5.1 INTRODUCTION

Oxidation of organic substrates by means of tellurium reagents is of current interest and is rapidly growing. Inorganic species such as Na₂TeO₃ as oxidising agent for thiols¹, TeCl₄-promoted oxidation of trialkyl phosphites² and organic derivatives such as bis(p-methoxyphenyl) telluroxide as mild and selective oxidizing reagent for conversion of thio- and selenocarboxyl compounds into their oxo analogous³, conversion of tertiary phosphines into tertiary phosphine oxides⁴, conversion of phenyl isothiocyanate into diphenyl urea⁴, conversion of thiourea into urea⁴, conversion of thiols into disulphides³ conversion of o- and p-diphenols into quinones⁴, conversion of acylhydrazine into acylhydrazide⁴, conversion of N-phenylhydroxylamine into nitroso benzene⁴, oxidation of benzophenone hydrazone into diphenyl diazomethane⁴. Bis(p-methoxyphenyl) tellurone⁵, arenetellurinic anhydrides⁶-⁸ and tellurinic acid⁹ as oxidising reagents for several functionalities are well established.

Aryltellurium(IV) halides are well know compounds, the tri- and dichlorides being the most familiar and useful for the synthetic purposes. These chlorides are easily accessible, crystalline compounds. Though the lewis acid character of aryltellurium(IV) halides has been recently utilised in synthetic reactions including chlorotelluration like lactonization of unsaturated carboxylic acids with aryltellurium trichlorides¹⁰,¹¹

\[
\text{Ar} = p\text{-MeOC}_6\text{H}_4
\]

R, R¹ = H, R² = H, Ph, Me, R² = H, Ph, Me
and dialkyttellurium dichlorides\textsuperscript{12}, synthesis of biaryls by Raney Ni-catalysed homocoupling of diaryltellurium dichlorides\textsuperscript{13} and aryltellurium trichlorides\textsuperscript{14}, cyclic etherification of unsaturated alcohols and allylphenols with ArTeX\textsubscript{3} and Ar\textsubscript{2}TeX\textsubscript{2}\textsuperscript{15}.

\[ n = 1, \text{R} = \text{H, Me} \quad \text{Ar} = p-\text{MeOC}_\text{6}H_4, p-\text{PhC}_6H_4 \]
\[ n = 2, \text{R} = \text{H} \quad p-\text{MeC}_6H_4 \]

and Pd(II)-catalysed arylation of olefins by means of different aryltellurium(IV) Chlorides\textsuperscript{16}.

Straightforward utilisation of oxidising property of these aryltellurium(IV) chlorides has not been claimed so far in synthetic organic chemistry\textsuperscript{17}. In view of this, we were interested in this property of ArTeCl\textsubscript{3} and Ar\textsubscript{2}TeCl\textsubscript{2}.

As part of a programme aimed at developing organic synthetic methods based on various organyl derivatives of tellurium\textsuperscript{18-22}, an efficient and operationally simple method is developed for the synthesis of diorganyl chlorophosphates from di- and triorganyl phosphites using new chlorine bearing reagents, aryltellurium(IV) chlorides. These reagents afforded diorganyl chlorophosphates at room temperature.

Organophosphorus compounds have attracted the attention of researchers because of their wide applications in industrial, agricultural, biochemical and medicinal areas\textsuperscript{23}. Naturally occurring organophosphorous compounds play an important role in the maintenance of life process\textsuperscript{24-28}. It is interesting to note that chemical, physical and biological properties of organophosphorus compounds are governed by the stereochemical disposition of substituents around the phosphorus atom. One such class of compounds is the diorganyl chlorophosphates. These chlorophosphate are used for the transformation of various functional groups\textsuperscript{29-34}. Recently, diethyl chlorophosphate has been used as an efficient reagent in cyclization reactions\textsuperscript{35} and in regioselective ring opening of epoxides\textsuperscript{36}.
Methods described in the literature for the preparation of diorganyl chlorophosphates, involve chlorination of the corresponding phosphites (diorganyl phosphites/triorganyl phosphites) with reagents such as elemental chlorine, phosgene, \( \text{SO}_2\text{Cl}_2 \), \( \text{S}_2\text{Cl}_2 \), perchlorofulvalene, and \( \text{N}-\text{chlorosuccinimide} \). Among these procedures, only a few can be considered as convenient laboratory methods for the synthesis of diorganyl chlorophosphates. Most of these reported methods either use reagents or produce undesired by-products, which are difficult to remove from the sensitive chlorophosphates, while others are time consuming, involve expensive and unstable reagents, and require harsh conditions. A modified method (the so-called Atherton-Todd Method) makes use of \( \text{CCl}_4 \) and a tertiary base to generate dialkyl chlorophosphates in situ, but has limited scope in the formation of P-N compounds. Our aim in this research work is to overcome the limitations and drawbacks of the reported methods.

In recent years, the uses of tellurium reagents have received considerable interest in organic synthesis. All this prompted us to explore the possibility of using stable, efficient and positive chlorine releasing reagents, aryltellurium(IV) chlorides. These have been used as efficient lewis acid catalyst for knoevenagel condensation in our laboratory. We investigated the oxidising behaviour of these aryltellurium(IV) chlorides namely \( p\)-methoxyphenyltellurium(IV) trichloride, \( p\)-hydroxyphenyltellurium(IV) trichloride, \( 3\)-methyl-4-hydroxyphenyltellurium(IV) trichloride and bis(\( p\)-methoxyphenyl)tellurium(IV) dichloride as alternative reagents for the conversion of di- and triorganyl phosphites into corresponding diorganyl chlorophosphates and report our results herein.

5.2 EXPERIMENTAL

5.2.1 Reagents and Solvents

Aryltellurium trchlorides, \( \text{ArTeCl}_3 \) ( \( \text{R} = \text{p-methoxyphenyl}, \text{p-hydroxyphenyl}, \text{3-methyl-4-hydroxyphenyl} \) ); diaryltellurium dichloride, \( \text{Ar}_2\text{TeCl}_2 \) ( \( \text{R} = \text{p-methoxyphenyl} \) ) were investigated for their oxidising property. \( p\)-Methoxyphenyltellurium trichloride and bis(\( p\)-methoxyphenyl)tellurium dichloride have been prepared by reaction of \( \text{TeCl}_4 \) with anisole. \( p\)-Hydroxyphenyl and 3-methyl-4-hydroxyphenyltellurium trichlorides have been
prepared by reaction of TeCl$_4$ with phenol$^{61, 62}$ and o-cresol$^{62, 63}$ respectively, as described in chapter-2.

Oxidation of trimethyl phosphite, triethyl phosphite, tri-n-propyl phosphite, di- and tri-n-butyl phosphites, tri-iso-butyl phosphite, triphenyl phosphite and tri-o-tolyl phosphite has been studied.

Carbon tetrachloride, benzene, acetonitrile, dichloromethane, ethyl acetate, n-hexane and petroleum ether were the solvents used for the preparation and purification of the compounds. These were purified by standard methods as described in chapter-2.

5.2.2 Methods

Boiling points were determined in fusion tube and are uncorrected. TLC plates of silica gel-G were used to monitor the reactions. The products were characterized by IR, and $^1$H NMR spectral studies.

5.2.3 Aryltellurium(IV) Trichlorides, ArTeCl$_3$, as Oxidising Reagents

$p$-Methoxyphenyltellurium(IV) trichloride-I

$p$-Hydroxyphenyltellurium(IV) trichloride-II

3-Methyl-4-hydroxyphenyltellurium(IV) trichloride-III

5.2.3.1 Oxidation of Trimethyl phosphite: Formation of Dimethyl chlorophosphate

To a solution of aryltellurium trichloride (0.55 mmol; 0.188 g, 0.179 g and 0.188 g for I, II and III respectively) in 5 mL of dichloromethane was added dropwise a solution of trimethyl phosphite (0.124 g, 1.0 mmol) in 5 mL of dichloromethane under nitrogen atmosphere at room temperature. The reaction mixture was stirred for 40-50 minutes till completion of the reaction. As reaction proceeded, the mixture became black due to
precipitation of tellurium metal. The contents were then filtered and the filtrate was concentrated to obtain crude product. The product was purified by silica gel column chromatography using EtOAc/n-hexane (1:2) as eluent in 75-85% yield which was identified to be dimethyl chlorophosphate by direct comparison with authentic sample.


IR ( cm⁻¹ ); 1270 ( P=O ), 1050 ( O-CH₃ ), 851 ( O-P ).

¹H NMR ( CDCl₃, δ ppm ); 3.7465-3.7742 ( d, 6H, CH₃ ).

5.2.3.2 Oxidation of Triethyl phosphite: Formation of Diethyl chlorophosphate

To a 0.55 mmol solution of aryltellurium trichloride in 5 mL of dichloromethane was added dropwise a solution of triethyl phosphite ( 0.166 g, 1.0 mmol ) in 5 mL of dichloromethane under nitrogen atmosphere at room temperature. The reaction mixture was stirred till completion for 40-50 minutes. The mixture became black due to precipitation of tellurium metal. The contents were then filtered and the filtrate was concentrated to give crude product. The product was purified by silica gel column chromatography using EtOAc/n-hexane (1:2) as eluent in 71-78% yield which was identified to be diethyl chlorophosphate by direct comparison with authentic sample.


IR ( cm⁻¹ ); 1264 ( P=O ), 1034, 977 ( O-C ), 882 ( O-P ).

¹H NMR ( CDCl₃, δ ppm ); 1.0015-1.0390 ( t, 6H, -CH₂CH₃ ), 3.7472-3.8207 ( m, 4H, -CH₂CH₃ ).
5.2.3.3 Oxidation of Tri-n-propyl phosphite: Formation of Di-n-propyl chlorophosphate

To a solution of aryltellurium trichloride (0.55 mmol) in 5 mL of dichloromethane was added dropwise a solution of tri-n-propyl phosphite (0.208 g, 1.0 mmol) in 5 mL of dichloromethane under nitrogen atmosphere at room temperature. The reaction mixture was stirred for 40-50 minutes till completion. As reaction proceeded, the mixture became black due to precipitation of tellurium metal. The contents were then filtered and the filtrate was concentrated to give crude product. The product was purified by silica gel column chromatography using EtOAc/n-hexane (1:2) as eluent in 70-80% yield which was identified to be di-n-propyl chlorophosphate by direct comparison with authentic sample.


IR (cm⁻¹); 1271 (P=O), 1011 (O-CH₂), 864 (O-P).

¹H NMR (CDCl₃, δ ppm); 0.9771-1.0229 (t, 6H, -CH₃), 1.6701-1.7588 (m, 4H-CH₂CH₂CH₃), 3.9668-3.0435 (q, 4H, -CH₂CH₂CH₃).
5.2.3.4 Oxidation of Tri-n-butyl phosphite: Formation of Di-n-butyl chlorophosphate

Added dropwise a solution of tri-n-butyl phosphite (0.250 g, 1.0 mmol) in 5 mL of dichloromethane to a solution of aryltellurium trichloride (0.55 mmol) in 5 mL of dichloromethane under nitrogen atmosphere at room temperature. The reaction mixture was stirred for 40-50 minutes. As reaction proceeded, the mixture became black due to precipitation of tellurium metal. The contents were then filtered and the filtrate was concentrated to give crude product. The product was purified by silica gel column chromatography using EtOAc/n-hexane (1:2) as eluent in 74-75% yield which was identified to be di-n-butyl chlorophosphate by direct comparison with authentic sample.


IR (cm⁻¹); 1264 (P=O), 1034 (O-CH₂), 882 (O-P).

¹H NMR (CDCl₃, δ ppm); 0.9174-0.9544 (t, 6H, -CH₃), 1.3734-1.4666 (m, 4H \(\text{CH}_2\text{CH}_2\text{CH}_3\)), 1.6309-1.7014 (q, 4H, -CH₂CH₂CH₂CH₃), 4.0048-4.0552 (q, 4H, \(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\)).

5.2.3.5 Oxidation of Tri-iso-butyl phosphite: Formation of Di-iso-butyl chlorophosphate

To a solution of aryltellurium trichloride (0.55 mmol) in 5 mL of dichloromethane was added dropwise a solution of tri-iso-butyl phosphite (0.250 g, 1.0 mmol) in 5 mL of
dichloromethane under nitrogen atmosphere at room temperature. The contents were stirred for 40-50 minutes till completion of the reaction. The mixture became black due to precipitation of tellurium metal. It was then filtered and the filtrate was concentrated to give crude product. The product was purified by silica gel column chromatography using EtOAc/n- hexane (1:2) as eluent in 70-78% yield which was identified to be di-iso-butyl chlorophosphate by direct comparison with authentic sample.

B. pt. 270-272 °C ( lit\(^6\) b. pt. 270 °C ).

IR ( cm\(^{-1}\) ); 1280 ( P=O ), 1024 ( O-CH\(_2\) ), 878 ( O-P ).

\(^1\)H NMR ( CDCl\(_3\), δ ppm ); 0.5894-0.6391 ( d, 12H, -CH\(_3\) ), 1.5852-1.6852 ( m, 2H, >CH- ), 3.4621-3.4946 ( t, 4H, -CH\(_2\) ).

5.2.3.6 Oxidation of Triphenyl phosphite: Formation of Diphenyl chlorophosphate

A solution of triphenyl phosphite ( 0.310 g, 1.0 mmol ) in 5 mL of dichloromethane was added dropwise to a solution of aryltellurium trichloride ( 0.55 mmol ) in 5 mL of dichloromethane under nitrogen atmosphere at room temperature. The reaction mixture was stirred for 70-80 minutes. As reaction proceeded, the mixture became black due to precipitation of tellurium metal. The contents were then filtered and the filtrate was concentrated to give crude product. The product was purified by silica gel column chromatography using EtOAc/n- hexane (1:2) as eluent in 65-80% yield which was identified to be diphenyl chlorophosphate by direct comparison with authentic sample.
IR ( cm\(^{-1}\) ): 1170 ( P=O ), 951 ( O-Ph ), 765 ( O-P ).

\(^1\)H NMR ( CDCl\(_3\), \(\delta\) ppm ): 7.1267-7.3140 ( m, 10H, PhH ).

5.2.3.7 Oxidation of Tritolyl phosphite: Formation of Ditolyl chlorophosphate

To a solution of aryltellurium trichloride ( 0.55 mmol ) in 5 mL of dichloromethane was added dropwise a solution of tritolyl phosphite ( 0.3523 g, 1.0 mmol ) in 5 mL of dichloromethane under nitrogen atmosphere at room temperature. The reaction mixture was stirred for 70-80 minutes. The mixture became black due to precipitation of tellurium metal. The contents were then filtered and the filtrate was concentrated to obtain crude product. The product was purified by silica gel column chromatography using EtOAc/n- hexane (1:2) as eluent in 65-80% yield which was identified to be ditolyl chlorophosphate by direct comparison with authentic sample.


IR ( cm\(^{-1}\) ): 1239 ( P=O ), 1018 ( O-Ph ), 876 ( O-P ).

\(^1\)H NMR ( CDCl\(_3\), \(\delta\) ppm ); 2.2697-2.2868 ( d, 6H, -CH\(_3\) ), 6.9538-7.2998 ( m, 8H, PhH ).
5.2.3.8 Oxidation of Di-n-Butyl phosphite: Formation of Di-n-butyl chlorophosphate

To a dichloromethane (5ml) solution of aryltellurium trichloride (0.55 mmol) a solution of di-n-butyl phosphite (0.1942 g, 1.0 mmol) in 5 mL of dichloromethane was added under nitrogen atmosphere at room temperature. The reaction mixture was stirred for 70-80 minutes till completion of the reaction. The mixture became black due to precipitation of tellurium metal. The contents were then filtered and the filtrate was concentrated to give crude product. The product was purified by silica gel column chromatography using EtOAc/n-hexane (1:2) as eluent in 72-74% yield which was identified to be di-n-butyl chlorophosphate by direct comparison with authentic sample.


IR (cm⁻¹): 1264 (P=O), 1034 (O-CH₂), 882 (O-P).

¹H NMR (CDCl₃, δ ppm): 0.9174-0.9544 (t, 6H, -CH₃), 1.3734-1.4666 (m, 4H, CH₂CH₂CH₂CH₃), 1.6309-1.7014 (q, 4H, -CH₂CH₂CH₂CH₃), 4.0048-4.0552 (q, 4H, CH₂CH₂CH₂CH₃).
5.2.4. Bis(p-methoxyphenyl)tellurium Dichloride, An$_2$TeCl$_2$ as an Oxidizing Reagent

5.2.4.1 Oxidation of Trimethyl phosphite: Formation of Dimethyl chlorophosphate

To a solution of bis(p-methoxyphenyl)tellurium dichloride (0.227 g, 0.55 mmol) in 5 mL of carbon tetrachloride was added dropwise a solution of trimethyl phosphite (0.124 g, 1.0 mmol) in 5 mL of carbon tetrachloride under nitrogen atmosphere at room temperature. The reaction mixture was stirred for 65 minutes. As reaction proceeded, the mixture became black due to precipitation of tellurium metal. The contents were then filtered and the filtrate was concentrated to give crude product. The product was purified by silica gel column chromatography using EtOAc/n-hexane (1:2) as eluent in 72% yield which was identified to be dimethyl chlorophosphate by direct comparison with authentic sample.


5.2.4.2 Oxidation of Triethyl phosphite: Formation of Diethyl chlorophosphate

To a solution of bis(p-methoxyphenyl)tellurium dichloride (0.227 g, 0.55 mmol) in 5 mL of carbon tetrachloride was added dropwise a solution of triethyl phosphite (0.166 g, 1.0 mmol) in 5 mL of carbon tetrachloride under nitrogen atmosphere at room temperature. The reaction mixture was stirred for 65 minutes. As reaction proceeded, the mixture became black due to precipitation of tellurium metal. The contents were then filtered and the filtrate was concentrated to obtain crude product. The product was purified by silica gel column chromatography.
chromatography using EtOAc/n-hexane (1:2) as eluent in 78% yield which was identified to be diethyl chlorophosphate by direct comparison with authentic sample.


5.2.4.3 Oxidation of Tri-n-propyl phosphite: Formation of Di-n-propyl chlorophosphate

To a stirred solution of bis(p-methoxyphenyl)tellurium dichloride (0.227 g, 0.55 mmol) in 5 mL of carbon tetrachloride was added a solution of tri-n-propyl phosphite (0.208 g, 1.0 mmol) in 5 mL of carbon tetrachloride under nitrogen atmosphere at room temperature. The contents were stirred for 65 minutes. As reaction proceeded, the mixture became black due to precipitation of tellurium metal. It was then filtered and the filtrate was concentrated to get crude product. The product was purified by silica gel column chromatography using EtOAc/n-hexane (1:2) as eluent in 75% yield which was identified to be di-n-propyl chlorophosphate by direct comparison with authentic sample.

5.2.4.4 Oxidation of Tri-n-Butyl phosphite: Formation of Di-n-butyl chlorophosphate

To a solution of bis(p-methoxyphenyl)tellurium dichloride (0.227 g, 0.55 mmol) in 5 mL of carbon tetrachloride was added dropwise a solution of tri-n-butyl phosphite (0.250 g, 1.0 mmol) in 5 mL of carbon tetrachloride under nitrogen atmosphere at room temperature. The reaction mixture was stirred for 65 minutes. As reaction proceeded, the mixture became black due to precipitation of tellurium metal. The contents were then filtered and the filtrate was concentrated to give crude product. The product was purified by silica gel column chromatography using EtOAc/n-hexane (1:2) as eluent in 90% yield which was identified to be di-n-butyl chlorophosphate by direct comparison with authentic sample.


5.2.4.5 Oxidation of Tri-iso-Butyl phosphite: Formation of Di-iso-butyl chlorophosphate

Added dropwise a solution of tri-iso-butyl phosphite (0.250 g, 1.0 mmol) in 5 mL of carbon tetrachloride to CCl₄ solution of bis(p-methoxyphenyl)tellurium dichloride (0.227 g, 0.55 mmol). The reaction mixture was stirred for 65 minutes under N₂ atmosphere. As reaction proceeded, the mixture became black due to precipitation of tellurium metal. The contents were then filtered and the filtrate was concentrated to obtain crude product. The product was purified by silica gel column chromatography using EtOAc/n-hexane (1:2) as eluent in 81% yield which was identified to be di-iso-butyl chlorophosphate by direct comparison with authentic sample.
5.2.4.6 Oxidation of Triphenyl phosphite: Formation of Diphenyl chlorophosphate

To a solution of bis(p-methoxyphenyl)tellurium dichloride (0.227 g, 0.55 mmol) in about 5 mL of carbon tetrachloride was added dropwise a solution of triphenyl phosphite (0.310 g, 1.0 mmol) in 5 mL of carbon tetrachloride under nitrogen atmosphere at room temperature. The reaction mixture was stirred for 90 minutes. As reaction proceeded, the mixture became black due to precipitation of tellurium metal. The contents were then filtered and the filtrate was concentrated to give crude product. The product was purified by silica gel column chromatography using EtOAc/n- hexane (1:2) as eluent in 80% yield which was identified to be diphenyl chlorophosphate by direct comparison with authentic sample.

B. pt. 312-314 °C (lit\(^6\). b. pt. 315 °C ).
5.2.4.7 Oxidation of Tritolyl phosphite: Formation of Ditolyl chlorophosphate

To a solution of bis(p-methoxyphenyl)tellurium dichloride (0.227 g, 0.55 mmol) in 5 mL of carbon tetrachloride was added dropwise a solution of tritolyl phosphite (0.352 g, 1.0 mmol) in 5 mL of carbon tetrachloride under nitrogen atmosphere at room temperature. The contents were stirred for 90 minutes. As reaction proceeded, the mixture became black due to precipitation of tellurium metal. The contents were then filtered and the filtrate was concentrated to give crude product. The product was purified by silica gel column chromatography using EtOAc/n-hexane (1:2) as eluent in 85% yield which was identified to be ditolyl chlorophosphate by direct comparison with authentic sample.


5.2.4.8 Oxidation of Di-n-Butyl phosphite: Formation of Di-n-butyl chlorophosphate

To a solution of dianisyltellurium dichloride (0.227 g, 0.55 mmol) in 5 mL of carbon tetrachloride was added dropwise a solution of di-n-butyl phosphite (0.194 g, 1.0 mmol) in 5 mL of carbon tetrachloride under an atmosphere of nitrogen at room temperature. The reaction mixture was stirred for 90 minutes till completion of reaction. As reaction proceeded, the mixture became black due to precipitation of tellurium metal. The contents were then filtered and the filtrate was concentrated to obtain crude product. The product was purified by silica gel column chromatography using EtOAc/n-hexane (1:2) as eluent in 78% yield which was identified to be di-n-butyl chlorophosphate by direct comparison with authentic sample.
5.3 RESULTS AND DISCUSSION

Starting from tellurium tetrachloride, p-methoxyphenyltellurium(IV) trichloride, p-hydroxyphenyltellurium(IV) trichloride, 3-methyl-4-hydroxyphenyltellurium(IV) trichloride and bis(p-methoxyphenyl)tellurium(IV) dichloride were prepared smoothly by a Friedel-Craft type condensation reaction of anisole\(^58-60\), phenol\(^61, 62\) and o-cresol\(^62, 63\) with TeCl\(_4\), where by the TeCl\(_3^+\) unit attacks a position para to a hydroxyl or methoxy group in the aromatic ring. The formation of these aryltellurium(IV) chlorides can be represented as

These readily accessible stable crystalline solids, aryltellurium(IV) trichlorides and dianisyltellurium dichloride have been investigated for their oxidising property towards five trialkyl phosphites (trimethyl phosphite, triethyl phosphite, tri-n-propyl phosphite, tri-n-butyl phosphites and tri-isoo-butyl phosphite); one dialkyl phosphite (di-n-butyl phosphites); and two triaryl phosphites (triphenyl phosphite and tri-o-tolyl phosphite). The oxidised products diorganyl chlorophosphates, their boiling points, yield and reaction conditions are compiled in the table 1, 2, 3 and 4.

Oxidative chlorination of di/triorganyl phosphites is the subject of active investigation. Koh and Oh reported\(^2\) the similar reactions of di- and triorganyl phosphites
with TeCl₄ as a preparative method for diorganyl chlorophosphates. For the purpose of investigation on oxidising property of aryltellurium(IV) trichlorides and diaryltellurium dichlorides, we extended the above reaction to aryltellurium(IV) chlorides [p-methoxyphenyltellurium(IV) trichloride, p-hydroxyphenyltellurium(IV) trichloride, 3-methyl-4-hydroxyphenyltellurium (IV) trichloride] and bis(p-methoxyphenyl)tellurium(IV) dichloride. This synthetic approach is based on the electrophilic nature of aryltellurium(IV) chlorides. Arbuzov-type reaction of di/triorganyl phosphites with chlorine bearing reagent ArTeCl₃ or Ar₂TeCl₂ lead to the formation of corresponding chlorophosphates.

where R’ = H, R; Ar = p-MeOC₆H₄, p-HOC₆H₄, and p-HO-o-MeC₆H₃

where R’ = H, R; Ar = p-MeOC₆H₄

We found that both alkyl and aryl phosphites reacted efficiently at room temperature to give the product in excellent yield. Aliphatic phosphites reacted a little more rapidly compared to aromatic phosphites. When R’ was aryl, prolongation of reaction time is necessary due to decrease in nucleophilicity of P(III) by aryl group while R’ was H (dialkyl phosphites) the decrease in nucleophilicity of P(III) or increase in reaction time is due to decrease in the number of electron donating ‘R’ group attached to P(III).

Comparative study of efficiency of TeCl₄, ArTeCl₃ and Ar₂TeCl₂ as oxidizing reagents clearly indicates that electrophilicity of tellurium decrease by substitution of more electronegative ‘Cl’ by aryl group. Further, as the number of aryl group increased the electrophilicity of Te(IV) decrease and oxidizing behaviour of the above reagents follows the order TeCl₄ > ArTeCl₃ > Ar₂TeCl₂.

Next, the effect of varying the aryl group in ArTeCl₃ on reaction time was investigated. The nature of substituent present in aromatic ring of aryltellurium trichloride
also influence the reaction time (table 1, 2 and 3). Electron withdrawing substituent increase the electrophilicity of ArTeCl₃ and decrease the reaction time while reverse is true for electron donating substituent i.e. the reaction is faster in case of hydroxyaryltellurium trichlorides than anisyltellurium trichloride. Among hydroxyaryltellurium trichlorides, p-HOC₆H₄TeCl₃ proved to be better oxidizing reagent than p-OH-m-MeC₆H₄TeCl₃. The order of reactivity of these ArTeCl₃ is as HOC₆H₄TeCl₃ > p-HO-m-MeC₆H₄TeCl₃ > p-MeOC₆H₄TeCl₃.

The result indicates that the above Arbuzov-type reaction initiates by nucleophilic attack of trivalent phosphorus species to aryltellurium(IV) chlorides. The reaction may proceed by the attack of phosphorus centre of trivalent organyl phosphite on the positive chlorine of (ArTeCl₂)⁺ Cl⁻ or (Ar₂TeCl)⁺ Cl⁻ which are the partially ionized forms of ArTeCl₃ and Ar₂TeCl₂ in solution⁵³ respectively. The probable mechanism for the reaction is represented as

\[ \text{Initally formed } Ar₂Te₂ \text{ or } Ar₂Te \text{ dissociates to } Te \text{ which is precipitated out as black powder. Highly electrophilic aryltellurium(IV) chloride and more nucleophilic phosphorus reagent promoted the reaction markedly.} \]
Table 1: *p*-Methoxyphenyltellurium(IV) Trichloride as Oxidising Reagent.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Substrate</th>
<th>Reaction time(^a) (min.)</th>
<th>Yield(^b) (%)</th>
<th>B. pt. (^c) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>40</td>
<td>75</td>
<td>162-163</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>40</td>
<td>73</td>
<td>217</td>
</tr>
<tr>
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<td></td>
<td>40</td>
<td>69</td>
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</tr>
<tr>
<td>4</td>
<td></td>
<td>40</td>
<td>74</td>
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<td></td>
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<td>70</td>
<td>270</td>
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<tr>
<td>8</td>
<td></td>
<td>70</td>
<td>72</td>
<td>279</td>
</tr>
</tbody>
</table>

\(^a\)Monitored by complete disappearance of starting material using TLC; \(^b\)isolated yield based on diorganyl chlorophosphate.
Table 2: *p*-Hydroxyphenyltellurium(IV) Trichloride as Oxidising Reagent.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Substrate</th>
<th>Product</th>
<th>Reaction time(^a) (min.)</th>
<th>Yield(^b) (%)</th>
<th>B. pt. (˚C)</th>
</tr>
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<tbody>
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<td></td>
<td></td>
<td>45</td>
<td>80</td>
<td>162-163</td>
</tr>
<tr>
<td>2</td>
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\(^a\)Monitored by complete disappearance of starting material using TLC; \(^b\)isolated yield based on diorganyl chlorophosphate.
Table 3: 3-Methyl-4-hydroxyphenyltellurium(IV) Trichloride as Oxidising Reagent.

<table>
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<tr>
<th>S. No.</th>
<th>Substrate</th>
<th>Product</th>
<th>Reaction time&lt;sup&gt;a&lt;/sup&gt; (min.)</th>
<th>Yield&lt;sup&gt;b&lt;/sup&gt; (%)</th>
<th>B. pt. (˚C)</th>
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</table>

<sup>a</sup>Monitored by complete disappearance of starting material using TLC; <sup>b</sup>isolated yield based on diorganyl chlorophosphate.
Table 4: Bis(p-Methoxyphenyl)tellurium(IV) Dichloride as Oxidising Reagent.

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<th>Substrate</th>
<th>Product</th>
<th>Reaction time&lt;sup&gt;a&lt;/sup&gt; (min.)</th>
<th>Yield&lt;sup&gt;b&lt;/sup&gt; (%)</th>
<th>B. pt. (°C)</th>
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<sup>a</sup>Monitored by complete disappearance of starting material using TLC; <sup>b</sup>isolated yield based on diorganyl chlorophosphate.
5.4 CONCLUSION

Oxidative chlorinating property of three aryltellurium trichlorides, ArTeCl$_3$ (Ar = p-methoxyphenyl, $p$-hydroxyphenyl, 3-methyl-4-hydroxyphenyl) and diaryltellurium dichloride, Ar$_2$TeCl$_2$ (Ar = p-methoxyphenyl) have been investigated for conversion of di- and triorganylphosphites into corresponding diorganyl chlorophosphates at room temperature. Phosphites investigated are: trimethyl phosphite, triethyl phosphite, tri-$n$-propyl phosphite, di- and tri-$n$-butyl phosphites, tri-iso-butyl phosphite, triphenyl phosphite and tri-$o$-tolyl phosphite.

The di- and triorganyl phosphites oxidised smoothly to afford the corresponding dialkyl/aryl chlorophosphates in considerable yield. It has been observed that aryltellurium trichlorides are stronger oxidising agents than the diaryltellurium dichloride.

*******
REFERENCES


