# CHAPTER II

PRELIMINARY WORK

Lead (IV) acetate is commonly used as a solution in acetic
acid or benzene, and its applications are continually being
extended. Oxidations by lead (IV) acetate have been frequently reviewed
the most recent one (13) being by R. Criegee, who introduced
the possible use of this reagent as an oxidant in the 1930's.
In the same volume as Criegee's review, a general account was
given by C.A. Bunton of the oxidative cleavage of glycols,
effected by lead (IV) acetate, periodic acid, iodoso compounds,
or sodium bismuthate.

Shiner, Wasmuth (14) discussed the relative rates
corresponding to both geometrical isomer and streoisomer of
diols, and also the advantage of lead (IV) acetate over that
of periodates.

The experiments on a number of substituted aromatic and
polynuclear compounds were carried out and gave good results
with lead (IV) acetate, for example 4, 4' - dimethoxybenzoin is
oxidized by lead (IV) acetate in anhydrous acetic acid at 50°C (15)
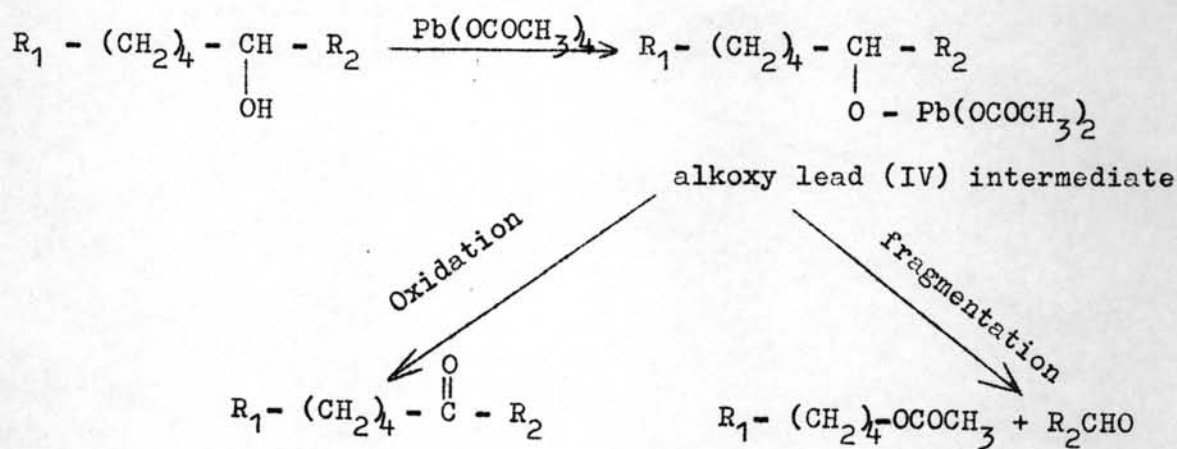The reaction is represented by
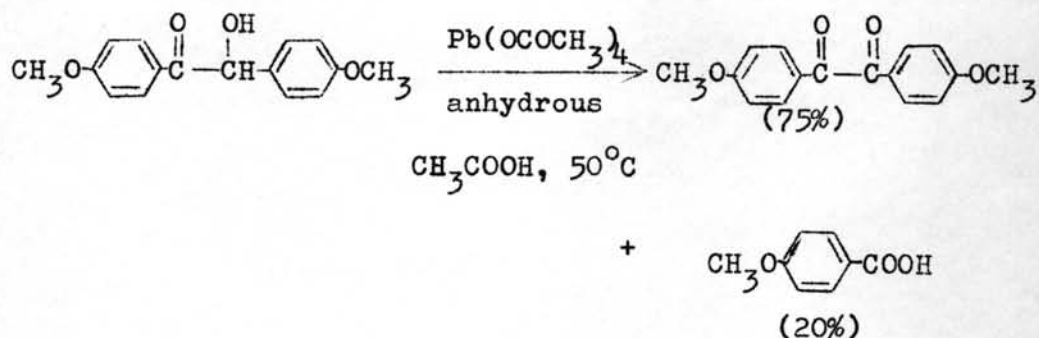
The oxidative cleavage of 1, 2 - diketones, α - hydroxy ketones, and α - ketoacids with lead (IV) acetate has been found to occur when the reaction medium contains a hydroxylic component such as water or ethanol (15)

Speer and Mahler (16) have found that the rates of thermal decomposition of various lead (IV) derivatives are in the following order:-

acetates and benzoates $<$ alkoxides - monoalkyl-acetates $<$ dialkyl and trialkylacetates. These decomposition rates are enhanced by the addition of donor ligands such as pyridine which can bond to the lead atom resulting in increasing its electron density and facilitating the loss of an acetate anion. They also discovered that the lead alkoxide intermediate could decompose thermally or photolytically in a variety of ways such as oxidation, fragmentation and so on. Both the structural features of the alcohol and the reaction conditions play important roles in determining which of the decomposition paths is favoured. In the presence of a donor solvent, e.g. pyridine if the lead alkoxide from a primary or secondary alcohol is generated, then the oxidation of an aldehyde or ketones

is dominant. The progress of this oxidation is easily followed because the red colour resulting from the interaction of pyridine with lead (IV) salt disappear when all of lead (IV) acetate has been consumed (17).

On the other hand in a non-basic solvent, the fragmentation of lead alkoxide intermediate formed becomes more favourable with alkoxide from secondary and tertiary alcohols, especially when the fragment lost is a relatively stable tertiary alkyl, benzyl or allyl. These can be generally written as:-

$$R_1 - (CH_2)_4 - \underset{\underset{OH}{|}}{CH} - R_2 \xrightarrow{Pb(OCOCH_3)_4} R_1 - (CH_2)_4 - \underset{\underset{O - Pb(OCOCH_3)_2}{|}}{CH} - R_2$$

alkoxy lead (IV) intermediate

Oxidation / fragmentation

$$R_1 - (CH_2)_4 - \overset{\overset{O}{||}}{C} - R_2 \qquad\qquad R_1 - (CH_2)_4 - OCOCH_3 + R_2CHO$$

The acetoxylation of phenol by lead (IV) acetate studied particularly by F. Wessely and his co-workers is a topic which is included in J.D. London's survey of method for the hydroxylation of phenol (18).

Two series of paper from the research schools of R.O.C. Norman (19) and M. Lj. Mihailovic (20) described the extensions of application of lead (IV) acetate, for example, the oxidations

of hydrazones and amines. Also included is the dicussion of the alternatives of one electron or two-electron transformation of the oxidant, a subject which has long been a cause of argument.

The oxidation of olefins with lead (IV) acetate has been suggested by R. Crigee (13). He explored briefly the oxidation of cyclohexene, styrene with lead (IV) acetate, thallium (III) acetate and mercury (II) acetate, and he expressed the view that the power of thallium (III) acetate is intermediate between lead (IV) acetate and mercury (II) acetate.

A variety of other functional groups found to be oxidized with lead (IV) acetate included disulphides (21), oximes (22), azines (23), N-acylhydrazines (24), carboxyl and carbonyl (25).

It is interesting to note that, there are quite a number of techniques whereby lead (IV) acetate is used as an oxidant such as its use in conjunction with iodine, in a reaction similar to Hunsdiecker degradation in which a carboxylic acid is converted to an alkyl iodide. Another variation is the use of lead (IV) acetate in conjunction with boron trifluoride whereby, α-acetoxylation of ketones occurs that is $-CH_2-CO-$ is converted to $-CH\ (OAc)-CO-$.

The discovery of thallium in 1861, did not represent a milestone in the development of modern chemistry. The use of thallium compound in organic chemistry was at that time virtually non-existing. Until the last decade, scientists have paid intensive

attention to thallium chemistry for the purpose of synthesis and found that many synthetic transformations are unique for thallium reagents.

In 1963, Anderson and Winstein (26) used thallium (III) acetate in acetic acid as an oxidizing agent for cyclohexene with the intention of studying a reaction mechanism. Cyclohexene were treated several days at room temperature with thallium (III) acetate, the products were identified both in acetic acid and water-acetic acid medium by vapour phase chromatography, infrared, nuclear magnetic resonance spectra and common chemical methods. Thallium (III) chloride, mercury (II) acetate, palladium (II) acetate and lead (IV) acetate were also used as oxidants, the mechanism of these reactions were discussed corresponding to different percentage yields.

Many papers were published from Hercules Powder Co. on the topics of the study of kinetics of thallium (III) ions on oxidation of olefins (27). Patrick studied the salt effect on the oxidation of ethylene by thallium (III) which yield acetaldehyde and ethylene glycol. The reaction was first order in thallium (III) ion, It was not retarded by acid and strongly accelerated by increasing salt concentration. The order of magnitude of the effect in various media, i.e., perchlorate $>$ sulphate $>$ nitrate can be explained by deactivation of the metal ion by ion-pair formation. The rate and the product distribution were found to be dependent upon the olefin structure (28). Based on the kinetics and rate effects, a reaction scheme

proceeding through an oxythallation adduct is proposed. The effect of olefin structure on product distribution is as expected. If the products arise by the decomposition of the postulated oxythallation intermediate assuming thallium (I) behaves as a normal leaving group, when in acetic acid, Thallium (III) acetate oxidizes olefin yielding 1, 1-and 1, 2-diacetates. He postulated the reactive species to be $Tl(OAc)_2(I)$ and found that the addition of strong acid to aqueous thallium (III) acetate accelerates the oxidation of olefins. At a very low acetate concentration the oxidation of thallium (III) and $Tl(OAc)_2(I)$ were probably unreactive (29).   005732

In 1966, J. McAdam Grimley and C.H. Brunaker (30) were able to identify the oxidation products of tartaric acid, glyoxal by thallium (III) in the presence of uranium (IV). Uranium (IV) is necessary for its function as a catalyst. It appears that uranium (IV) tartaric acid complexes formed facilitate both the oxidation of tartaric acid and uranium (IV).

Thallium organic acid complexes were potentiometrically investigated by T orapava, Batyrshima and Galeeva (31). They determined instability constant of various complexes and dissociation constant of the acids. At pH 1.5 and higher, salts of glycolic, lactic acid and some dicarboxylic acid, e.g. malic and succinic acid do not reduce. Thallium (III), the hydroxyl group in the anion of oxy acid, in an acid medium, does not take part in the formation of complexes.

Acyl transfer accompanying the oxidation of monocarboxylic
esters of hydroquinone was studied by Clark and Erant (32). They
found that the oxidation of monobenzoates of hydroquinones was
accompanied by benzoyl transfer. Oxidizing agents used were
cerium (IV) ion, thallium (III) ion, N-bromosuccinimide, bromine
or high potential quinone, and lithium periodate. There is
evidence that acylium intermediates were formed in the oxidation
with cerium (IV) ion. Thallium (III) ion oxidations are catalyzed
by thallium (I) ion and acyl transfer in these cases appears to
require attack of solvent on a thallium (III) ion-substrate
complexes.

Ulrtrup Jene (33), carried out some researches on the
influence of some organic π-electron system on the rate of the
electron transfer reaction of a number of organic compounds
containing a conjugated double bond system in $HClO_4$. The in-
stability constant of complexes of the individual reactions with
the compound were also determined. For several carboxylic acids
and amines, a retardation was observed, due to the formation of
thermodynamic stable complexes of thallium (III) and iron (II).

Chip and Grossert (34) found that an acyl-thallation can
serve as a route for the preparation of 1, 4-benzoquinones in
90% hydrogen peroxide-trifluoroacetic acid. From the year 1972,
a number of papers about thallium in organic synthesis have been
published. Alexander McKillop and Edward C. Taylor (5) have
given a review on thallium in organic synthesis. They summarized

all the applications of thallium in organic transformation, many
of which are specific and unique and fifty-four references were
listed.