PART A:

SYNTHETIC STUDIES ON LEAD (IV) ACETATE OXIDATIONS: STUDIES ON 1,2-CARBONYL TRANSPOSITIONS AND RELATED REACTIONS

PART B:

DEVELOPMENT OF GENERAL METHODS FOR THE SYNTHESIS OF DIARYL METHANES AND STILBENES FROM AZINES

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CERTIFICATE

This is to certify that the work described in this thesis has been carried out by Mr. Felix Mathew Vattakunnel under my supervision. He has satisfactorily completed the Pre-Ph.D. courses prescribed and the period of two years of investigational work for the award of Ph.D. degree in Chemistry.

This work described in this thesis is original and has not been submitted for any other degree or diploma in this or any other University.

19/6/95

(B. Myrboh)
Supervisor

CONTENTS

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Felix Mathew

FELIX MATHEW VATTAKUNNEL

PREFACE

Lead(IV) acetate is a versatile oxidising agent widely used in organic synthesis. The work that has been carried out in the laboratory revolves mainly around lead(IV) acetate oxidation of various ketones - saturated, unsaturated, cyclic and acylic.

The thesis is devided into 5 chapters. The first four Chapters discuss synthetic studied on lead(IV) acetate oxidations. First Chapter gives a general introduction on lead(IV)acetate oxidations. In the second Chapter, synthesis of methyl 4-phenyl-3-butenoate using lead(IV) acetate and boron trifluoride etherate-methanol combination has been discussed. In Chapter II the ring contraction of benzylidene cycloalkanone using lead(IV) acetate and triethyl orthoformate perchloric acid combination to afford the ring contracted cyclic esters is discussed. In continuation of the studies concerning the carbonyl transposition and ring contraction, the methodology discussed in Chapter III has been extended to unsaturated acylic ketones, saturated cyclic ketones and cyclopropyl methyl ketones. The details of the reaction and the products obtained are discussed in Chapter IV.

The synthetic utility of benzalazine for the preparation of diarylmethanes and stilbenes is the subject matter of the fifth and last Chapter.

Each Chapter is divided into Introduction, Results and Discussion and Experimental Section. The entire documentation in this thesis is supported by appropriate references at the end of each Chapter.

PART A

CHAPTER I

LEAD(IV) ACETATE OXIDATIONS

I. 1 GENERAL INTRODUCTION

Lead (IV) acetate (LTA) is a versatile oxidising agent widely used in organic synthesis. Its reaction with organic molecules generally involves the reduction of lead(IV) to lead(II) either through ionic or radical mechanisms. Synthetic applications of this reagent as it is now commercially available has since been increased in recent years. These results have been published in a number of reviews highlighting its synthetic applications. For instance, they include the reactions of lead(IV) acetate with olefines,[1] oxidative decarboxylations with lead(IV) acetate[2], oxidation of alcohols by LTA,[3] reaction of LTA with azomethines[4] and the LTA oxidation of sugars with emphasis on glycol cleavage.[5] Also a number of

useful general reviews on LTA have appeared. Fieser and Fieser[6] have discussed the uses of LTA for a broad range of synthetic processes, while Aylward[7] has reviewed the general behaviour of LTA towards organic nitrogen compounds. The reactions of LTA with steroids and intramolecular cyclization of alcohols with LTA[8,9] have also been discussed.

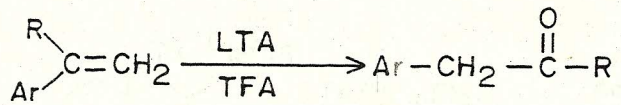
A general review by Criegee[10] on the behaviour of LTA towards O-H, C-H and single and multiple carbon-carbon bonds as well as some reactions involving organic compounds of sulphur, nitrogen and phosphorus have also been appeared. The initial work developed by Criegee laid the foundation for the development and growth of LTA as an important synthetic reagent.[11] The mechanistic aspects of LTA reactions have been included in the general reviews of oxidations.[12,13]

It is interesting to note that despite an array of diverse synthetic applications of lead(IV)acetate in organic synthesis, there are only a few synthetically useful processes based on oxyplumbation in contrast to oxymercuration[14,15] and oxythallation.[16], studies which have led to the development of a series of reactions of immense synthetic utility in recent years.

Metallation and oxymetallation reactions have been observed with the salts of only a few metals, namely mercury(II), thallium(III), lead(IV), palladium(II), gold(III) and platinum(II) which are known to posses 'soft acid' character.[17] Lead(IV) is isoelectronic with mercury(II) and thallium(III). The redox potential of lead(IV) is lowest in the series[18] and consequently the relative oxidising ability of the three metal ions is in the order Hg(II), Tl(III) and Pb(IV). A comparative study of oxymetallation of olefins with the acetates of the three metals have shown that while stable oxymercuration adducts[14] are formed with Hg(II) acetate, oxythallation adducts have been isolated only occasionally,[11,19] while the treatment of olefins with lead(IV)acetate gives complex mixture of products[10] which often renders these reactions of little synthetic value. Although oxyplumbation adducts have been postulated as intermediates in these reactions, direct evidence for the key organolead intermediate have not been obtained except as organic derivative of lead from the reaction of pregnenolene and diaacetatedifluoro lead(IV), $Pb(OAC)_2F_2$, which is particularly significant. Attempts have been made in recent years to direct these oxidations towards products formed through electrophilic oxyplumbation by employing more electrophilic lead(IV) salts. Thus, although styrene gives very low yield of phenylacetaldehyde (a product of oxyplumbation reaction) by oxidation with Pb(IV)

acetate under vigorous condition. However, excellent yields of aryl acetaldehyde (2) and other ketones are obtained when 1 are oxidised with lead(IV) acetate in trifluoroacetic acid, which contains lead(IV) with four trifluoroacetate ligands[21] (Scheme 1). Similarly, several oxidations involving LTA in hydrofluoric acid and lead(IV) diacetate difluoride, which has been shown to be highly useful fluorinating agent, have been reported.[22,23]

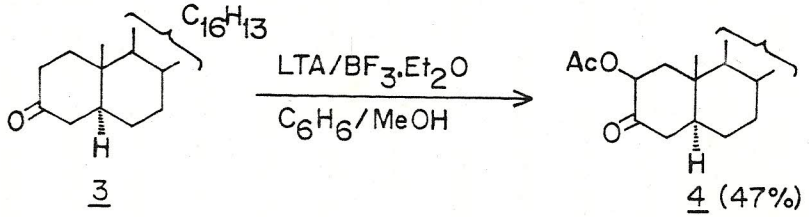
Ketones containing an α-methine moiety readly yield α-acetoxyketones on oxidation with lead(IV) acetate.[24] The enol form is considered to be the reactive species in these reactions. Boron trifluoride is shown to have a strong catalysing effect on the acetoxylation and this has been explained in terms of keto-enol tautomerism,though its effect could also arise from the interaction with the reagent. Although α-acetoxylation is the predominant pathway in the oxidation of ketones with lead(IV) acetate, products resulting through oxidative rearrangement have also been reported in some cases. Thus Henbest and co-workers[25] observed that 5α-cholestan-3-one (3) on treatment with lead(IV)acetate in benzene/methanol in the presence of boron trifluoride etherate yielded besides the normal acetoxylation product (4) (47%) a ring contracted product, methyl A-norcholestane-2α-carboxylate (5) in low yields (7%) (Scheme 2). Subsequently Fujimoto and co-workers[26] accomplished ring contraction of α-santonin in preparative yield using



1 2

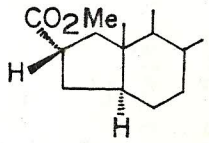
R = H, alkyl, aryl

Scheme—1



3

4 (47%)

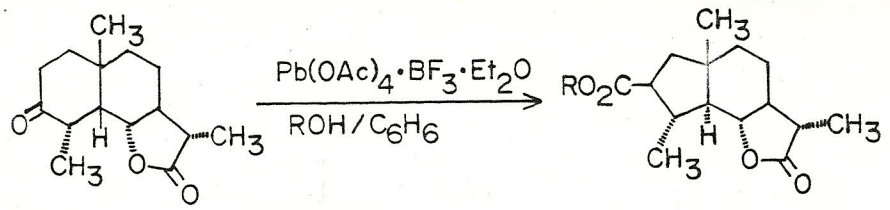


5 (7%)

Scheme-2

lead(IV)acetate / boron trifluoride etherate in benzene methanol combination. Thus 6 on oxidation yielded 7 as major products (Scheme 3). These authors have postulated the formation of 7 via enol ether (9), which on oxyplumbation followed by subsequent rearrangement of the adduct 10 yields 7 (Scheme 4).

Willgerodt developed in 1887 a method for the preparation of phenyl acetic acid by reacting ammonium sulphide and the acetophenones under pressure at about 200°C, which later became known as the Willgerodt reaction.[27] Extention of this reaction was hampered by modest yields of the carboxylic acid. Several modifications were subsequently extended to improve upon the yields of the products. Since the conversion of the aryl ketones to the corresponding phenyl acetic acid was of synthetic use, substantial modification of this reaction was first introduced by Kindler[28,29] in 1923, wherein the use of pressure was avoided and by introducing anhydrous aliphatic amines at a maximum temperature of 180°C, he was able to considerably improve the yield. This method was continued to be used although it could not be extended to the acetophenones which undergo polymerization under these condition. However, an excellent modification of this reaction was introduced by Taylor and McKillop[30] in 1971, when they were able to convert acetophenones to the corresponding methyl aryl acetates at room temperature in modest to excellent yields. Their method involves the oxidation of the

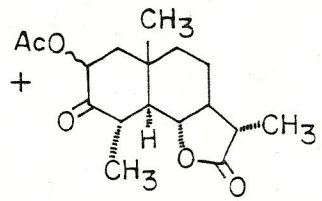


6

7 a, R=Me

b, R=Et

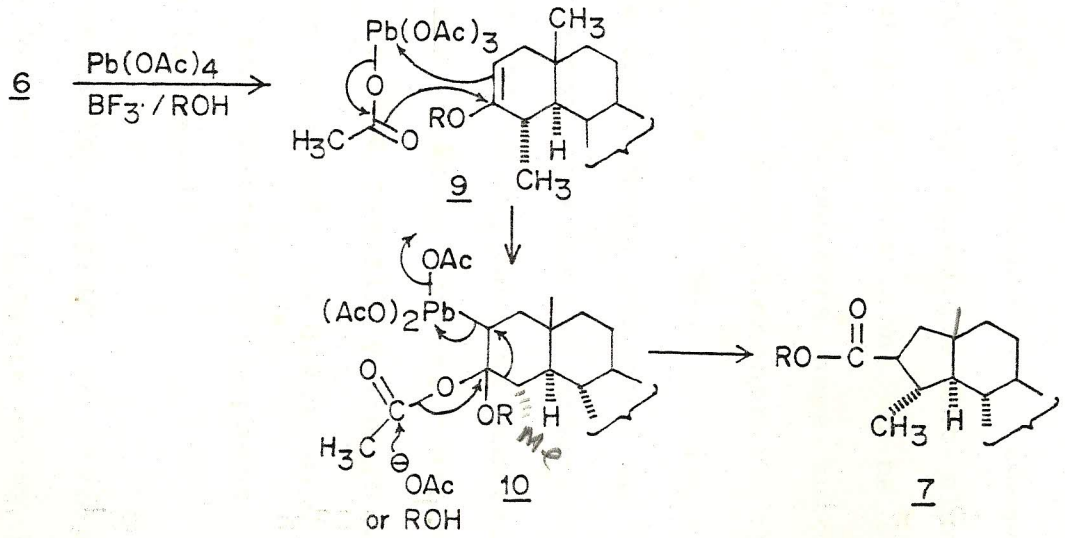
c, R=$CH_2C_6H_5$



8 a, α-OAc

b, β-OAc

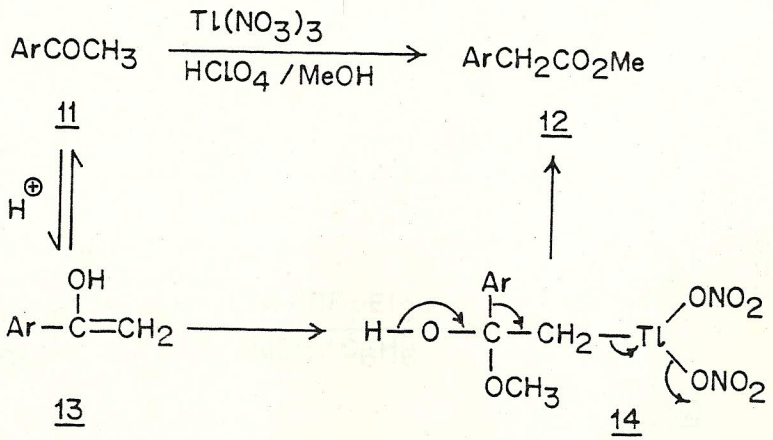
Scheme-3


6
Pb(OAc)4
BF3·/ROH
Pb(OAc)3
CH3
O
RO
H3C
O
H
CH3
9
OAc
(AcO)2Pb
O
O
C
H3C
OR
H
Me
OAc
or ROH
10
RO
O
C
CH3
H
7

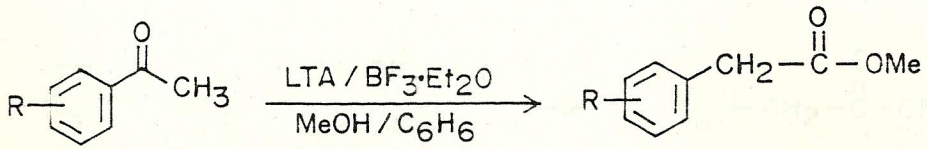
Scheme – 4

acetophenones (11) using thalium (III) nitrate (TTN) in the presence of perchloric acid and methanol, when they obtained the corresponding phenyl acetate (12), in excellent yield (Scheme 5). A mechanism involving oxythallation adduct (14) via enol (13) has been suggested for this rearrangement (Scheme 5). Thallium and its compounds are not only expensive but also extremely toxic requiring careful handling precautions to be strictly observed. Subsequently, Myrboh and co-workers have successfully reported similar conversion of the acetophenones to the corresponding phenylacetates by oxidation with lead(IV) acetate in presence of methanol and boron trifluoride etherate in dry benzene. Thus when methanol and boron trifluoride etherate added to a well stirred suspension of LTA in dry benzene containing acetophenone and stirred for 8 hours, work-up of the reaction mixture yielded the desired product in 86% overall yield (Scheme 6). The same methodology has been extended to desoxybenzoin (15), 2-acetyl naphthalene (17), and 2-acetylthiophene (19) to their corresponding esters (Scheme-7).

The plausible mechanism appears to involve the initial enolization of the ketones (11) assisted by boron trifluoride etherate followed by oxyplumbation to give 23, which by subsequent aryl group migration rearranges to 12 with the precipitation of lead(II)acetate (Scheme 8). The mechanism is analogus to the oxythallation of the acctophenones[30] in the

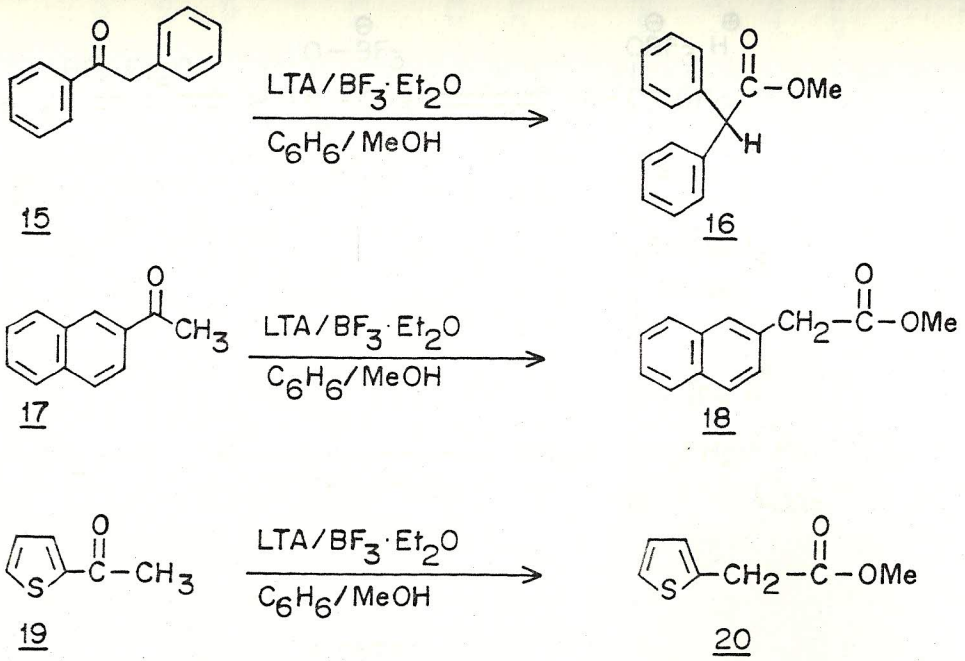

ArCOCH3
Tl(NO3)3
HClO4 / MeOH
ArCH2CO2Me
11
12
H⊕
OH
Ar–C=CH2
13
Ar
H–O–C–CH2–Tl
OCH3
ONO2
ONO2
14

Scheme — 5

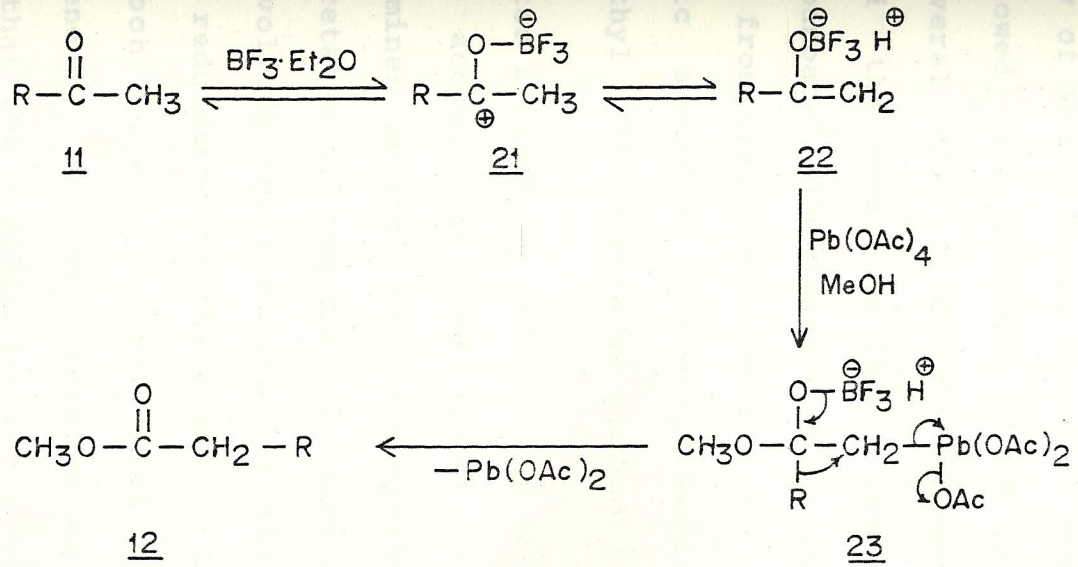


11 12

Scheme – 6



Scheme–7

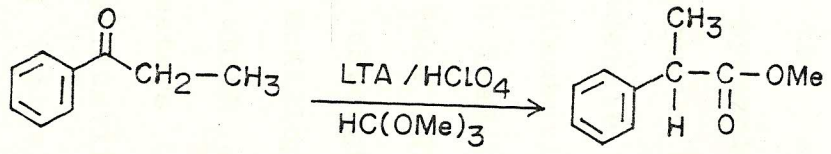


Scheme — 8

presence of perchloric acid and methanol as reproted by McKillop and co-workers (Scheme 5).

When the same reaction was extended to propiophenone (24) in order to prepare methyl α-methyl phenyl acetate (25), a majority of the starting material was recovered unchanged while GLC showed the presence of 25 as minor product (5%) along with several other products. Subsequently a Japanese group has reported the result on the facile preparation of alkyl 2-arylpropanoate[32] (Pharmaceutically important as antiinflamatory drugs) from aryl ethyl ketones 24 and lead(IV) acetate using catalytic amount of perchloric acid and trimethyl orthoformate or triethyl orthoformate as solvent in 78% yield (Scheme 9).

Later a paper by CeKovic and co-workers[33] appeard in which lead(IV) acetate was used under similar conditions to convert the enamines derived from acetophenones to the corresponding phenylacetates in comparable yields. However, the additional step involving the formation of moisture sensitive enamines become redundant in the light of the observations, the method by Myrboh et al.[31] provided direct convertion of the acetophenones to the corresponding phenylacetates. It may be noted that the enamine derived from p-nitroacetophenone failed to undergo the rearrangement. However their method has been shown to be of practical importance for ring contraction of the enamine derived form cycloalkanones analogous to the Favorski

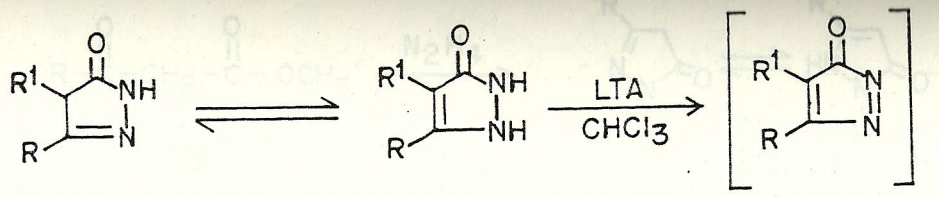


24 25

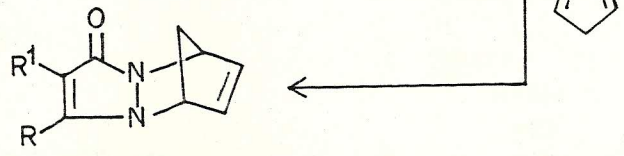
Scheme—9

type of rearrangement, while the reaction of enamines of cyclohexanone and tetralone with lead(IV) acetate and boron trifluoride etherate yielded mixture of several products from which the desired carboxylates could not be isolated.

In continuation of lead(IV)acetate oxidation Myrboh et al.[34] reported the oxidation of 2-substituted and 2,3-disubstituted-5-pyrazolones with lead(IV)acetate in methanol which affords 2-alkynoic and 2,3-alkadienoic (allenic) esters respectively in moderate to high yields. Previously it was reported that 3,4-disubstituted-5-pyrozolones (26) underwent dehydrogenation with lead(IV) acetate in chloroform to give the unstable pyrazol-3-one (27) which has been trapped in the presence of dienes through the Diels-Alder reaction (Scheme 10).[35] Taylor and McKillop have reported [36] the conversion of 5-pyrazolones (26) which are readily prepared in quantitative yield from β-ketoesters (29), to the esters of β-alkynoic acids (32) by thallium(III)nitrate in methanol (Scheme 11). A mechanism involving initial thallation of enemine tautomer of 5-pyrazolone (26) followed by a sequence of reactions as depicted in Scheme 12, has been suggested for this transformation. The β-ketoesters (33) which are alkylated on the α-carbon atom are converted under similar conditions (by initial treatment with hydrazine followed by addition of Tl(III)nitrate) to the allenic esters (35) (Scheme 12).[37] Since the 4-position



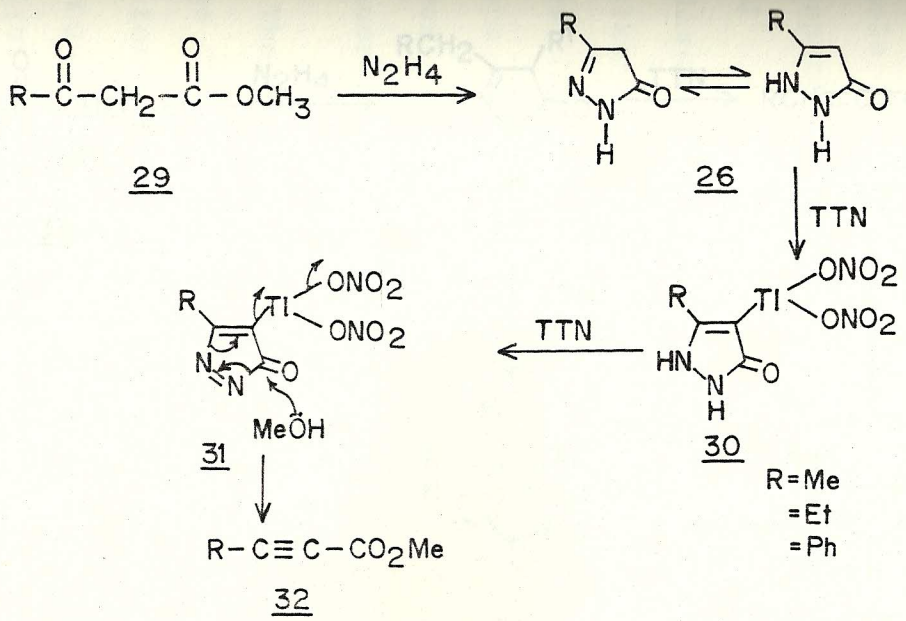
26a 26b 27



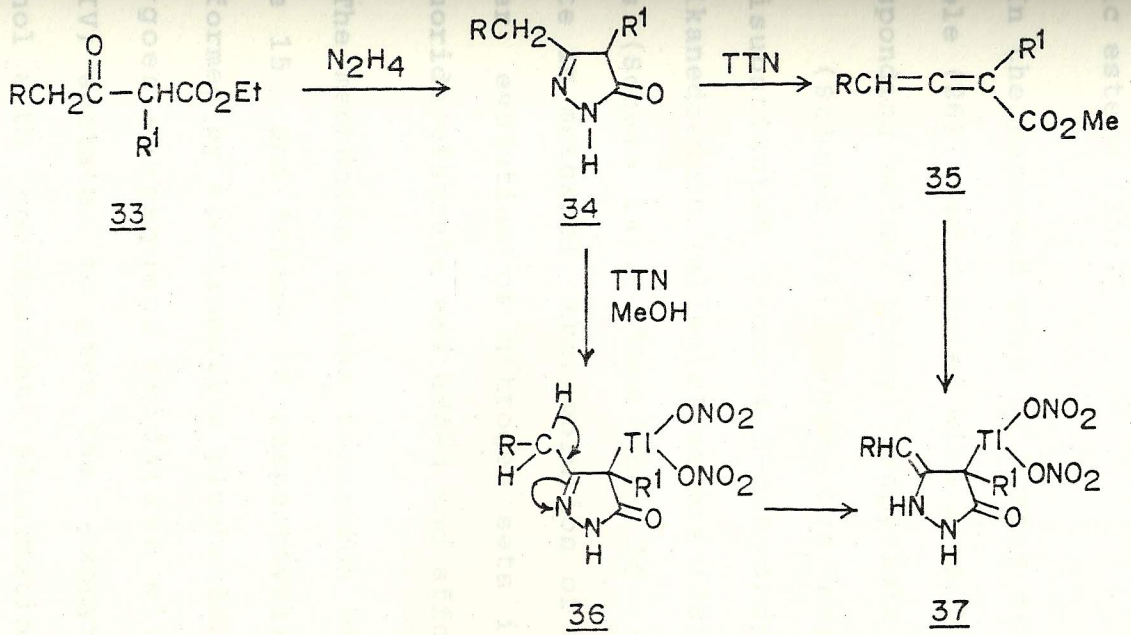
28

R, R^1 = H, CH_3, C_6H_5

Scheme—10


R–C(=O)–CH2–C(=O)–OCH3
N2H4
29
26
TTN
30
TTN
31
MeOH
R–C≡C–CO2Me
32
R=Me
=Et
=Ph

Scheme-11

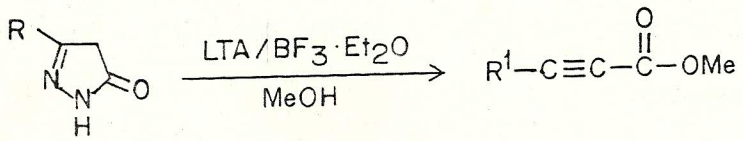

RCH2C(=O)CHCO2Et
R1
N2H4
RCH2
R1
N
N
H
O
TTN
RCH=C=C
R1
CO2Me
33
34
35
TTN
MeOH
H
R-C
H
Tl
ONO2
ONO2
R1
N
N
H
O
RHC
HN
36
37

Scheme — 12

now blocked by an alkyl substituent, deprotonation occurs from the 3-substituent of the pyrazolone thus leading to the observed allenic esters (35).

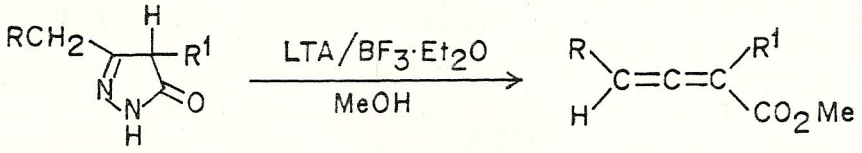
In the reported work by Myrboh et al.[34] the 5-oxo-3-phenyl pyrazole (26) was reacted with lead(IV) acetate in methanol, the corresponding methyl phenyl propyolate (32) was obtained in 40% yield (Scheme 13). When the reaction was extended to 3,4-disubstituted 5-oxo-4,5-dihydropyrazoles, the expected 2,3-alkanedienoic (allenic) esters (35) were formed in excellent yields (Scheme 14). Thus when 34 was treated with lead(IV) acetate in methanol the evolution of nitrogen was not observed. However, evolution of nitrogen sets in immediately when boron trifluoride etherate was added and afforded 35 in 60% yield.

The mechanism of the formation of 32 and 35 is shown in Scheme 15 and Scheme 16 respectively. The intermediate adduct (38) formed by electrophilic plumbation of enamine tautomer 26b undergoes subsequent oxidation with a second molecule of lead(IV) acetate to give the oxopyrazole (40). Solvolysis by methanol with concomitant elimination of nitrogen and lead(II) acetate yields the 2-alkynoic esters (32) directly. When the 4-position in 38 is blocked by an alkyl group, deprotonation occurs from 3-substituent of intermediate pyrazolone adduct (38) affording 39 (Scheme 16). The intermediate 39 on subsequent



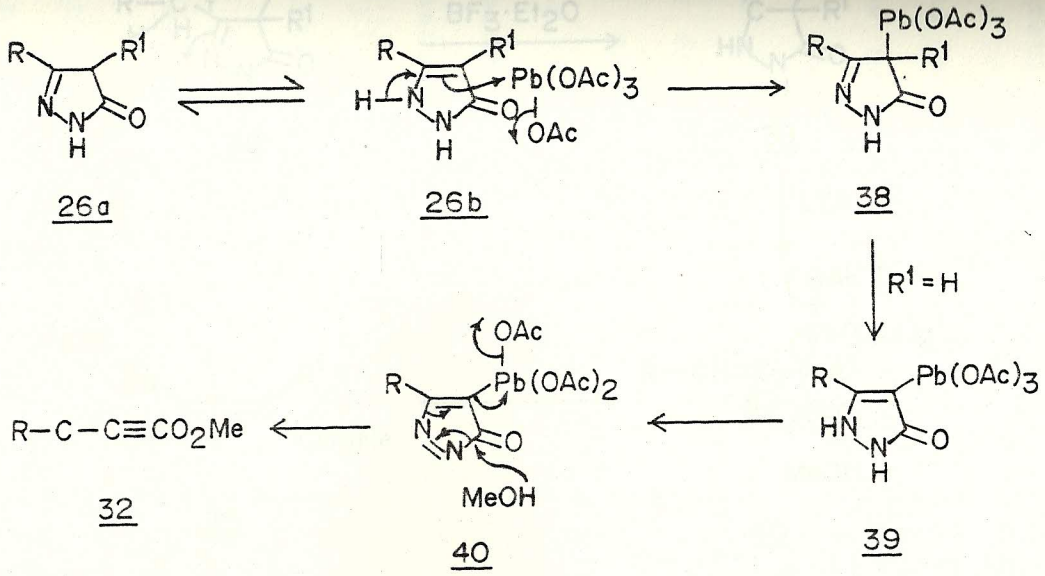
26 32

Scheme—13

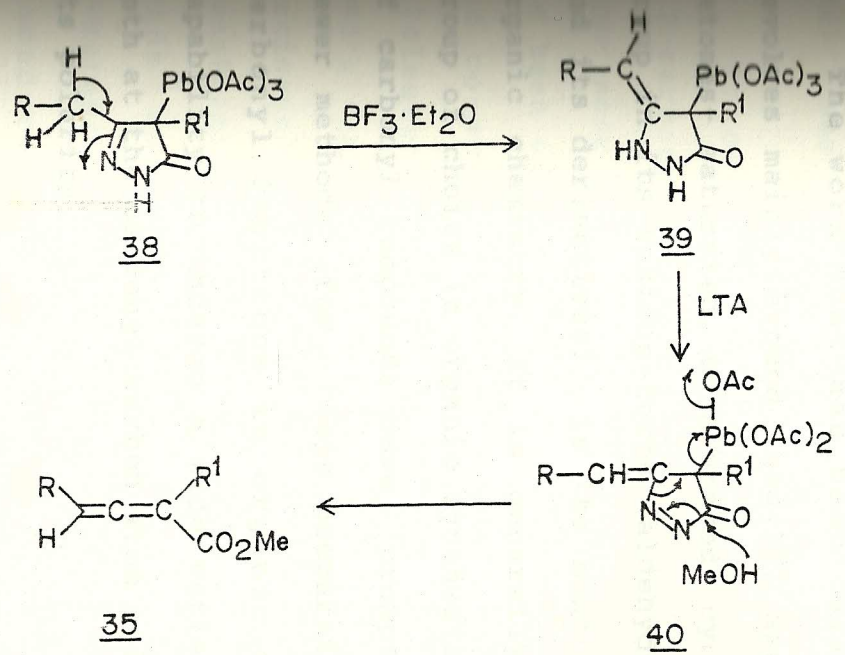


34 35

Scheme—14


R
R1
N
N
H
O
26a
Pb(OAc)3
OAc
26b
38
R1 = H
39
Pb(OAc)2
MeOH
40
R–C–C≡CO2Me
32

Scheme—15



Scheme—16

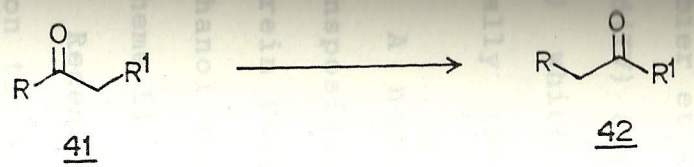
dehydrogenation followed by methanolysis yields the allenic esters (35). The role of boron trifluoride etherate in the formation of 35 apparently is to facilitate the deportonation-isomerization of intermediate 38 (Scheme 16).

The work that has been carried out in our laboratory revolves mainly around lead(IV) acetate oxidations of various ketones- saturated, unsaturated, cyclic and acylic. The carbonyl group in its various forms (aldehydes, ketones, carboxylic acids and its derivatives) is the most important functional unit in organic chemistry. It is generally considered as a functional group of choice in organic synthesis. The unparalleled importance of carbonyl compounds have prompted a continuous search for newer methods for their preparations. The versatility of the carbonyl functions in organic synthesis is based on its capability to undergo a wide variety of bond forming reactions both at the carbonyl carbon atom and at the sites influenced by its polarity.

Since the begining of the 20th century, there has been a constant interest in finding suitable methods for the transposition of a carbonyl group from its original position to carbon atom α,β and to it. The most common transposition is the exchange of a carbonyl function with an adjacent methylene group referred to as 1,2-carbonyl transpositions. (Scheme 17).

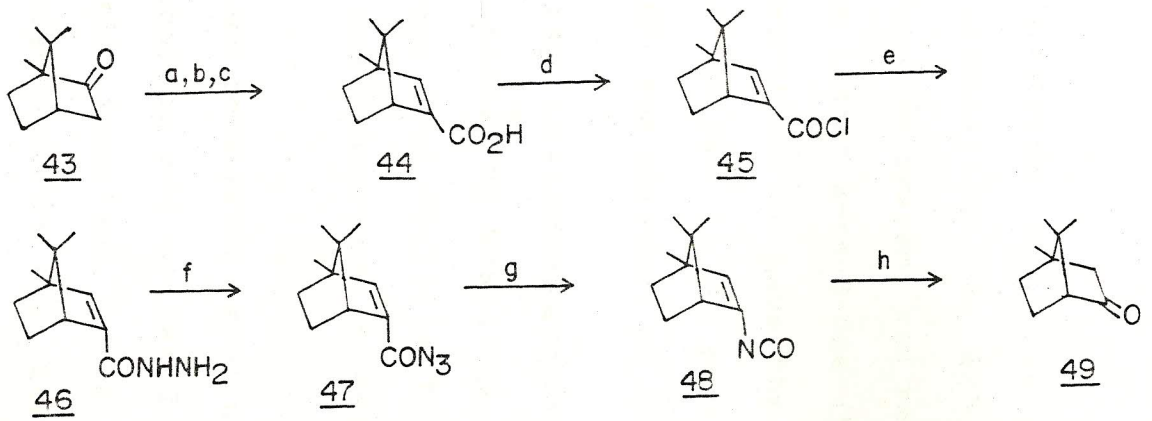
A survey of the literature revealed that a successful attempt at 1,2-carbonyl transposition was simultaneously reported by Perkin[38] and Bredt[39] in 1911. The study refers to the transposition of (d) Camphor (43) to 1-epicamphor (49) (Scheme 18). The requisite starting material unsaturated carboxylic acid (44) was readily available [40] from (d) camphor in four steps.

Since then other methods were developed dealing with 1,2-carbonyl transposition in the terpene systems.[41,42] The importance of 1,2-carbonyl transposistion in the steroid field has been well documented and recognised. As early as 1944 Ruzika and co-workers developed a method for the conversion of cholestan-3-one to cholestan-2-one.[43] But it was not until 1950's that a ketone transposition technique was applied to the cortisone problem. Here also the methodology found its success in transforming readly available 12-ketosteroids occurring in bile acids and sapogenins to the otherwise inaccessible 11-ketosteroids. Subsequently, numerous ketone transposition procedures have appeared in the literature as solution to problems especially in steroid chemistry and have employed a wide spectrum of organic reagents in the transposition step. A recent example lies in the work of Oka and Hara[44] who have very effectively utilized a 1,2-carbonyl transposition in their synthetic work leading to the synthesis of biologically active salamander alkaloids. The key step in this sequence was the



41 42

Scheme—17



43 44 45 46 47 48 49

a. $NaNH_2$,Et_2O, CO_2 ; b. Electrolytic Reduction ; c. $(CH_3CO)_2O/\Delta$; d. $SOCl_2$;

e. NH_2NH_2 ; f. HNO_2 ; g. Pyrolysis ; h. HCl .

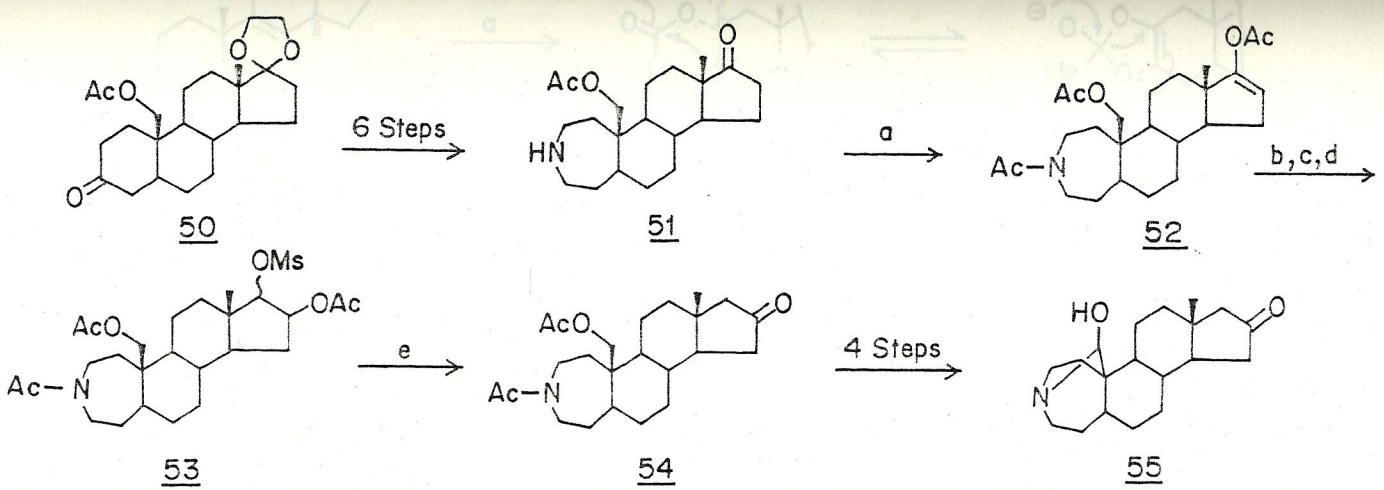
Scheme—18

conversion of α-acetoxy mesylate (53) to 54 on treatment with methanolic potassium hydroxide. The latter was then converted by these authors in four steps to cycloneosamandione (55) (Scheme 19).

Another method involving the use of lead(IV) acetate-borontrifluoride combination to achieve a 1,2-carbonyl transposition in a saturated system was reported by A. Leblache-Combier et al.[45] Thus lanost-8-en-3-one (56) on treatment with lead(IV) acetate-borontrifluoride gave the vicinal acetoxyketone (57) which isomerizes to (59) in the presence of basic alumina. Finally the product 60 was obtained as shown in Scheme 20.

A novel one-step transformation for 1,2-carbonyl transposition was reported by McKillop, Swann and Taylor,[30] wherein they have found that thallium(III) nitrate in acidic methanol rearranged acetophenones to methyl phenyl acetates (Scheme 5).

Recently Myrboh and co-workers have used lead(IV) acetate, boron trifluoride etherate and methanol combination in the synthesis of biologically important Indane-1-Carboxylates[46] (65). Here a 1,2-carbonyl transposition was obtained by a smooth ring contraction of the tetralones (61) to the Methyl Indane-1-Carboxylates (65) in moderate yields (Scheme 21).



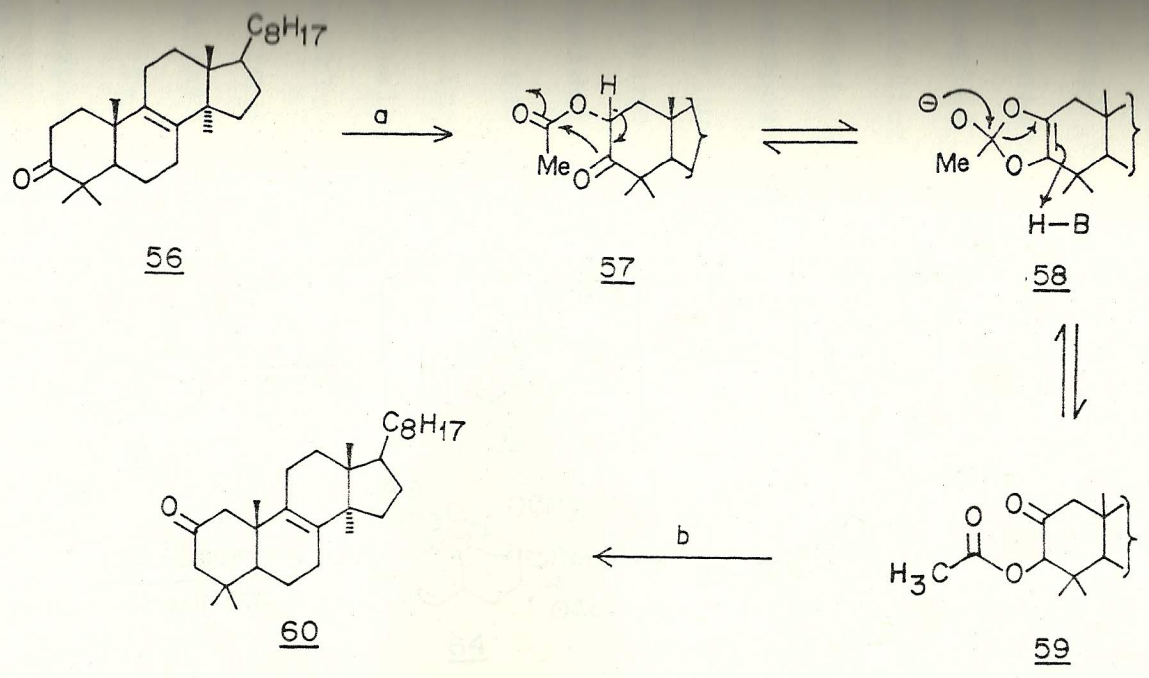
50 51 52

53 54 55

a. Isoprenyl acetate, $H^{\oplus}$; b. $Pb(OAc)_4$, CH_3CO_2H, trace $(CH_3CO)_2O$;

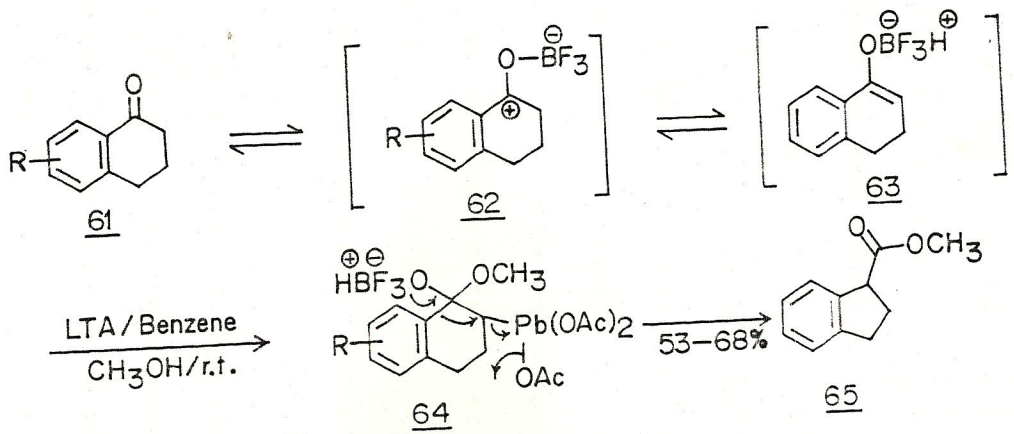
c. $NaBH_4$, CH_3OH; d. MsCl, C_5H_5N; e. KOH, CH_3OH.

Scheme –19



a. $Pb(OAc)_4 - BF_3$ b. $Ca - NH_3$

Scheme—20



Scheme – 21

The examples available on the 1,2-carbonyl transposition using lead(IV) acetate and other isoelectronic oxidising agents have been done on saturated carbonyl compounds and no attempt has been made to affect similar conversion on the α,β-unsaturated ketones using lead(IV) acetate. This fact has prompted us to carry out investigations based on lead(IV) oxidation of unsaturated ketones and cyclopropyl ketones with a view to develop general methods for these type of carbonyl transposition. In Chapter II synthesis of Methyl-4-phenyl-3-butenoate using lead(IV) acetate and boron trifluoride etherate methanol combination has been discussed. The structural elucidation of the products were done on the basis of analytical data and spectral evidences are also discussed.

In Chapter III the ring contraction of benzylidene cycloalkanone using lead(IV) acetate and triethyl orthoformate perchloric acid combination to afford the ring contracted cyclic esters. The details concerning the ring contraction and analysis of the products are discussed there.

In continuation of our studies concerning the carbonyl transposition and ring contraction, we have extended the same methodology discussed in Chapter III to unsaturated acylic ketones, saturated cyclic ketones and cyclopropyl methyl ketones. The details of the reaction, and the confirmation of the products formed are discussed on the bases of analytical data and spectral evidence in Chapter IV.

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