-1-ene shows that the oxidation of phenylpropenes had occurred. This observation was made after eight months and this indicates that the reaction was slow, however, the insensitivity of the n.m.r. spectrophotometer was also a draw back.

2.3.2   U.V. STUDIES

Since the absorption spectra of the reactants (phenylprop-1-enes) and products (benzaldehydes) were considerably different, u.v. spectrophotometry could have been employed to follow the changes in concentration of either the products or the reactants during the reaction (provided Beer's law was obeyed over the concentration range). Unlike the n.m.r. spectrophotometric method, the u.v. spectrophotometric method is very sensitive and gives good results even in very dilute solutions. Further, only minute quantities of the material would be required for analysis. Also useful accessories like time-drive and repetitive scanning attachments were available in

our instrument and this simplified the technique. In
addition u.v. studies would have acted as a back-up for
the n.m.r. results.

Ethanol is u.v. inactive in wavelengths greater
than 200 nm., therefore it is a suitable solvent for
the reaction under study.

Before any study was done it was necessary to
prepare calibration curves. In the preparation of
these calibration curves, it was verified that
4-methoxyphenylprop-1-ene and 4-methoxybenzaldehyde
in absolute ethanol obeyed the Beer's law at wavelengths
273 nm. and 259 nm., and from the plots of
absorbance against concentration the extinction
coefficients for each of the compounds at those
different wavelengths were as follows:-

Table 1

COMPOUND	EXTINCTION COEFFICIENT AT WAVELENGTH .	
	273 nm	259 nm
4 - METHOXYPHENYLPROP-1-ENE	21875	9032
4- METHOXYBENZALDEHYDE	16250	8333

The analysis of the mixtures was based on the fact that absorbances are additive and therefore the absorbance of a mixture of absorbing substances is equal to the sum of the separate absorbances.

For any mixture which contains substances which absorb in the u.v., the measured absorbance (D) at any wavelength (λ) can be given by the equation:

$$D_\lambda = \log\frac{Io}{I} = (\varepsilon_1 C_1 + \varepsilon_2 C_2 \, ----- \, + \, \varepsilon_n C_n)l \qquad (77)$$

where: lo is the incident light; I is the transmitted light; ε's are the extinction coefficients of the various pure components at any given wavelength C's are corresponding concentrations and l is the cell length.

Since the cell length is constant, for two components and at wavelengths λ_1 and λ_2 the measured absorbances for the mixture may be expressed as follows:

$$D_{\lambda_1} = \lambda_1 \varepsilon_1 C_1 + \lambda_1 \varepsilon_2 C_2 \qquad (78)$$

$$D_{\lambda_2} = \lambda_2 \varepsilon_1 C_1 + \lambda_2 \varepsilon_2 C_2 \qquad (79)$$

Solving the two simultaneous equations gives
the following equations:

$$C_1 = \frac{\lambda_2 \varepsilon_2 \, D_{\lambda_1} - \lambda_1 \varepsilon_2 \, D_{\lambda_2}}{\lambda_1 \varepsilon_1 \, \lambda_2 \varepsilon_2 - \lambda_1 \varepsilon_2 \, \lambda_2 \varepsilon_1} \qquad (80)$$

$$C_2 = \frac{\lambda_1 \varepsilon_1 \, D_{\lambda_2} - \lambda_2 \varepsilon_1 \, D_{\lambda_1}}{\lambda_1 \varepsilon_1 \, \lambda_2 \varepsilon_2 - \lambda_1 \varepsilon_2 \, \lambda_2 \varepsilon_1} \qquad (81)$$

In selecting the analytical wavelengths λ_1 and
λ_2, it is desirable to choose wavelength λ , where
one component absorbs strongly and the other weakly.[129]

This method does not require the total
concentration of the mixture to be known, but if
one concentration is known then, obviously the other
can be deduced from the relation $(C = C_1 + C_2)$.

Solving the two simultaneous equations gives the following equations:

$$C_1 = \frac{\lambda_2 \epsilon_2 \, ^D\lambda_1 - \lambda_1 \epsilon_2 \, ^D\lambda_2}{\lambda_1 \epsilon_1 \lambda_2 \epsilon_2 - \lambda_1 \epsilon_2 \lambda_2 \epsilon_1} \qquad (80)$$

$$C_2 = \frac{\lambda_1 \epsilon_1 \, ^D\lambda_2 - \lambda_2 \epsilon_1 \, ^D\lambda_1}{\lambda_1 \epsilon_1 \lambda_2 \epsilon_2 - \lambda_1 \epsilon_2 \lambda_2 \epsilon_1} \qquad (81)$$

In selecting the analytical wavelengths λ_1 and λ_2, it is desirable to choose wavelength λ , where one component absorbs strongly and the other weakly.[129]

This method does not require the total concentration of the mixture to be known, but if one concentration is known then, obviously the other can be deduced from the relation $(C = C_1 + C_2)$.

Further, the mass of the sample need not be known
before its dilution for spectrophometric determination
if it is known that the mixture contains no other
components, or only spectroscopically inactive ones.[130]

In our calibration, the λmax 273 nm for
4-methoxybenzaldehyde and λmax 259 nm for
4-methoxyphenylprop-1-ene were chosen as the wave-
lengths for analysis.

A comparison of real and experimental (calculated)
concentrations showed that experimental concentrations
for 4-methoxybenzaldehyde and 4-methoxyphenylprop-1-ene
were obtained with an average percentage error of
18% and 12% respectively. This can be explained by the
fact that, each of these two compounds relatively absorbs
u.v. strongly in both analytical wavelengths.

From n.m.r. studies it was observed that
oxidation of 4-methoxyphenylprop-1-ene using mercury (II)
chloride in absolute ethanol formed acetal and
therefore inorder to use our u.v. calibration curves
it was necessary to modify our experimental conditions.
Furthermore, it was observed that mercury(II) chloride
dissolved in absolute ethanol was absorbing within
the spectrophotometric range of interest.

2.4   CONCLUSION

Industrially it is known that, 4-methoxyphenyl-
prop-l-ene, 4-hydroxy-3-methoxyphenylprop-lene, and
3,4-methylenedioxyphenylprop-l-ene may be oxidized to
their respective benzaldehydes and ethanal by ozone,
acidic dichromate, nitric acid and nitrobenzene.
3,4-Methylenedioxyphenylprop-l-ene (isosafrole)
may also undergo this reaction by using a mixture of
dilute nitric and sulphuric acids in methylbenzene,[131]
furthermore the oxidation of this compound using :
chromic acid is reported to have been enhanced by
manganese compounds.[132]

In our study, oxidation of the conjugated
phenylpropenes using mercury (II) chloride in the
different solvents was found to occur with cleavage
of the carbon-carbon double bond and aldehydes or
carboxylic acids were formed by further aerial
oxidation. Those phenylpropenes which were non-
conjugated like safrole needed to be isomerized to
isosafrole so as to undergo this oxidation reaction.

This reaction requires enhanced concentrations
of oxygen in solution and its uptake can be used to

follow the mechanism. Although most of the reactions
investigated gave low yields, attempted n.m.r.
studies indicated that the aldehydes are produced in
as much high yields as 80%. Furthermore, addition of
oxygen was found to enhance the reaction and
consequently this reaction can be of synthetic importance.
However, further studies on conditions of this reaction
are necessary.

3.0   GENERAL EXPERIMENTAL SECTION

All melting points were determined in
capillaries using Gallenkamp's Melting Point Apparatus
and are uncorrected.   The refractive index was
determined using an Abbé Refractometer (Bellingham
and Stanley).   Infrared spectra were measured using
a Perkin-Elmer 598 Spectrophotometer and ultraviolet
spectra were measured using a Pye Unicam SP 800 and
Beckman U.V. 5270 Spectrophotometers.   Nuclear
magnetic resonance spectra were measured using a
Perkin-Elmer Nuclear Magnetic Resonance Spectrophoto-
meter R 12B.   Thin Layer Chromatography (TLC) was done
using pre-coated aluminium oxide F-254 (type E) plates
and detection was made using a UVS.11 Mineral Light
Lamp (INC. San Gabriel, California).

3.1   SYNTHESIS OF ISOSAFROLE AND OTHER REQUIRED
COMPOUNDS

3.1.0   EXTRACTION OF 4-METHOXYPHENYLPROP-1-ENE
(ANETHOLE) FROM ILLICIUM VERUM

Illicium verum (star anise) seeds (1500 g)
were ground and steam distilled for a total of twenty

four hours. The distillate obtained contained a colourless oil, which decomposed on standing. The crude oil which separated from the distillate was removed and the distillate extracted with diethyl ether (4 x 50 ml.). The oil and diethyl ether extracts were combined and dried over anhydrous sodium sulphate. After filtration, the etherial solution was concentrated by evaporation to give a crude oil (9.11 g.). An attempt to purify the crude oil by distillation resulted in decomposition.

Comparison of the infrared and n.m.r. spectra of the crude oil with the literature[102] reported spectra of anethole, indicated that the crude oil contained anethole as a major product.

3.1.2   DEHYDRATION OF PHENYLPROPAN-1-OL

Phenylpropan-1-ol (2.7 g, 0.2 mole) phosphoric acid 85% (5 ml.) were mixed and heated to the mixtures boiling point and the distillate collected.

The distillate was washed with a saturated solution of sodium chloride (20 ml), and the organic layer was separated, dried over anhydrous sodium sulphate, decanted and was redistilled. This gave phenylprop-1-ene (14.16 g, 60%) as a colourless oil, b.p. 175°C.

The i.r. spectrum showed a band at vmax 1630 cm^{-1}, but no band at vmax 3300 cm^{-1} and compared well with a literature spectrum.[104] The n.m.r. showed signals at:-

δ, 7.5 - 6.8 doublet, 5H, aromatic;

δ, 6.3 - 5.8 multiplet 2H, ArC$\underline{H}$ = C$\underline{H}$;

and δ, 1.8 - 1.4 doublet, 3H, C$\underline{H}_3$.

3.1.3 METHYLATION OF 4-HYDROXY-3-METHOXYPHENYLPROP-I-ENE (ISOEUGENOL)

Isoeugenol (18.309g), iodomethane (7 ml.) propan-2-one (300 ml.) and anhydrous potassium carbonate (14 g.) were mixed together and set aside for 2 hours, after which time, a further quantity of iodomethane (15 ml.) was added. The reaction mixture was then heated under reflux for 1 hour and was again left overnight. The excess iodomethane and propanone were

distilled off and an i.r. spectrum of the crude compound
was obtained. This showed the presence of a strong
O-H stretch centred at νmax 3450 cm^{-1} indicating
that complete methylation had not taken place.

The reaction mixture of isoeugenol and
3,4-dimethoxyphenylprop-l-ene, was separated by
chromatography using a wet column of aluminium oxide
and petroleum ether (b.p. 40-60°C) as an aluent. The
progress of separation was followed by T.L.C. The
3,4-dimethoxyphenylprop-l-ene which, eluted first,
showed no band at νmax 3450 cm^{-1} in the i.r. and the
spectrum compared well with that reported in the
literature.[105]

The n.m.r. showed signals at δ,
6.7 - 6.5, multiplet, 3H aromatic;   ,
6.1 - 5.8, multiplet, IH, ArC$\underline{H}$ = CH ; δ,
3.9 - 3.4, multiplet IH, ArCH = C$\underline{H}$-; δ,
3.62, singlet, 6H, OC$\underline{H}_3$; δ, 1.7, doublet,
3H, - CH - C$\underline{H}_3$;

3.1.4 PREPARATION OF 3,4-METHYLENEDIOXYPHENYL-PROPAN-1-OL[133]

Freshly cleaned pieces of magnesium ribbon
(4.85 g.) were added to sodium-dried, diethyl ether
(100 ml.) and a few drops of bromoethane added. After
vigorous shaking a crystal of iodine was added and the
reaction was seen to begin. Bromoethane (22 ml.)
was added slowly until all the magnesium had been
consumed. A solution of 3,4-methylenedioxybenzaldehyde
(11.2 g.) in diethyl ether (30 ml.) was added slowly
to the solution of the Grignard reagent over a period
of one hour. The reaction mixture was left stirring
overnight and treated with saturated aqueous ammonium
chloride solution until a separation of the salts
had occurred. The salts were filtered off, washed
with diethyl ether and the washings combined with the
filtrate. The etherial solution was dried over
anhydrous magnesium sulphate, filtered and concentrated
by evaporation. The infrared spectrum showed a strong
peak at νmax 1700 cm^{-1} suggesting that there was some
residual 3,4-methylenedioxybenzaldehyde. This was
removed by washing the mixture with excess concentrated
aqueous sodium hydrogen sulphite. The aqueous layer

was extracted with diethyl ether (4 x 50 ml.) and
was dried over anhydrous magnesium sulphate. The
etherial mixture was concentrated by evaporation to
give 3,4-methylenedioxyphenylpropan-1-ol (11.062 g,
81%).

The i.r. spectrum showed absorptions at νmax
3360 cm^{-1}, broad intermolecular hydrogen bonded O-H
stretch; and νmax 1235 cm^{-1} a strong O-C stretch.[134]

3.1.5 DEHYDRATION OF 3,4-METHYLENEDIOXYPHENYL-PROPAN-1-OL[135]

3,4-Methylenedioxyphenylpropan-1-ol (7 g.)
was dissolved in absolute ethanol (100 ml.). To
this, a solution of potassium hydroxide (76 g.) and
water (76 ml.) were slowly added, during which time
a deep green precipitate was formed. The reaction
mixture was stirred for 32 hours, after which time
it was heated under reflux for a further 1 hr. After
cooling and acidifying, the mixture was extracted
with chloroform (3 x 25 ml.). The chloroform extract
was dried over anhydrous magnesium sulphate, filtered
and was concentrated under reduced pressure. Crude
3,4-methylenedioxyphenylprop-1-ene (5.1 g) was obtained
as a yellow oil.

The i.r. spectrum of the crude oil showed
absorptions at νmax 1635 cm^{-1}, moderate conjugated
C = C stretch band. The spectrum was consistent with
that reported by Grasselli 1973[106] for the same
compound. Examination by thin layer chromatography
showed the oil to contain some of the starting
material.

3.1.6   SYNTHESIS OF METHYLENEDIOXYBENZENE[109]

A mixture of dichloromethane (50 ml.) and
dimethyl sulphoxide (250 ml.) were heated under
reflux to a temperature of about 125°C, with continuous
stirring of the mixture, under an atmosphere of
nitrogen. Aliquots of catechol (20 x 2.75 g) and
aliquots of sodium hydroxide (20 x 2.075 g) were
added over a period of 105 minutes. After a further
20 minutes, dichloromethane (10 ml) and sodium
hydroxide (1.5 g.) was added and the reaction mixture,
heated for a further 70 minutes. Water (50 ml.) was
then added and the reaction mixture distilled.
Further quantities of water were added periodically,
during which time the benzene-water azeotrope,
distilled off between 98° - 100°C. A total of 300 ml

of azeotrope was collected.

On cooling the azeotrope, methylenedioxybenzene separated as a heavy oil and was removed. The aqueous residue was extracted with diethyl ether (3 x 50 ml.) and the diethyl ether extract and methylenedioxybenzene residues were combined. The etherial solution was dried over anhydrous sodium sulphate and the solvent ether removed by distillation. This gave crude methylenedioxybenzene (26.4 g, 43%) which was used without further purification.

On treatment of the methylenedioxybenzene produced with alcoholic Ferric (III) chloride, a red colouration was obtained. Catechol, under the same conditions, gave a deep blue solution. This examination indicated that the oil did not contain free hydroxyl groups associated with catechol.[136] The refractive index of the unpurified oil was 1.540 (literature, 1.5398).[137] Its infrared spectrum showed no absorptions in the region νmax 3550 - 3200 cm^{-1}, confirming that the hydroxyl group was absent. Two strong bands, one centred at νmax 1235 cm^{-1} and the other centred at νmax 1035 cm^{-1}, were consistent with the expected assymmetrical and symmetrical ph-0-C

bond stretching frequencies.[138] The infrared spectrum of the methylenedioxybenzene produced was identical with a spectrum reported in literature by Pouchert.[137]

3.1.7   PURIFICATION OF BENZOYL CHLORIDE[139]

A commercial grade of benzoyl chloride (121 g) in benzene (33.4 ml.) was washed with two portions of cold sodium hydrogen carbonate solution (33.4 ml.). The benzene layer was separated, dried over anhydrous calcium chloride and the resulting solution distilled. The fraction of boiling point range 194-197°C (72.93 g.) was collected.

3.1.8   PREPARATION OF PROPANOYL CHLORIDE[140]

Propionic acid (19 ml.) and purified benzoyl chloride (44 ml.) were heated under reflux for 10 minutes. The highly volatile propionyl chloride (15 ml, 67%) was distilled off at 47°C under atmospheric pressure.

3.1.9 ATTEMPTED PREPARATION OF 3,4-METHYLENEDIOXY-PHENYLPROPAN-1-ONE

Methylenedioxybenzene (20.02 g.), propanoyl chloride (14 ml.) and alcoholic boron triflouride solution (27.4 ml., 14% BF_3) were heated under reflux for 12 hours. The reaction mixture was cooled, water (100 ml.) added, and allowed to stand for 30 minutes. This was then extracted with diethyl ether (4 x 50 ml.) and the ether extract was washed with aqueous sodium hydrogen carbonate. The etherial layer was separated and dried over anhydrous sodium sulphate. The solvent diethyl ether, was removed by distillation and an oil (12.4 g, 42%) was obtained. This was used without further purification.

The infrared spectrum showed a strong C = O stretch at νmax 1745 cm^{-1} (literature for conjugated ArCOR νmax 1685-1666 cm^{-1}).[111] This high value of νmax 1745 cm^{-1} suggest that the oil was not the required ketone.

3.1.10   ATTEMPTED REDUCTION OF THE CRUDE OIL

          PRODUCED ON ACYLATION OF METHYLENEDIOXY-

          BENZENE

The crude oil (12.4 g.), isopropanol (33.3 ml)
and a solution of sodium borohydride (1.2 g.)
dissolved in isopropanol (13.4 ml) were heated under
reflux for 12 hours, and cooled. The reaction mixture
was acidified with dilute hydrochloric acid and
extracted with chloroform (3 x 50 ml.). The
chloroform solution was dried over anhydrous sodium
sulphate. After filtration the chloroform solution
was evaporated to give a colourless oil (9.92 g.,
72%). This was used without further purification.

The infrared spectrum of the oil showed a
strong $C = O$ stretch at νmax at 1715 cm^{-1} implying
reduction of the phenylpropanone was not complete.
There was also a broad $O-H$ stretch intermolecular
hydrogen bonded band centred at νmax 3380 cm^{-1} and
also $O-H$ in plane bending band at νmax 1355 cm^{-1}.

3.1.11   ATTEMPTED DEHYDRATION OF THE CRUDE OIL
          PRODUCED BY REDUCTION OF ACYLATED METHYLENE-
          DIOXYBENZENE

          The crude oil (9.92 g.) and potassium
hydrogen sulphate (0.5229 g.) were heated under reflux
for 20 minutes and the mixture was distilled between
81-84°C.

          An infrared spectrum of the distillate showed
it was not the required compound while a nuclear magnetic
resonance (n.m.r.) of the residue after distillation
showed two major peaks at δ, 6.67 (aromatic protons)
and δ, 5.8 (methylenedioxy protons). The number of
these protons was confirmed by the integral area of
the peaks. This suggests that the material was
methylenedioxybenzene and indicates the original
acylation had not taken place.

3.1.12   ATTEMPTED PREPARATION OF 3,4-METHYLENEDIOXY-
          PHENYLPROPAN-1-ONE[141]

          Anhydrous, finely-powdered, aluminium (III)
chloride (27 g.), dry carbon disulphide (7.5 ml) and
methylenedioxybenzene (25 g.) were mixed and cooled in an
ice and water mixture. Redistilled, propionyl chloride

(17.8 ml.) was slowly added with frequent shaking of the flask to ensure thorough mixing. When all the propionyl chloride had been introduced, the flask was heated on a water bath for about two hours, until hydrogen chloride gas ceased to be evolved. The mixture was cooled, poured onto water (170 ml.) containing a little crushed ice. The resulting mixture was shaken and a little concentrated hydrochloric acid added to dissolve the undissolved solids. The aqueous layer was separated and discarded. The organic layer was washed with dilute sodium hydroxide solution followed by washing with water. The organic layer was separated and dried over anhydrous magnesium sulphate. The solvent was removed by distillation to yield a resinous, intractable gum.

3.1.13   ATTEMPTED DEHYDRATION OF 3,4-METHYLENE-
DIOXYPHENYLPROPAN-1-OL

3,4-Methylenedioxyphenylpropan-1-ol (10.8 g.) and phosphoric acid 85% (1.5 ml.) were placed in a Dean and Stark[142] apparatus. The reaction mixture was heated under reflux for 30 minutes after which the reaction mixture turned yellow, polymerized, and decomposed.

3.1.14 ATTEMPTED DEHYDRATION OF 3,4-METHYLENE-DIOXYPHENYLPROPAN-1-OL

3,4-Methylenedioxyphenylpropan-1-ol (18.5 g.)
was dissolved in toluene (150 ml.) and concentrated
phosphoric acid (3 ml.) was added. The mixture was
placed in a Dean and Stark apparatus and heated until
there was no more water produced.

The toluene was removed by distillation and the
residue extracted with diethyl ether (3 x 25 ml.)
and the etherial solution dried over anhydrous
magnesium sulphate. The ether solution was decanted
and concentrated by evaporation to give a sticky
brown mass which was thought to be polymeric in nature.

3.2 ATTEMPTED ISOMERISATION OF 3,4-METHYLENEDIOXY-PHENYLPROP-2-ENE (SAFROLE)

3,4-Methylenedioxyphenylprop-2-ene (6.8964 g.)
and potassium hydroxide (0.0378 g.) were heated under
reflux under atmosphere of nitrogen for 5.5 hr.
Nitrogen gas was continuously bubbled through the
reaction mixture during this period. This caused

considerable evaporation of the propene there being
insufficient remaining for further sampling after
5.5 hrs. The reaction was followed by changes in
refractive index.

Table 2

TIME (MIN)	REFRACTIVE INDEX AT 20°C
0	1.5350
20	1.5345
60	1.5355
185	1.5345
305	1.5380
330	1.5380

As the refractive index of pure safrole at 20°C
is 1.5350 (Literature 1.5370)[143] and that of isosafrole
is 1.5735,[143] these results indicate that very little
isosafrole was produced under these conditions.

3.2.1 ATTEMPTED ISOMERISATION OF 3,4-METHYLENE-

DIOXYPHENYLPROP-2-ENE FOLLOWED BY FRACTIONAL

DISTILLATION

 3,4-Methylenedioxyphenylprop-2-ene (4.8131 g.)
and potassium hydroxide (0.0300 g.) were heated under
reflux under an atmosphere of nitrogen for 2 hours.
The reaction mixture was then distilled and the distillate
was collected in portions whose refractive index
was determined.

Table 3

PORTIONS	· REFRACTIVE INDEX AT 25.5°C
1	1.5330
2	1.5345
3	1.5361
4	1.5380
5	1.5380
6	1.5390

3.2.2   ISOMERISATION OF 3,4-METHYLENEDIOXYPHENYL-
PROP-2-ENE

3,4-Methylenedioxyphenylprop-2-ene (3.222 g.)
and potassium hydroxide (0.061 g.) were heated under
reflux for 30 hours and the reaction was followed by
a change of refractive index. The results were as
tabulated below:-

Table 4

TIME IN HOURS	REFRACTIVE INDEX
0	1.5350
1	1.5350
2	1.5350
3	1.5360
4	1.5370
5	1.5370
6	1.5380
7	1.5390
8	1.5400
.	.
22	1.5525
23	1.5530
24	1.5535
25	1.5530
26	1.5535
27	1.5540
28	1.5555
29	1.5585
30	1.5640

The reaction was accompanied by a substancial amount of decomposition and no isosafrole was detected.

3.2.3 ATTEMPTED ISOMERISATION OF 3,4-METHYLENE-
DIOXYPHENYLPROP-2-ENE UNDER ALKALINE CONDITIONS

3,4-Methylenedioxyphenylprop-2-ene (2.19 g.) and (10 ml.) of alcoholic solution of potassium hydroxide (0.1948 g) dissolved in absolute ethanol (100 ml.) were heated under reflux for 21 hours. The reaction was followed by T.L.C. using benzene-tetrachloromethane (in the ratio 1:2) as the solvent medium.

Thin layer chromatography showed the presence of two compounds, one of which was fast running and was identified as safrole while the other was thought to be isosafrole.

The infrared and n.m.r. spectra of aliquots of the reaction mixture taken after different reaction times indicated that little isosafrole had been produced.

3.2.4   <u>ATTEMPTED ISOMERISATION OF 3,4-METHYLENEDIOXY-</u>
<u>PHENYLPROP-2-ENE (SAFROLE) UNDER ACIDIC</u>
<u>CONDITIONS</u>

3,4-Methylenedioxyphenylprop-2-ene (2.19 g.)
absolute ethanol 5 ml. and a drop of concentrated
hydrochloric acid were heated under reflux for 21 hours
and the reaction was followed by TLC and infrared
spectroscopy. Neither technique showed any evidence
of isomerisation having occured. An n.m.r. spectrum
of the last aliquot again showed no evidence for
isomerisation having occured.

3.2.5   <u>ATTEMPTED PHOTOCHEMICAL ISOMERISATION OF</u>
<u>3,4-METHYLENEDIOXYPHENYLPROP-2-ENE</u>

3,4-Methylenedioxyphenylprop-2-ene (4.38 g.)
was put into a silica cell and was placed in sunlight
for several days. The refractive index was determined
every hour, however, no change in refractive index
(1.535) was observed.

3.3 HYDROCHLORINATION OF 3,4-METHYLENEDIOXYPHENYL-PROP-2-ENE (SAFROLE)

Dry hydrogen chloride gas was bubbled through neat 3,4-methylenedioxyphenylprop-2-ene (1.0082 g.) for 1 hour. The reaction was followed by decolourisation of bromine water. After one hour, the reaction mixture was dissolved in diethyl ether, dried over anhydrous sodium sulphate, was filtered and the filtrate was concentrated in vacuo on a rotatory evaporator. The infrared and n.m.r. spectra were consistent with the sample being safrole.

3.3.1 HYDROCHLORINATION OF 3,4-METHYLENEDIOXY-PHENYLPROP-2-ENE (SAFROLE) IN SOLUTION

Dry hydrogen chloride gas was bubbled through 3,4-methylenedioxyphenylprop-2-ene (1.0032 g.) in dry tetrachloromethane (0.9548 g.) at $0^{\circ}C$. After 40 minutes, the reaction mixture changed from yellow to blue and an aliquot of this mixture decolourised bromine solution in tetrachloromethane. The infrared and n.m.r. spectra of this mixture were consistent with the sample being safrole.

3.3.2 HYDROCHLORINATION OF 3,4-METHYLENEDIOXY-PHENYLPROP-2-ENE IN DICHLOROMETHANE

Dry hydrogen chloride gas was bubbled through 3,4-methylenedioxyphenylprop-2-ene (0.5332 g.) in dichloromethane (8 ml.) at 0^OC for 1 hour. The reaction was followed by testing with bromine in tetrachloromethane which was always decolourised. Infrared and n.m.r. spectra did not show any evidence for hydrochlorination.

3.3.3 HYDROCHLORINATION OF 3,4-METHYLENEDIOXY-PHENYLPROP-2-ENE IN NITROMETHANE

Dry hydrogen chloride gas was bubbled through 3,4-methylenedioxyphenylprop-2-ene (0.50 g.) in anhydrous nitromethane (10 ml.) at 0^OC for 1 hour. The reaction was followed by testing with bromine in tetrachloromethane which was always decolourised. Infrared and n.m.r. spectra did not show any evidence for hydrochlorination.

3.4 STUDIES ON OXIDATION OF PHENYLPROP-1-ENES USING MERCURY (II) CHLORIDE

3.4.1 OXIDATION OF 4-METHOXYPHENYLPROP-1-ENE (ANETHOLE) USING MERCURY (II) CHLORIDE

4-Methoxyphenylprop-1-ene (7.41 g.) mercury (II) chloride (16.4 g.), were mixed and set aside. During a period of 52 days, the reaction mixture had formed a sweet smelling mixture which, consisted of an oily brown substance and a white crystalline substance.

An attempt to separate the sweet smelling oily mixture by steam distillation failed to give good results. However, a test of the aqueous mixture resulting from steam distillation with 2,4-dinitrophenyl-hydrazine showed a red crystalline precipitate and this indicated presence of an aldehyde or ketone.

The carbonyl compound was separated by treating the aqueous mixture with sodium hydrogen sulphite and the resulting solid complex was obtained by filtration, and was decomposed with aqueous sodium carbonate solution, extracted with diethyl ether, dried over anhydrous sodium sulphate, decanted and was

concentrated under vacuum on a rotatory film evaporator. 4-Methoxybenzaldehyde (0.274 g, 3.7%) was obtained.

The significant bands in the i.r. spectrum of the compound were:-

νmax 2840 cm^{-1}, (aldehydic C-H stretch)

and νmax 1715 (Ar - C = 0 stretch). The spectrum compared well with one of the authentic sample, 4-methoxybenzaldehyde.

The n.m.r. in tetrachloromethane gave the following absorptions at:-

δ, 9.8 - 9.6, 1 H, singlet CHO; δ, 7.9-7.4

and δ, 7.1-6.6, two doublets, 4H,

aromatic and δ, 4.0-3.6, singlet,

CH$_3$0. The n.m.r. was identical to that of authentic compound, 4-methoxybenzaldehyde.

3.4.2   OXIDATION OF 4-METHOXYPHENYLPROP-1-ENE
         USING MERCURY (II) CHLORIDE

4-Methoxyphenylprop-1-ene (2.059 g.), mercury (II) chloride (3.778 g.), dimethyl sulphoxide (41.8 ml.) and water 1.4 ml. were shaken together until all the mercury (II) chloride had dissolved.

The reaction mixture was set aside for one week and a small sample tested with 2,4-dinitrophenylhydrazine solution. An orange-red precipitate was obtained.

After standing for several months the reaction mixture was filtered and the residue was washed with excess ethanol. The filtrate was treated with excess 2,4-dinitrophenylhydrazine solution, and 4-methoxybenzaldehyde 2,4-dinitrophenylhydrazone crystallized from the solution. This hydrazone (0.8615 g, 20.5%) had a m.p. of 226°C. An authentic hydrazone prepared in dimethyl sulphoxide melted at 226°C and the mixed m.p. was undepressed.

3.4.3   OXIDATION OF 4-METHOXYPHENYLPROP-1-ENE
(ANETHOLE) USING MERCURY (II) CHLORIDE

4-Methoxyphenylprop-1-ene (1 g.), mercury(II) chloride (2.2130 g.) and absolute ethanol (22.5 ml.) were shaken together until all the mercury (II) chloride had dissolved and the mixture was set aside for about one month.

The reaction mixture was dissolved in excess ethanol, filtered, and the filtrate treated with

excess sodium hydrogen sulphite. The mixture was
stirred and set aside for about 30 minutes. The
hydrogen sulphite complex which crystallized from
the solution was separated by filtration under vacuum.
It was then decomposed, using a 10% aqueous solution
of sodium carbonate (100 ml.). The aqueous mixture
was extracted with diethyl ether, dried over anhydrous
sodium sulphate, filtered and the filtrate concentrated
under vacuum using a rotatory evaporator. 4-Methoxy-
benzaldehyde (15%) was obtained as a pale yellow oil.

The infrared spectrum of the oil showed
absorptions at:-
$\qquad$ vmax 2840 cm^{-1}, aldehydic C-H stretch
$\qquad$ and vmax 1715 cm^{-1}, Ar C = 0 stretch.
This spectrum was compared with a spectrum of an authentic
sample, 4-methoxybenzaldehyde and the two spectra
were found to be identical. The n.m.r. showed signals at:-
$\qquad$ δ, 9.75, singlet, 1H, CHO; δ, 7.6-7.4
$\qquad$ and 7.1-6.9 doublets, 4H, aromatic
$\qquad$ and δ, 4.0-3.6, singlet, CH$_3$O.

3.4.4   OXIDATION OF 4-METHOXYPHENYLPROP-1-ENE
         (ANETHOLE) USING MERCURY (II) CHLORIDE IN
         THE PRESENCE OF OXYGEN

         4-Methoxyphenylprop-1-ene (0.5046 g.) mercury (II)
chloride (1.2555 g.) and absolute ethanol (11.5 ml.)
were shaken together until all the mercury (II) chloride
had dissolved. Oxygen was bubbled into the flask which
was then sealed with a vaccine turnove (suba-seal)
and set aside.

    After a few days a brown colouration appeared
and a colourless precipitate was deposited. Using
a syringe, sample of the head space vapours were
removed from above the reaction mixture and these
vapours bubbled through 2,4-dinitrophenylhydrazine
solution. A yellow precipitate was observed.
2,4-Dinitrophenylhydrazone of ethanal was prepared
and compared with the yellow precipitate produced
above, using thin layer chromatography. Both precipitates
were shown to have identical R.F. values when alumina
plates were used as an eluent.

    The reaction mixture was dissolved in excess
ethanol, filtered and treated with 2,4-dinitrophenyl-
hydrazine solution. After one hour, the orange-red

hydrazone of 4-methoxybenzaldehyde was separated
by filtration under vacuum and dried to give 0.0597 g.
of the hydrazone. This corresponds to a percentage
yield of 4-methoxybenzaldehyde of 12.9%

3.4.5   OXIDATION OF 4-METHOXYPHENYLPROP-1-ENE
          (ANETHOLE) USING MERCURY (II) CHLORIDE

          Mercury (II) chloride (2.2177 g.) was
dissolved in a minimum quantity of water (35 ml).
To this solution 4-methoxyphenylprop-1-ene (1.0012 g.)
was added followed by ethanol (32.8 ml.) to dissolve
the emulsion which had formed. The experiment was
set aside for two months. The reaction mixture was
washed with excess ethanol, filtered and the filtrate
treated with 2,4-dinitrophenylhydrazine solution.
After 30 minutes the hydrazone produced was removed
by filtration under vacuum. The crystals were
recrystallized using glacial ethanoic acid to produce
crystals which melted at $176^{O}C$. 4-Methoxybenzaldehyde
2,4-dinitrophenylhydrazone prepared from an authentic
sample of 4-methoxybenzaldehyde and recrystallized
from glacial ethanoic acid melted at $234^{O}C$.

The residue from filtration was not soluble in ethanol, ethanoic acid, dimethyl sulphoxide, chloromethane, hexane or dichloromethane.

3.4.6 OXIDATION OF 4-METHOXYPHENYLPROP-1-ENE USING MERCURY (II) CHLORIDE

4-Methoxyphenylprop-1-ene (0.1143 g.) and ethanol (1 ml.) were mixed together, and shaken to form a solution. Water (0.2 ml.) was added until there was a slight trace of emulsion, mercury(II) chloride was then added and shaken until all the mercury (II) chloride had dissolved. The experiment was set aside for several weeks.

The reaction mixture formed a black solid which dissolved in diethyl ether. The ether solution was filtered and the filtrate was dried over anhydrous magnesium sulphate and concentrated under vacuum using a rotatory film evaporator, to produce an ether soluble material (0.402 g.). A residue of ether insoluble material (0.091 g.) was also obtained.

The i.r. spectrum for the diethyl ether soluble material showed absorptions at:-

vmax 3500 cm^{-1}, broad intermolecular
hydrogen bonded O-H stretch, vmax 1170 cm^{-1}
C-O stretch which is typical of a
secondary alcohol.[144] The n.m.r. for both diethyl
ether soluble and insoluble materials showed aromatic
and methoxy protons, however, alkenic proton absorptions
were not observed.

3.4.7   OXIDATION OF 4-METHOXYPHENYLPROP-1-ENE

(ANETHOLE) USING MERCURY (II) CHLORIDE

4-Methoxyphenylprop-1-ene (0.5175 g.), was
dissolved in ethanol (2 ml.). Water (0.3 ml) was
added until an emulsion was formed. To this emulsion,
mercury (II) chloride (0.9497 g.) suspended in water
(0.3 ml.) was added. This mixture was shaken but
only very little mercury (II) chloride dissolved.
The experiment was set aside. After several weeks, the
reaction mixture formed a black crystalline mixture
which was extracted with diethyl ether (5 x 25 ml.),
filtered and the filtrate was dried over anhydrous
magnesium sulphate. The supernatent liquid was decanted
and concentrated under vacuum using a rotatory
evaporator to produce an ether soluble material (1.0992 g.).

An ether insoluble material (0.2594 g.) was also
obtained.   The i.r. spectrum of the ether soluble
material showed absorptions at:-

νmax 3600-3200 cm^{-1}, broad, OH stretch (water) and
νmax 1625 cm^{-1}, weak, C = C stretch.

The n.m.r. spectrum of the same material showed
signals at:-

δ, 7.2-6.4, multiplet, aromatic protons; δ,
6.0-5.8, multiplet, C = C - $\underline{H}$, δ, 4.0-3.8
singlet, $C\underline{H}_3O$ and δ, 2.3-2.0, doublet C = C—$\underline{CH}_3$

3.4.8   OXIDATION OF 4-METHOXYPHENYLPROP-1-ENE
           USING MERCURY (II) CHLORIDE (FOR DETERMINING
           THE YIELD)

Mercury (II) chloride (5.0412 g.), water
(96.2 ml.) ethanol 92.2 ml. and 4-methoxyphenylprop-1-ene
(2.7515 g.) were shaken together until all the
mercury (II) chloride had dissolved. After several
days the reaction mixture was filtered. A portion of
the filtrate 10 ml. was treated with 2,4-dinitrophenyl-
hydrazine solution.   The hydrazone produced was
recrystallized from glacial ethanoic acid and dried

under vacuum to give a hydrazone (0.06416 g, 20%)
of m.p 201-206°C. An authentic sample, 4-methoxybenzal-
hyde 2,4-dinitrophenylhydrazone melted at 234°C.
Mixed m.p. was 219°C.

3.4.9   PREPARATION OF 4-METHOXYBENZALDEHYDE
        MERCURY (II) CHLORIDE COMPLEX

Mercury (II) chloride (1.0251 g.) was
dissolved in absolute ethanol (30 ml.). To this
4-methoxybenzaldehyde (0.5965 g.) dissolved in ethanol
(5 ml.) was added. The solution was concentrated on
a hot water bath and was set aside to stand for
several minutes after which 4-methoxybenzaldehyde
mercury (II) chloride crystallized from the solution.

The n.m.r. showed signals at:-
δ, 9.75, singlet, 1H, CHO; δ, 7.9-7.6
doublet, 2H, aromatic; δ, 7.1-6.8,
doublet, 2H, aromatic and δ, 4.25
singlet, 3H, CH$_3$O.

3.4.10   OXIDATION OF 3,4-DIMETHOXYPHENYLPROP-1-ENE
USING MERCURY (II) CHLORIDE

3,4-Dimethoxyphenylprop-1-ene (1.6312 g.) mercury (II) chloride (2.448 g.) , diethyl ether (28 ml.) and water (1 ml.) were shaken together until all the mercury (II) chloride had dissolved. The mixture was set aside for several weeks, during which time it was tested with 2,4-dinitrophenylhydrazine solution, which gave a red-orange crystalline precipitate.

An attempt to separate the carbonyl compound by steam distillation was not successful, and a solid material and an aqueous mixture resulted. These aqueous and solid mixtures were extracted with diethyl ether and filtered. The etherial mixture was dried over anhydrous magnesium sulphate, was concentrated under vacuum using a rotatory evaporator and a solid material (4.023 g.) resulted. An ether insoluble residue of (0.4253 g.) was also obtained. An infrared spectrum of the diethyl ether soluble material showed absorptions at:-

νmax 3300-2500 cm^{-1}, a broad 0 - H stretch and

νmax 1720-1660 cm^{-1}, a strong C = 0 stretch.

This infrared spectrum compared well with the reported
spectrum of 3,4-dimethoxybenzoic acid.[145] It was also
identical with the spectrum of 3,4-dimethoxybenzoic
acid produced by permanganate oxidation of 3,4-dimethoxy-
phenylprop-1-ene.

The n.m.r. spectrum in d_6 dimethyl sulphoxide
showed absorptions at:-

δ, 7.0 - 6.2, a multiplet, 3H, aromatic and

δ, 3.9 - 3.6, a singlet, 6H, $\underline{CH_3}O$. No low
field absorption, normally associated with hydrogen
bonded hydroxyl groups, were observed. A similar
phenomenon was observed with the n.m.r. spectrum in d_6
dimethyl sulphoxide of an authentic sample of
3,4-dimethoxybenzoic acid.

3.4.11   OXIDATION OF 3,4-DIMETHOXYPHENYLPROP-1-ENE
          USING POTASSIUM PERMANGANATE

3,4-Dimethoxyphenylprop-1-ene (4 g.) was
dissolved in benzene (25 ml.) and 18-crown-6- (1, 4, 7,
10, 13, 16 - hexaoxacyclooctadecane) (1 g.) was
added to the resulting mixture. Potassium permanganate
(4 g.) was then added and the mixture was heated under
reflux for about 3 hours. Sulphur dioxide was passed

through the mixture to remove the precipitated manganese dioxide. The solution was acidified with dilute hydrochloric acid and extracted with diethyl ether. The ether solution was dried over anhydrous sodium sulphate, evaporated to give a residue of . (0.5 g.). A small portion of this residue was purified by sublimation to give a colourless material m.p. 181-182°C (Literature 179-180°C).[145]

The i.r. spectrum showed absorptions at:-
vmax 3300-2500 cm^{-1}, broad O-H stretch
and 1680-1660 cm^{-1}, a strong C = O stretch.
The n.m.r. spectrum in d_6 dimethyl sulphoxide showed signals at:-
δ, 7.5-6.9, multiplet, 3H, aromatic
and δ, 3.9-3.5, singlet, 6H, CH$_3$0.
No low fields absorptions were observed beyond δ, 7.5.

3.4.12   OXIDATION OF PHENYLPROP-1-ENE USING
          MERCURY (II) CHLORIDE

Phenylprop-1-ene (5.028 g.), mercury (II) chloride (11.6256 g.) diethyl ether (128 ml.) and water (4.3 ml.) were shaken together until all the

mercury (II) chloride had dissolved. The reaction
mixture was set aside and after several weeks was
tested with 2,4-dinitrophenylhydrazine solution. A
red precipitate was observed. The reaction mixture
was dissolved in excess diethyl ether, filtered and
the filtrate dried over anhydrous magnesium sulphate.
The etherial solution was concentrated using a
rotatory evaporator. An ether, soluble, material
(2.8851 g.) and an ether insoluble, material (1.7627 g.)
were obtained.

The infrared spectrum for the ether soluble
material showed absorptions at:-

νmax 3300-2500 cm^{-1}, a broad O-H stretch

band and νmax 1700 cm^{-1}, a strong C = O

stretch band. These absorptions are typical
of carboxylic acids. The spectrum of this material
compared well with the spectrum of benzoic acid.[146]

The n.m.r. spectrum in d_6 dimethyl sulphoxide
showed signals at:-

δ, 8.1 - 7.9, and δ, 7.6 - 7.0, both
multiplets, 5H, aromatic. No low field absorptions
associated with hydrogen bonded hydroxyl groups, were
observed. An n.m.r. spectrum for benzoic acid in

tetrachloromethane showed signals at similar
chemical shifts as above, but had an additional signal
at δ, 11.45, singlet, 1H, C - O$_2$ - $\underline{H}$ proton. This
absorption, however, disappeared on addition of a
drop of d$_6$ dimethyl sulphoxide.

3.4.13   OXIDATION OF 3,4-METHYLENEDIOXYPHENYLPROP-1-ENE
           (ISOSAFROLE) USING MERCURY (II) CHLORIDE

        The unpurified reaction product (4 g.),
from the preparation of isosafrole using the Grignard
route, mercury (II) chloride (6.72 g.) and ethanol
(71.1 ml.) were shaken until all the mercury (II)
chloride had dissolved. The mixture was set aside for
about 2 months, during which time yellow crystals and
oily red substance were formed. This oily liquid
was decanted, and the crystalline material recrystallized
from diethyl ether to produce colourless crystals
(5.2262 g.) m.p. 160°C (with decomp) (Literature 158°C)[101]

        The n.m.r. spectrum was consistent with the compound
being 3,4-methylenedioxybenzaldehyde mercury (II)
chloride and compared well with the spectrum reported
by Ormand.

3.4.14   PREPARATION OF 3,4-METHYLENEDIOXYBENZALDEHYDE MERCURY (II) CHLORIDE COMPLEX (PIPERONAL MERCURIC CHLORIDE)

Mercury (II) chloride (4.0 g.) was dissolved in diethyl ether (100 ml.) and a solution of piperonal (2.219 g.) dissolved in diethyl ether (50 ml.) was added.   The mixture was set aside to stand for several minutes, after which time piperonal mercuric chloride crystallized from the solution as clourless crystals of m.p. 157-8°C (Literature 158°C)[101]

The n.m.r. showed signals at:-

δ, 9.75, a singlet, IH, ArCHO;

δ, 7.55-7.0, a multiplet, 3 H, aromatic,

and δ, 6.7, a singlet 2H, 0-CH$_2$-0

3.4.15   OXIDATION OF 3,4-METHYLENEDIOXYPHENYLPROP-1-ENE (ISOSAFROLE) USING MERCURY (II) CHLORIDE

The unpurified reaction product (0.7621 g.) from the preparation of isosafrole using Grignard route, mercury (II) chloride (1.29 g.) and ethanol (14.5 ml.) were shaken together until all the mercury (II) chloride had dissolved. The experiment was set

for several days, was tested with 2,4-dinitrophenyl-
hydrazine solution and formed a red-orange precipitate.

After several weeks, the reaction mixture was
dissolved in excess ethanol, filtered and the filtrate
treated with 2,4-dinitrophenylhydrazine solution.
The hydrazone obtained was recrystallized from glacial
ethanoic acid and crystals (0.0590 g., m.p. 219-223°C)
was obtained in 4% yield based on the aldehyde. An
authentic sample, (3,4-methylenedioxybenzaldehyde
2,4-dinitrophenylhydrazone) which had been crystallized
from ethanol melted at 264°C.

3.4.16   OXIDATION OF 4-HYDROXY-3-METHOXYPHENYLPROP-1-ENE
         (ISOEUGENOL) USING MERCURY (II) CHLORIDE

4-Hydroxy-3-methoxyphenylprop-1-ene
(18.85 g.) diethyl ether (300 ml.), water (10 ml.)
and mercury (II) chloride (32.8 g.) were mixed
together and set aside for one week, after which time,
it was tested with 2,4-dinitrophenylhydrazine solution,
which gave a red-orange precipitate. During a period
of several months, a sweet smelling oxidation product
was produced and an attempt to separate this material
by steam distillation was unsuccessful. The reaction

mixture was then extracted with diethyl ether (4 x 50 ml.)
and the etherial solution was dried over anhydrous
magnesium sulphate. The ether solution was decanted
and concentrated under reduced pressure on a rotatory
film evaporator. An ether soluble residue (7.1255 g.)
and ether insoluble residue (4.023 g.) was obtained.
The ether soluble residue was further purified by
column chromatography using silica gel as the adsorbent
and trichloromethane as the eluent. The eluate
was examined by thin layer chromatography and the
fractions containing the faster running component
were combined and evaporated to give a pale yellow
solid. Recrystallisation from 95% ethanol gave a
colouress crystalline material m.p. 167-168°C. An
alcoholic solution of this compound with silver nitrate
solution gave immediately a white precipitate which on
standing turned brown. This indicated presence of
chlorine in the compound. Addition of hydrogen
sulphide in propan-2-one to an acidified, alcoholic,
solution of the compound, gave no precipitate. A
second portion of acidified solution failed to give
a precipitate of mercuric iodide on treatment with
iodine.

The infrared spectra for both the diethyl ether soluble and diethyl insoluble material were similar, but not identical.

The significant peaks in the i.r. spectrum of the crystalline compound m.p. 167-168°C were:-

$v$max 3450 cm^{-1} 0-H stretch, $v$max 2980-2840 cm^{-1}, C-H stretch and $v$max 1600 cm^{-1}, C = C stretch or C $\equiv$ C stretch. However, the absorption centred at $v$max 3000 cm^{-1} and is present in isoeugenol was conspicously missing.

The n.m.r. spectrum for the same compound in d_3 trichloromethane gave the following absorptions at:-

δ, 6.8-6.45, multiplet, 3H, aromatic protons; δ, 5.6-5.4, singlet, 1H, (OH proton which disappears on addition of D_2O); δ, 4..0-3.8, two signals, (3H), OC$\underline{H}_3$; δ, 2.9-2.3, multiplet, 1H, ph-C$\underline{H}$-Cl; δ, 1.8-1.5, multiplet, 1H, Cl-C$\underline{H}$-CH$_3$; δ, 1.15-0.90, doublet, 3H, C$\underline{H}_3$. But absorptions at δ, 5.9 - 5.3, multiplet, C$\underline{H}$ = C$\underline{H}$ present in isoeugenol were missing while the CH$_3$ protons in isoeugenol appears at δ, 1.25-1.6 and therefore this absorption is shifted to higher fields in our compound.

Ultraviolet (u.v.) spectra for both the crystalline compound and isoeugenol in 95% ethanol showed λmax at 300 nm and on addition of a drop of aqueous sodium hydroxide, the unknown had λmax at 297 nm while isoeugenol had λmax at 294 nm. There was also an increase in $E_{1\ cm}^{1\%}$ for both the unknown compound (527%) and isoeugenol (261%)

3.4.17 OXIDATION OF 3,4-METHYLENEDIOXYPHENYLPROP-1-ENE (SAFROLE) USING MERCURY (II) CHLORIDE

Safrole (1.7812 g.), mercury (II) chloride (2.9851 g.) diethyl ether (33 ml.) and water (1.1 ml.) were shaken until all the mercury (II) chloride had dissolved. The mixture was then set aside.

After several weeks the reaction mixture was tested with 2,4-dinitrophenylhydrazine solution, however, no hydrazones were formed. The reaction mixture was dissolved in excess diethyl ether, filtered, dried over anhydrous magnesium sulphate, filtered and the filtrate concentrated under vacuum using a rotatory evaporator.

The i.r. spectrum showed absorptions at:-

νmax 3600-3200 cm^{-1}, broad, OH

stretch (water); νmax 1630-1610 cm^{-1},

sharp, C = C stretch and νmax 1350 cm^{-1},

O-H in-plane bending vibration. The n.m.r

spectrum showed the aromatic, alkenic and methylenedioxy

protons at their expected chemical shifts.

Thin layer chromatography showed the mixture to

be unreacted safrole.

3.5   MECHANISTIC STUDIES

3.5.1   OXIDATION OF 4-METHOXYPHENYLPROP-1-ENE

(ANETHOLE) USING MERCURY (II) CHLORIDE

UNDER CONTROLLED CONDITIONS

4-Methoxyphenylprop-1-ene (2.2203 g),

mercury (II) chloride (1.0013 g) and absolute ethanol

(23 ml.) were shaken together until all the mercury (II)

chloride had dissolved.

The reaction mixture was divided into two

equal portions and were placed into two separate

250 ml. round-bottomed flasks. The flasks were

sealed with an adaptor which narrowed down to a

capillary tube, the end of which was placed in a

reservoir of mercury. One flask remained at room temperature, the other was placed in a heated water bath at 40°C. The mercury rise in each capillary was measured daily for five days.

After the fifth day, the flasks were opened and air allowed to diffuse into the system. The flasks were then resealed and a further uptake of oxygen was observed in both cases. The results are as tabulated below:-

Table 5

DAY	ROOM TEMP ^{O}C	MERCURY RISE IN CAPILLARY (CM)	
		ROOM TEMP	WATER BATH TEMP 40°C
1	23°C	2	2
2	23°C	3.9	5.1
3	24.5	4.2	6.8
4	26.5	3.1	8.1
5	23.5	1.9	8.3

Excess sodium hydrogen sulphite solution was
added to the reaction which was carried out at higher
temperature. The hydrogen sulphite compound was
separated by filtration, and decomposed with 10%
aqueous sodium carbonate solution. The aqueous mixture
was extracted with diethyl ether (3 x 25 ml) and the
ether extracts, combined, dried over anhydrous sodium
sulphate and concentrated under vacuum. This gave
pale yellow oil whose infrared characteristics were:-

νmax 3000 - 2780 cm^{-1}, C-H stretch and

νmax 1715 cm^{-1}, strong C = O stretch. The
n.m.r. spectrum of the oil in tetrachloromethane showed
absorptions at:-

δ, 9.75, singlet, 1H, CHO;

δ, 7.9-7.4 and δ, 7.1-6.6, both are
two doublets, 4H, aromatic, and

δ, 4.0-3.6, singlet, 3H, CH$_3$O

3.5.2   NUCLEAR MAGNETIC RESONANCE (n.m.r.) STUDIES
          ON THE REACTION OF SOME PHENYLPROP-1-ENES WITH
          MERCURY (II) CHLORIDE

3.5.2.1   ATTEMPTED CALIBRATION USING DIETHYL ETHER
          AS A SOLVENT

          The following mixtures of 4-methoxybenzaldehyde
and 4-methoxyphenylprop-1-ene were made and diethyl
ether 1 ml. added. The mixtures were shaken until
they were homogeneous. From each solution a sample
(1 ml.) was removed and placed in an n.m.r. tube.
The n.m.r. spectrum of each sample was then determined.
After the height and area of the aldehydic (CHO) peak
were determined in each spectrum, this peak was
cut off and weighed.

The results are as tabulated below:

Table 6

TUBE NO.	4-METHOXYBENZALDEHYDE (CHO PEAK)					4-METHOXYPHENYL-PROP-1-ENE ($CH_2=CH_2$)			MASS RATIO $CH_2=CH_2$ to CHO
	Conc. μg/ml	Height cm.	Integral area	Area cm^2	Mass μg	Conc. μg/ml	height cm.	integral area	
1	537.1	9.60	6.1	2.40	17.0	124.4	1.10	1.20	1:4.82
2	311.4	4.90	3.1	1.23	10.5	300.0	3.70	5.15	1:1.05
3	719.0	8.25	5.8	4.13	16.6	338.0	2.85	3.60	1:2.13
4	618.8	8.40	6.1	4.20	16.8	72.3	0.60	0.60	1:9.43

From this data the following graphs were drawn:-

(a) Concentration of both aldehyde and alkene against the heights of the aldehydic and alkenic peaks respectively.

(b) Concentration of aldehyde against the mass of the aldehydic peak.

(c) Concentration of both aldehyde and alkene against peak integral areas of aldehydic and olefinic peaks respectively.

(d) Concentration of aldehyde against calculated peak areas of the aldehydic peak.

However, these graphs did not give good calibration
curves.

3.5.2.2 REPEATED CALIBRATION USING d_6 DIMETHYL
SULPHOXIDE AS A SOLVENT

The following mixtures of 4-methoxybenzal-
dehyde (anisaldehyde) and 4-methoxyphenylprop-1-ene
(anethole) were weighed in n.m.r. and d_6 dimethyl
sulphoxide (0.5 ml.) added to each tube. The mixtures
were shaken and n.m.r. spectra determined.

The results are as tabulated below:-

Table 7

TUBE NO.	4-METHOXYBENZALDE-HYDE CHO PEAK			4-METHOXYPHENYL-PROP-1-ENE CH_3 PEAK			SUM OF AREA OF $CH_{3/3}$ AND CHO	$\frac{CHO\ AREA}{CORRECTED\ TOTAL\ AREA} \times 100$	EXPECTED PERCENTAGE
	CONC. µg/ml.	HEIGHT cm	AREA cm^2	CONC. µg/ml.	HEIGHT cm	AREA cm^2	cm^2	%	%
1	111.7	2.8	0.42	903.3	15.30	6.77	2.68	15.8	11.0
2	203.4	2.9	0.55	800.4	11.40	5.45	2.37	23.2	20.3
3	301.2	5.4	1.02	702.6	12.50	6.95	3.34	30.5	30.0
4	400.8	6.2	1.17	607.4	10.10	5.28	2.93	39.9	39.8
5	500.8	7.9	1.82	498.7	8.60	3.35	2.94	61.9	50.1
6	606.1	9.4	2.18	404.3	6.85	3.10	3.21	67.9	60.0
7	698.8	11.1	3.23	313.4	5.30	2.28	3.99	80.9	69.0

The following parameters were plotted:-

(a)   Concentration of both 4-methoxyphenylprop-l-ene
      and 4-methoxybenzaldehyde against CH$_3$ and CHO
      calculated peak areas (Fig(iii) page 114)

(b)   Concentration of both 4-methoxyphenylprop-l-ene
      and 4-methoxybenzaldehyde against CH$_3$ and CHO
      measured peak heights. (Fig (ii) page 113).

3.5.2.3   AN ATTEMPT TO FOLLOW THE MECHANISM OF THE
          REACTION OF PHENYLPROP-l-ENES WITH MERCURY (II)
          CHLORIDE USING n.m.r. SPECTROSCOPY

          The following experiments were set:-

(a)   4-Hydroxy-3-methoxyphenylprop-l-ene (0.1005 g.)
      was placed in an n.m.r. tube and to this 1 ml.
      of a solution of mercury (II) chloride (0.5477 g)
      dissolved in d$_6$ dimethylsulphoxide (5 ml) was added. The
      mixture was shaken and occasionally the tube
      was opened to allow air to enter. The n.m.r
      spectrum was determined at regular intervals.

          There was no noticeable change in the
      spectra after eight months.

(b)   3,4-Dimethoxyphenylprop-1-ene (0.110 g.) and
        1 ml. of a solution of mercury (II) chloride
        (0.5477 g.) dissolved in d_6 dimethyl sulphoxide
        (5 ml.) were placed in an n.m.r. tube and set
        aside. Occasionally the tube was opened to allow
        air to enter. The n.m.r. spectrum of the mixture
        showed a signal at δ, 9.7, singlet, CHO. Also
        there was a change of ratio of aromatic to
        allylic methyl proton integral areas from 1:1
        to 2:1. The CHO signal was detected in high
        sensitivity but its area and height could not be
        used with calibration curves.

(c)   4-Methoxyphenylprop-1-ene (0.1067 g.) and 1 ml.
        of a solution of mercury (II) chloride (0.5477 g.)
        dissolved in d_6 dimethyl sulphoxide (5 ml.)
        were place in n.m.r. tube and set aside.
        Occasionally the tube was opened to allow air
        to enter. The n.m.r. spectra was determined at
        regular intervals. After eight months the n.m.r.
        spectrum of the mixture showed a signal at δ,
        9.7, singlet, CHO. There was also a change of
        ratio of aromatic to allylic methyl proton
        integral areas from 4:3 to 7:3. Using the
        calibration curve and the area of the signal,
        the reaction had taken place with approximately

80% yield.

3.5.2.4   OXIDATION OF 4-METHOXYPHENYLPROP-1-ENE
USING MERCURY (II) CHLORIDE

4-Methoxyphenylprop-1-ene (0.9915 g.)
mercury (II) chloride (2.1962 g.) and absolute ethanol
(22.3 ml.) were put together and shaken until Mercury (II)
chloride had dissolved. After a week the reaction
mixture was tested with 2,4-dinitrophenylhydrazine
solution and gave an orange-red precipitate. An
aliquot of this reaction was drawn, placed in an n.m.r.
tube and on determining n.m.r. spectrum showed a
signal at δ, 5.35, singlet, (RO-C$\underline{H}$-OR)[147] which
disappeared on addition of acid and another signal
appeared at δ, 9.75, singlet, C$\underline{H}$O.

3.5.3   ULTRAVIOLET (U.V.) CALIBRATION FOR
PHENYLPROP-1-ENE OXIDATION USING MERCURY (II)
CHLORIDE

Different mixtures (see table 8) of
4-methoxybenzaldehyde (anisaldehyde) and
4-methoxyphenylprop-1-ene (anethole) were prepared by
putting different masses of the two compounds in
volumetric flasks and diluting the mixtures with

absolute ethanol. Ultraviolet spectra were obtained
for each mixture.

The results were summarised in the table below:-

Table 8

NUMBER OF THE FLASK	MASS OF THE COMPOUND (g.)		MOLES OF THE COMPOUND X10^{-4}	
	4-METHOXY-BENZALDE HYDE	4-METHOXY PHENYL-PROP-1-ENE	4-METHOXY-BENZALDE-HYDE	4-METHOXY-PHENYLPROP-1-ENE
1	0.0269	-	1.98	-
2	-	0.0178	-	1.20
3	0.0144	0.0347	1.06	2.34
4	0.0181	0.0368	1.33	2.49
5	0.0300	0.0730	2.21	4.93
6	0.0307	0.0300	2.26	2.03
7	0.0478	0.0124	3.51	8.38

ULTRAVIOLET SPECTRAL DATA FOR MIXTURE NUMBER 1

Table 9

DILUTION MOL/LITRE $X10^{-6}$	ABSORBANCE (A) AT		CALCULATED EXTINCTION COEFFICIENTS (ϵ) $X10^4$ AT	
	$\lambda = 273$ nm	$\lambda = 259$ nm	$\lambda = 273$ nm	$\lambda = 259$ nm
12.7	0.18	0.10	1.420	0.787
25.3	0.43	0.26	1.700	1.030
31.6	0.48	0.29	1.520	0.918
63.3	0.89	0.55	1.410	0.869

From this data, a graph of absorbance against concentration was plotted (Figure (iv)) and the molar extinction coefficient from the graph were:-
at λ= 273, 16250, λ = 259, 833.

ABSORBANCE AGAINST CONCENTRATION OF PURE
4-METHOXYBENZALDEHYDE

Slope at $\lambda = 273 = \varepsilon_{273}$

$= \dfrac{0.52}{32} \times 10^6$

$= 16250$

Slope at $\lambda = 259$ nm

$= \varepsilon_{259}$

$= \dfrac{0.2 \times 10^6}{24} = 8333$

⊖ At $\lambda = 273$ nm.

◇ At $\lambda = 259$ nm.

Fig(iv)   Conc. $\left(\dfrac{mol}{l}\right) \times 10^{-6}$ ⟶
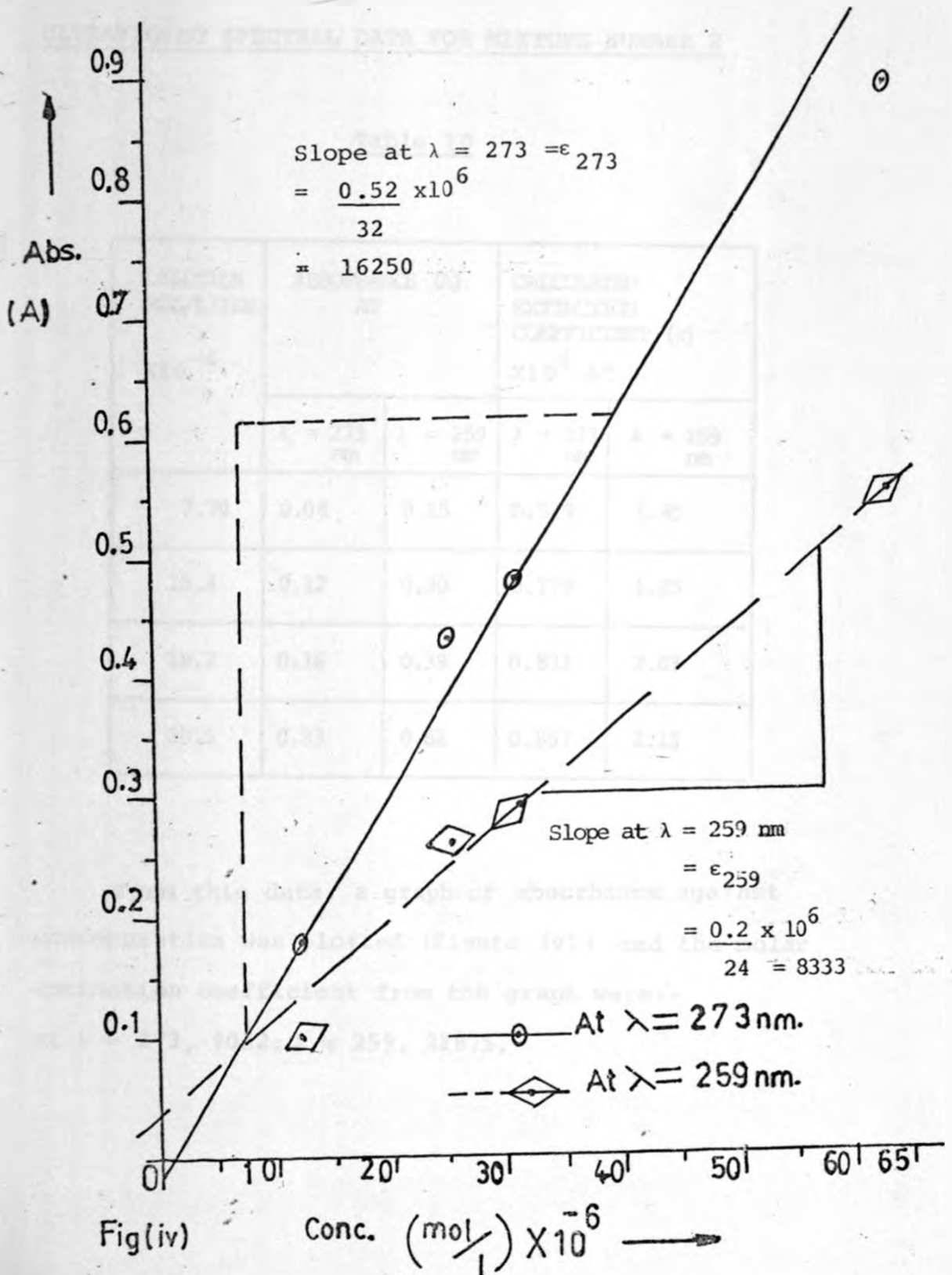
ULTRAVIOLET SPECTRAL DATA FOR MIXTURE NUMBER 2

Table 10

DILUTION MOL/LITRE X10^{-6}	ABSORBANCE (A) AT		CALCULATED EXTINCTION COEFFICIENT (ϵ) X10^4 AT	
	λ = 273 nm	λ = 259 nm	λ = 273 nm	λ = 259 nm
7.70	0.04	0.15	0.519	1.95
15.4	0.12	0.30	0.779	1.95
19.2	0.16	0.39	0.833	2.03
38.5	0.33	0.82	0.857	2.13

From this data, a graph of absorbance against concentration was plotted (figure (v)) and the molar extinction coefficient from the graph were:-

at λ = 273, 9032; λ = 259, 21875.

ABSORBANCE AGAINST CONCENTRATION OF 4-METHOXYPHENYLPROP-1-ENE

Slope at $\lambda = 259$ nm $= \varepsilon_{259}$

$= \dfrac{0.35}{16 \times 10^{-6}}$

$= 21875$

At $\lambda = 259$ nm.

At $\lambda = 273$ nm.

Slope at
$\lambda = 273$ nm
$= \varepsilon_{273}$
$= \dfrac{0.28}{31 \times 10^{-6}}$
$= 9032$

0.9 0.8 0.7 Abs. (A) 0.6 0.5 0.4 0.3 0.2 0.1

0 10 20 30 40 50

Fig(v) Conc $\left(\dfrac{mol}{l}\right) \times 10^{-6}$
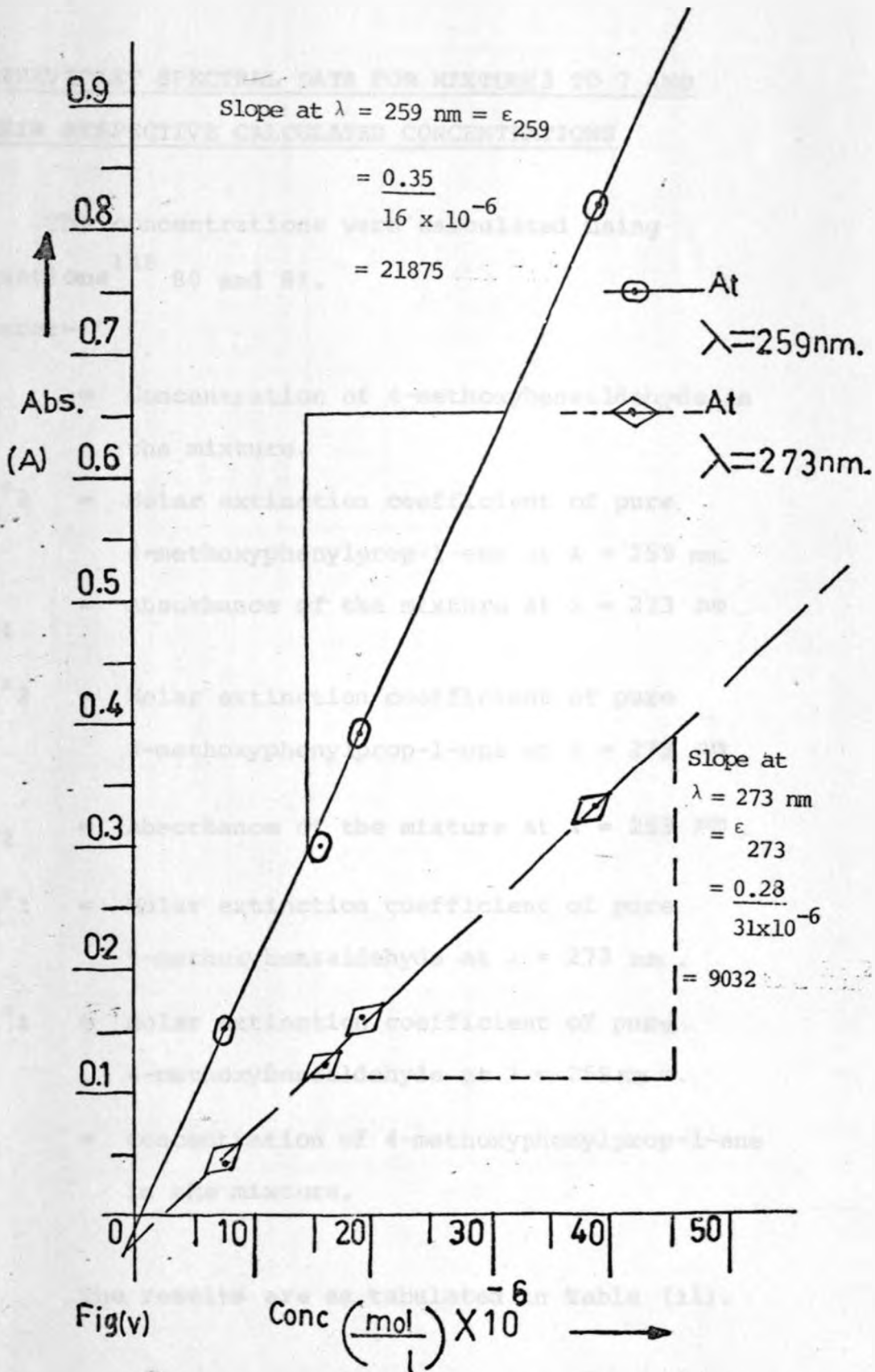
ULTRAVIOLET SPECTRAL DATA FOR MIXTURE 3 TO 7 AND
THEIR RESPECTIVE CALCULATED CONCENTRATIONS

The concentrations were calculated using
equations[148] 80 and 81.

where:-

C_1 = Concentration of 4-methoxybenzaldehyde in
the mixture.

$\lambda_2 \varepsilon_2$ = Molar extinction coefficient of pure
4-methoxyphenylprop-1-ene at λ = 259 nm.

D_{λ_1} = Absorbance of the mixture at λ = 273 nm.

$\lambda_1 \varepsilon_2$ = Molar extinction coefficient of pure
4-methoxyphenylprop-1-ene at λ = 273 nm

D_{λ_2} = Absorbance of the mixture at λ = 259 nm.

$\lambda_2 \varepsilon_1$ = Molar extinction coefficient of pure
4-methoxybenzaldehyde at λ = 273 nm.

$\lambda_2 \varepsilon_1$ = Molar extinction coefficient of pure
4-methoxybenzaldehyde at λ = 259 nm.

C_2 = Concentration of 4-methoxyphenylprop-1-ene
in the mixture.

The results are as tabulated in Table (11).

Table 11

NUMBER OF THE FLASK	CONCENTRATION IN THE MIXTURE AFTER DILUTION MOL/L X10^{-6}		ABSORBANCE (A) AT		CALCULATED CONCENTRATIONS MOL/L X10^{-6}		PERCENTAGE ERROR (%)	
	4-METHOXY-BENZALDE-HYDE	4-METHOXY-PHENYL-PROP-1-ENE	= 273 nm	= 259 nm	4-METHOXY-BENZALDE-HYDE	4-METHOXY-PHENYL-PROP-1-ENE	4-METHOXY-BENZALDE-HYDE	4-METHOXY PHENYL-PROP-1-ENE
3	10.6	23.4	0.34	0.56	8.5	22.4	22.6	6.9
4	13.3	24.9	0.44	0.66	13.1	25.6	1.5	2.8
5	22.1	8.8	0.38	0.38	17.4	10.7	21.3	21.6
6	22.6	20.3	0.48	0.62	17.5	21.7	22.6	6.9
7	35.1	8.4	0.55	0.46	27.8	10.3	20.8	21.6

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