Investigation of some \( p \)-methoxyphenyltellurium(IV) trichloride catalysed knoevenagel reaction

Rimpi, Sapana Garg and Krishan K. Verma*

Department of Chemistry, M. D. University, Rohtak, India

ABSTRACT

\( p \)-Methoxyphenyltellurium trichloride has been prepared by condensation of tellurium tetrachloride with anisole. This \( p \)-methoxyphenyltellurium trichloride has been investigated as a catalyst in knoevenagel reactions between non-enolisable aldehydes and active methylene compounds to yield the corresponding olefinic products. This paper reports the reaction of ethylcyanoacetate, malononitrile and cyanoacetamide with aromatic aldehydes, \( \text{ArCHO} \) ( \( \text{Ar is C}_6\text{H}_5, 4-\text{ClC}_6\text{H}_4, 4-\text{CH}_3\text{OC}_6\text{H}_4, \text{and C}_6\text{H}_5-\text{CH}=\text{CH} \) ). The products are obtained in excellent yield and high purity and have been identified by comparison of their properties with those of authentic samples.

Keywords: \( p \)-Methoxyphenyltellurium trichloride, Knoevenagel condensation, non-enolisable aldehyde, active methylene compounds.

INTRODUCTION

Knoevenagel condensation is now a very well established method [1] for the synthesis of substituted alkenes and is of importance because of its use in various synthetic transformations. The reaction is usually carried out in the presence of a base with non-enolisable aldehydes and ketones. It may be carried out either in homogeneous or heterogeneous phase. The usual catalysts [2] are ammonia and ammonium salts, primary and secondary amines and their salts. Subsequently the use of \( \text{TiCl}_4 \) and base [3], aluminium oxide [4], \( \text{AlPO}_4-\text{Al}_2\text{O}_3 \) [5] and doped xonotlite [6] have been reported. Silica gel functionalised with amine groups has been used under heterogeneous catalysis conditions [7]. However, Lehnert’s modification [3] of this method requires the equivalent of \( \text{TiCl}_4 \) and base, which severely limits the scope of this method in large scale preparations. Tellurium and its compounds in recent years have attracted considerable...
interest in the field of organic synthesis [8-11]. Khan et al [12] reported some tellurium tetrachloride catalysed knoevenagel reactions. In this paper we report the use of \( p \)-methoxyphenyltellurium trichloride as a catalyst in similar reactions.

**MATERIALS AND METHODS**

All products are known compounds and were characterized by melting points, IR and \(^1\)H NMR spectral studies. \(^1\)H NMR spectra were recorded on a Bruker AVANCE II-400MHz NMR spectro-meter using TMS as internal standard (CDCl\(_3\) solution). IR spectra were recorded in KBr on FT-IR Bruker Tensor 27. TLC plates of Silica Gel-G were used to monitor the reactions. All products were identified by comparison of their properties [13,14] with those of authentic samples.

**Preparation of \( p \)-methoxyphenyltellurium trichloride [15]**

Anisole (5.4 g, 50 mmol) and TeCl\(_4\) (13.5 g, 50 mmol) in CCl\(_4\) (40 mL) were heated under reflux for 2 h. Evolution of HCl occurred and heavy crystalline TeCl\(_4\) progressively converted in to yellow flakes of trichloride. The product was filtered off and washed with CCl\(_4\). The crude product was recrystallised from glacial HOAc as yellow needles. Yield 90%, m.p. 182 °C.

**General Experimental Procedure for Knoevenagel Condensation**

A mixture of carbonyl compound (I) (0.01 mol), the active methylene compound (II) (0.01 mol), and \( p \)-methoxyphenyltellurium(IV) trichloride (0.001 mol) was thoroughly mixed at room temperature. After being stirred for 5 minutes, the mixture was heated and continuously stirred at 90-100 °C at a magnetic stirrer with hot plate for specific time (Table). The reaction was cooled at room temperature and treated with a solution of 1% aqueous ethyl alcohol. The product was extracted with methylene chloride and washed with water. After drying over anhydrous Na\(_2\)SO\(_4\), the solvent was evaporated to obtain the product (III) in high purity.

**Physical Data**

(E)-2-Cyano-3-phenyl propenamide (1)

\(^1\)H NMR: \( \delta \) 8.2 (s, IH, H-olefinic), 7.87-7.97 (m, 2H, PhH), 7.27-7.58 (m, 3H, PhH), 6.88 (bs, 1H, NHCO), 6.62 (bs, 1H, NHCO); IR (KBr): 3399, 3164, 2218, 1692, 1597, 1573, 1370, and 684 cm\(^{-1}\).

(E)-2-Cyano-3-(4-chlorophenyl)-2-propenamide (2)

\(^1\)H NMR: \( \delta \) 8.19 (s, IH, H-olefinic), 7.89-7.97 (m, 2H, PhH), 7.63 (bs, 1H, NHCO), 7.40-7.82 (m, 2H, PhH), 7.05 (bs, 1H, NHCO); IR (KBr): 3455, 3153, 2211, 1702, 1600, 1586, 1380, 1092, 852 cm\(^{-1}\).

2-(Phenylmethylene) malononitrile (3)

\(^1\)H NMR: \( \delta \) 7.86-7.98 (m, 2H, PhH), 7.79 (s, 1H, H-olefinic), 7.29-7.63 (m, 3H, PhH); IR (KBr): 3184, 2222, 1592, 1693, 1383, 754, 679 cm\(^{-1}\).

2-[(4-Chlorophenyl)methylene] malononitrile (4)

\(^1\)H NMR: \( \delta \) 8.19 (s, 1H, H-olefinic), 7.90-7.97 (m, 2H, PhH), 7.40-7.50 (m, 2H, PhH); IR (KBr): 3184, 2222, 1592, 1693, 1383, 754, 679 cm\(^{-1}\).
3154, 2211, 1601, 1587, 1486, 1381, 1092, 825 cm\(^{-1}\).

2-[(4-Methoxypheyl)methylene] malononitrile (5)

\(^1\)H NMR: \(\delta\) 7.81-7.97 (m, 2H, PhH), 7.65 (s, 1H, H-olefinic), 6.86-7.02 (m, 2H, PhH), 3.88 (s, 3H, OCH\(_3\)); IR (KBr): 3100, 2924, 2851, 2223, 1605, 1571, 1278, 1180, 833 cm\(^{-1}\).

2-[(E)-3-Phenyl-2-propenylidene] malononitrile (6)

\(^1\)H NMR: \(\delta\) 8.5 (d, 1H, H-olefinic), 7.50-7.80 (m, 2H, PhH), 7.3-7.49 (m, 2H, H-olefinic), 7.10-7.20 (m, 3H, PhH); IR (KBr): 3029, 3057, 2223, 1671, 1577, 1607, 699, 752 cm\(^{-1}\).

Ethyl (E)-2-cyano-3-phenyl-2-propenoate (7)

\(^1\)H NMR: \(\delta\) 8.25 (s, 1H, H-Olefinic), 7.97-7.99 (t, 2H, PhH), 7.47-7.57 (m, 3H, PhH), 4.35-4.40 (q, 2H, CH\(_2\)CH\(_3\)), 1.37-1.41 (t, 3H, CH\(_2\)CH\(_3\)); IR (KBr): 3064, 3030, 2981, 2939, 2224, 1724, 1606, 1574, 1449, 1264, 1204, 1091, 768, 686 cm\(^{-1}\).

Ethyl (E)-2-cyano-3-(4-chlorophenyl)-2-propenoate (8)

\(^1\)H NMR: \(\delta\) 8.25 (s, 1H, H-olefinic), 7.97-7.99 (t, 2H, PhH) 7.47-7.57 (m, 3H, PhH), 4.38-4.40 (q, 2H, CH\(_2\)CH\(_3\)), 1.37-1.41 (t, 3H, CH\(_2\)CH\(_3\)); IR (KBr): 3036, 2989, 2925 2854, 2211, 1723, 1612, 1589, 1491, 1262, 1199, 1080, 832 cm\(^{-1}\).

Ethyl (E)-2-cyano-3-(4-methoxyphenyl)-2-propenoate (9)

\(^1\)H NMR: \(\delta\) 8.16 (s, 1H, H-olefinic), 7.98-8.00 (m, 2H, PhH), 6.97-6.99 (m, 2H, PhH), 4.33-4.38 (q, 2H, CH\(_2\)CH\(_3\)), 3.82 (s, 3H, OCH\(_3\)), 1.36-1.40 (t, 3H, CH\(_2\)CH\(_3\)); IR (KBr): 3194, 3073, 2980, 2937, 2841, 2221, 1716, 1591, 1566, 1512, 1463, 1263, 1175, 1090, 834 cm\(^{-1}\).

RESULTS AND DISCUSSION

Developments of new synthetic reactions utilizing characteristics of tellurium and its compounds have recently attracted much attention [8-11]. Tellurium (IV) chloride has been exploited as a catalyst [12] in Knoevenagel reaction. The potential of substituted tellurium (IV) trichloride as catalyst in this reaction has not been reported so far.

While exploring alternative methods for conversion I + II = III, we discovered that p-methoxyphenyltellurium(IV)trichloride efficiently catalyses the reaction in a matter of minutes to produce olefinic product in high yields and good purity. The results of the reactions of ethyl cyanoacetate, malononitrile and cyanoacetamide with a variety of aromatic aldehydes have been
described. These proceeded smoothly without solvent in the presence of a catalytic amount of \( p \)-methoxyphenyltellurium(IV) trichloride (Table). Only (E) isomers were produced. However, the yields of products are low and reactions time are more as compared to \( \text{TeCl}_4 \) catalysed \[12\] knoevenagel condensation reactions.

Table: Reaction time, melting point and yield of the product (III) in Knoevenagel condensations of (I) and (II) in the absence of solvent

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Ar</th>
<th>R</th>
<th>Reaction time (^a) (min)</th>
<th>Yield (^b) (%)</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{C}_6\text{H}_5 )</td>
<td>CONH₂</td>
<td>65</td>
<td>85</td>
<td>75-78</td>
</tr>
<tr>
<td>2</td>
<td>4-Cl-( \text{C}_6\text{H}_4 )</td>
<td>CONH₂</td>
<td>30</td>
<td>80</td>
<td>155-153</td>
</tr>
<tr>
<td>3</td>
<td>( \text{C}_6\text{H}_5 )</td>
<td>CN</td>
<td>55</td>
<td>80</td>
<td>80-83</td>
</tr>
<tr>
<td>4</td>
<td>4-Cl-( \text{C}_6\text{H}_4 )</td>
<td>CN</td>
<td>50</td>
<td>70</td>
<td>166-167</td>
</tr>
<tr>
<td>5</td>
<td>4-( \text{CH}_3\text{O-C}_6\text{H}_4 )</td>
<td>CN</td>
<td>120</td>
<td>85</td>
<td>110-113</td>
</tr>
<tr>
<td>6</td>
<td>(E)-( \text{C}_6\text{H}_5\text{-CH}=\text{CH} )</td>
<td>CN</td>
<td>125</td>
<td>82</td>
<td>115-116</td>
</tr>
<tr>
<td>7</td>
<td>( \text{C}_6\text{H}_5 )</td>
<td>COOEt</td>
<td>120</td>
<td>78</td>
<td>45-48</td>
</tr>
<tr>
<td>8</td>
<td>4-Cl-( \text{C}_6\text{H}_4 )</td>
<td>COOEt</td>
<td>60</td>
<td>75</td>
<td>89-92</td>
</tr>
<tr>
<td>9</td>
<td>4-( \text{CH}_3\text{O-C}_6\text{H}_4 )</td>
<td>COOEt</td>
<td>130</td>
<td>85</td>
<td>85-86</td>
</tr>
</tbody>
</table>

\(^a\): Monitored by complete disappearance of starting material using TLC. 
\(^b\): Yields are of pure isolated product. All the products identified by comparison of their melting point [13], IR [14] and NMR [13] spectra with those of authentic samples.

CONCLUSION

The \( p \)-methoxyphenyltellurium trichloride has been investigated as an efficient catalyst in knoevenagel condensation between non-enolisable aldehydes and active methylene compounds to yields the corresponding olefinic products in excellent yields and high purity.

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Dianisyltellurium (IV) Dichloride Promoted Oxidation Reactions of Di- and Triorganyl Phosphites

Sapana Garg, Rimpi and Verma KK*

Department of Chemistry, M. D. University, Rohtak-124001, India

ABSTRACT

Oxidation reactions of di- and triorganyl phosphites were carried out by using bis (p-anisyl) tellurium (IV) dichloride in carbon tetrachloride at ambient temperature. The di- and triorganyl phosphites were oxidized smoothly to afford the corresponding dialkyl/aryl chlorophosphates in considerable yield. The reaction probably proceeds by the attack of phosphorus centre of trivalent alkyl/aryl phosphite on the positive chlorine of \([\text{Ar}_2\text{TeCl}]^{2+}\) which is partially ionized form of dianisyltellurium(IV) dichloride in solution. During this reaction metallic tellurium is precipitated. All the products have been identified by comparison of their physical properties (boiling point, spectral studies) with those of authentic samples.

Keywords: Bis(p-anisyl)tellurium(IV) Dichloride, Diorganyl Phosphites, Triorganyl Phosphites Diorganyl Chlorophosphates

*Corresponding author
INTRODUCTION

As part of a programme aimed at developing organic synthetic method based on various organic derivatives of tellurium [1], we have found an efficient action of An$_2$TeCl$_2$ on the oxidation of di-and triorganyl phosphites using carbon tetrachloride as a solvent in nitrogen atmosphere giving rise to corresponding diorganyl chlorophosphate. During this reaction metallic tellurium is precipitated. The phenomenon means that oxidation reduction occurred in the reaction.

Though the Lewis acid character of Ar$_2$TeCl$_2$ has been recently utilized in the synthetic reactions [2, 3] including chlorotelluration [4], straight forward utilization of its oxidizing property has not been claimed so far in synthetic organic chemistry [5]. We were interested in the later property of Ar$_2$TeCl$_2$ and have now found a novel oxidative chlorination reaction which involves the oxidation-reduction reaction of a di- or triorganyl phosphite with Ar$_2$TeCl$_2$. Mukaiyama and co-workers [6] reported a similar type of the reaction where trivalent phosphorus compounds were reacted with Hg (II) or Hg (I) resulting in the formation of P (V) and Hg (0). KOH and OH [7] reported similar reaction of diorganyl or triorganyl phosphites with TeCl$_4$ as a preparative method for diorganyl chlorophosphates.

MATERIALS AND METHODS

The $^1$H NMR spectra were recorded in CDCl$_3$ on a Bruker AVANCE II Spectrometer operating at 400 MHz using TMS as internal standard. Infrared spectra were recorded in KBr pellets using a Bruker Tensor-27 FT-IR spectrophotometer. TLC plates of silica gel-G were used to monitor the reactions. All the products are known compounds and were characterized by IR, $^1$H NMR spectral studies and identified by comparison of their properties with those of authentic samples.

**Synthesis of bis(p-anisyl)tellurium(IV) dichloride [8]**

Anisole (64.8 g, 0.6 mol) and TeCl$_4$ (27.0 g, 0.1 mol) were heated at 160 °C for 6 h. The mixture was allowed to crystallize under vacuum to yield 30.6 g of bis (p-anisyl)tellurium(IV) dichloride. The product was recrystallized from acetonitrile as colourless crystals. M.pt 175-178 °C, (Lit m.pt 181-182°C) [8].

**Typical experimental procedure for the oxidative chlorination reaction**

To a solution of An$_2$TeCl$_2$ (0.227 g, 0.55 mmol) in 5 mL of carbon tetrachloride was added dropwise a solution of di-or triorganyl phosphite (1.0 mmol) in 5 mL of carbon tetrachloride under nitrogen atmosphere at 35-40 °C. The reaction mixture was stirred for about 1 – 1.5 h. 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 diorganyl chlorophosphate. The crude product was purified by silica gel column chromatography using EtOAc/n-hexane (1:2) as eluent in 72-85% yield. The results of reaction
with a variety of di- and triorganyl phosphites are listed in Table 1. The authenticity of the products was established by their spectral studies.

Dimethyl chlorophosphate (1), ( b.pt 162-163 °C ), ¹H NMR ( 400 MHz, CDCl₃ ) δ: 3.7465-3.7740 ( d,6H, CH₃ ). IR (KBr): 1270, 1050, 851 cm⁻¹.

Diethyl chlorophosphate (2), ( b.pt  217 °C ), ¹H NMR ( 400 MHz, CDCl₃ ) δ: 1.0015-1.0390( t, 6H, CH₃ ), 3.7472-3.8207 ( m, 4H,C₃H₂CH₃ ). IR (KBr): 1276, 1034, 822 cm⁻¹.

Di-n-propyl chlorophosphate (3), ( b.pt  231 °C ), ¹H NMR ( 400 MHz, CDCl₃ ) δ:  0.9771-1.0222 ( t, 6H, CH₃ ), 1.6701-1.7588 ( m, 4H,CH₂C₃H₂CH₃ ), 3.9668-4.0435 ( q, 4H, CH₂CH₂CH₃ ). IR (KBr): 1271, 1011, 864 cm⁻¹.

Di-n-butyl chlorophosphate (4), ( b.pt  279 °C ), ¹H NMR ( 400 MHz, CDCl₃ ) δ: 0.9174-0.9544 ( t, 6H, CH₃ ), 1.3734-1.4666 ( m, 4H, CH₂CH₂CH₂CH₃ ), 1.6309-1.7014 ( quin., 4H, CH₂CH₂CH₂CH₃ ), 4.0048-4.0552 ( q, 4H, CH₂CH₂CH₂CH₃ ). IR (KBr): 1231, 1031, 846 cm⁻¹.

Di-iso-butyl chlorophosphate (5), ( b.pt  270 °C ), ¹H NMR ( 400 MHz, CDCl₃ ) δ: 0.5894-0.6391 ( d, 12H, CH₃ ), 1.5852-1.6852 ( m, 2H, >CH- ), 3.4621-3.4946 ( t, 4H, -CH₂ ). IR (KBr): 1280, 1046, 878 cm⁻¹.

Triphenyl chlorophosphate (6), (b.pt 314-316 °C), ¹H NMR (400 MHz, CDCl₃) δ: 7.1267-7.3140 ( m, 10 H, ArH ). IR (KBr): 1177, 951, 765 cm⁻¹.

Ditolyi chloride or di- o- cresyl chlorophosphate (7), ( b.pt – 260 °C ) ¹H NMR ( 400 MHz, CDCl₃ ) δ: 2.2697-2.2867 ( d, 6H, -CH₃ ), 6.9538-7.2998 ( m, 8H, ArH ). IR (KBr): 1230, 1032, 735 cm⁻¹

RESULTS AND DISCUSSION

The oxidative chlorination of di- and triorganyl phosphites to yield the diorganyl chlorophosphate may be represented by Equation:

$$\text{(RO)₈POR'} + \text{Ar₂TeCl₂} \xrightarrow{\text{CCl₄, N₂, r.t.}} \text{(RO)₂P(O)Cl} + \text{Ar₂Te/Te}$$

R'=H,R ;  Ar= anisyl

Usual aliphatic or aromatic di- and triorganyl phosphites are easily converted to corresponding diorganyl chlorophosphates in good yield. The reaction may proceed by the attack of phosphorus centre of trivalent organyl phosphite on the positive chlorine of ( Ar₂TeCl )⁺ Cl⁻ which is the partially ionized form of Ar₂TeCl₂ in solution [9]. Initially formed An₂Te dissociates to Te which is precipitated out as black powder. The probable mechanism for the reaction is represented by Figure 1.
This reaction is the new region of dianisyltellurium(IV) dichloride chemistry in which dianisyltellurium(IV) dichloride can be used as an oxidizing and chlorinating agent for phosphorus nucleophiles such as di- or triorganyl phosphites.

CONCLUSION

The present chlorination is a novel type of redox reaction accompanying oxidation of P (III) to P (V) and reduction of Te (IV) to Te (II) / Te (0) and an alternative to the previously reported methods [6,7] for the formation of diorganyl chlorophosphates.

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Telluride Catalyzed Pinacolization of Aromatic Aldehydes

SAPANA GARG, RIMPI and K.K.VERMA*

Department of Chemistry, Maharshi Dayanand University, Rohtak-124001, India
vermakk123@rediffmail.com

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Abstract: The coupling reaction of aldehyde leading to pinacols was carried out by using disodium telluride and diaryl telluride in presence of potassium hydroxide in methanol solution at room temperature. These tellurides catalyze the pinacolization reactions to form α-glycols in considerable yield. All the products have been identified by comparison of their properties with those of authentic samples. It has been observed that disodium telluride is better catalyst as compare to diaryl tellurides and bis (p-methoxyphenyl) telluride is better catalyst as compared to bis(hydroxyaryl) tellurides.

Keywords: Tellurium, Pinacolization, Aromatic aldehydes

Introduction

1, 2 Diols are very useful synthons for a variety of organic synthesis1-2. They can be used as intermediates for the preparation of ketones and alkenes. More importantly, the pinacol coupling has been applied to the synthesis of biologically active natural compounds3. The reductive coupling of carbonyl compounds is an important method for the formation of 1, 2 diols. A number of types of reagents such Mg-Mgl24, Zn-ZnCl25, a number of transition metals6, lanthanides6, actinides6, Ti(II) and Ti(III) reagents have received much attention7-8. Olefin formation reaction is known to compete with these reagents9.

Pinacolization of aromatic aldehydes using Zn/montmorillonite K 10-ZnCl2 in aqueous THF under ultrasound10, vanadium-catalysed11, Te-KOH12 and Al-KOH13 has been reported. Tellurides find use in organic synthesis, both as a reagent for reductions14 and as a source of Tellurium in the synthesis of organotellurium compounds15. We herein report the results of tellurides catalyzed pinacol coupling reaction of aromatic aldehydes.

Experimental

Aldehydes were purified by distillation prior to use. Infrared spectra were recorded in KBr pellets using a Bruker Tensor 27 FT-IR Spectrophotometer. 1H NMR spectra were recorded in DMSO-d6 on a Bruker AVANCE II spectrometer operating at 400 MHz. TLC plates of silica gel-G was used to monitor the reactions. All products are known compounds and were characterized by IR, 1H NMR spectral studies and identified by comparison of their properties with those of authentic samples.
Preparation of disodium telluride\textsuperscript{16}
Hydrazine hydrate 80\% (0.50 mL, 7.1 mmol) was added drop wise using a syringe to stirred mixture of finely grounded Te (0.64 g, 5 mmol) and powdered NaOH (0.40 g, 10 mmol) in DMF (10 mL) at 50-60 °C stirred for 3 h, filtered and dried giving the white crystalline telluride, yield 0.688 g.

Preparation of bis(p-anisyl) telluride\textsuperscript{17}
Anisyltellurium dichloride (8.3 g, 0.02 mol) suspended in EtOH/H₂O (150:15 mL) was heated under reflux and hydrazine (3.2 g, 0.1 mol) was added drop wise. Vigorous evolution of N₂ was observed. Addition of hydrazine was stopped when no further evolution of N₂ was observed. The mixture was then poured into H₂O (700 mL) and extracted with ether (2×300 mL). The extracts were washed with H₂O, dried and evaporated, giving the telluride in 6.2 g yield, m.p. 53-54 °C.

Preparation of bis(4-hydroxyphenyl) telluride\textsuperscript{17}
Bis(p-hydroxyphenyl)tellurium dichloride (7.73 g, 0.02 mol) suspended in EtOH/H₂O (150:15 mL) was heated under reflux and hydrazine (3.2 g, 0.1 mol) was added drop wise (vigorous evolution of N₂). When further addition of hydrazine caused no evolution of N₂, the mixture is poured into H₂O (700 mL) and extracted with ether (2×300 mL). The extracts were washed with H₂O, dried and evaporated, giving the telluride in 5.9 g yield, m.p. 148-150 °C.

Preparation of di-3-methyl-4-hydroxyphenyl telluride\textsuperscript{17}
Bis(3-methyl-4-hydroxyphenyl)tellurium dichloride (8.3 g, 0.02 mol) suspended in EtOH/H₂O (150:15 mL) was heated under reflux and hydrazine (3.2 g, 0.1 mol) was added drop wise till no further evolution of N₂. The mixture was poured into H₂O (700 mL) and extracted with ether (2×300 mL). The extracts were washed with H₂O, dried and evaporated giving telluride 6.4 g, m.p. 143-144 °C.

General procedure for Pinacolization of aromatic aldehydes using telluride (Na₂Te or Ar₂Te) - KOH as catalyst
Aldehyde (5 mmol) was dissolved in methanol (7.5 mL), 10 mmol of telluride (Na₂Te or Ar₂Te) and KOH (1.40 g, 25 mmol) were added and the reaction mixture was stirred. The reaction became vigorous immediately after the addition of KOH. The reaction mixture was filtered to remove the catalyst. 50 mL water was added to the filtrate. A solid precipitated out which was filtered. Some of the diols were obtained by extracting the filtrate with CH₂Cl₂ (3×20 mL), drying with anhydrous Na₂SO₄ and evaporating the solvent.

Spectral data
1, 2-Diphenyl-1, 2-ethanediol (1) (DMSO, 400MHz) \(^1\)H NMR: δ 2.50(s, 2H, OH), 4.60(s, dl) and 5.20(s, meso) (2H, PhCH-), 6.70-7.29 (m, 10H, Ar) IR (KBr): 3498, 3394, 1041, 1012 cm\(^{-1}\).

1, 2-Bis (4-chlorophenyl)-1, 2-ethanediol (2) (DMSO, 400MHz) \(^1\)H NMR: δ 2.49(s, 2H, OH), 4.57(s, dl) and 5.17(s, meso) (2H, PhCH-), 6.72-7.17(m, 8H, Ar). IR (KBr): 3499, 3394, 1042 cm\(^{-1}\).

1, 2-Bis (2, 4-dichlorophenyl)-1, 2-ethanediol (3) (DMSO, 400MHz) \(^1\)H NMR: δ 2.51(s, 2H, OH), 4.56(s, dl) and 5.02(s, meso) (2H, PhCH-), 7.04-7.18 (m, 8H, Ar). IR (KBr): 3498, 3389, 1196, 1041, 775, 745 cm\(^{-1}\).
1, 2-Bis (2, 6-dichlorophenyl)-1, 2-ethanediol (4) (DMSO, 400MHz) $^1$H NMR: $\delta$ 2.70(s, 2H, OH), 4.62 (s, dl) and 5.09(s, meso) (2H, PhCH-), 7.09-7.25(m, 6H, Ar). IR (KBr): 3498, 3394, 1042, 1010, 776, 747 cm$^{-1}$.

1, 2-Bis (3-chlorophenyl)-1, 2-ethanediol (5) (DMSO, 400MHz) $^1$H NMR: $\delta$ 2.39(s, 2H, OH), 4.72(s, 2H, PhCH-), 6.37-7.19(m, 8H, Ar) IR (KBr): 3499, 1196, 1023, 776 cm$^{-1}$.

1, 2-Bis (2-chlorophenyl)-1, 2-ethanediol (6) (DMSO, 400MHz) $^1$H NMR: $\delta$ 3.05(s, 2H, OH), 4.72(s, 2H, PhCH-), 6.37-7.19(m, 8H, Ar) IR (KBr): 3498, 3394, 1197, 1042, 776 cm$^{-1}$.

1, 2-Bis (4-bromophenyl)-1, 2-ethanediol (7) (DMSO, 400MHz) $^1$H NMR: $\delta$ 2.99(s, 2H, OH), 4.69(s, dl), and 5.63(s, meso)(2H,PhCH-),6.77-7.26(m,8H,Ar). IR (KBr): 3498, 3394, 1195, 1042, 698 cm$^{-1}$.

1, 2-Bis (2-bromophenyl)-1, 2-ethanediol (8) (DMSO, 400MHz) $^1$H NMR: $\delta$ 3.12(s, 2H, OH), 4.69(s, dl) and 5.68(s, meso)2H,PhH-),6.85-7.45(m,8H,Ar). IR (KBr): 3498, 3394, 1195, 1041, 698 cm$^{-1}$.

1, 2-Bis (4-methoxyphenyl)-1, 2-ethanediol (9) (DMSO,400MHz) $^1$H NMR: $\delta$ 2.40(s, 2H, OH), 3.76(s, 3H, OCH$_3$) 4.52(s, dl) and 4.60(s, meso) (2H, PhCH-), 6.83-7.23(m, 8H, Ar). IR (KBr): 3350, 1280, 1156, 1039, 1000 cm$^{-1}$.

1, 2-Bis (4-methylphenyl)-1, 2-ethanediol (10) (DMSO, 400MHz) $^1$H NMR: $\delta$ 2.22(s, 3H, OH), 3.00(s, 3H, OH) 4.68(s, dl) and 5.39(s, meso) (2H, PhCH-), 6.70-7.21(m, 8H, Ar). IR (KBr): 3498, 3394, 1194, 1041 cm$^{-1}$.

1, 2-Bis (3-methylphenyl)-1, 2-ethanediol (11) (DMSO, 400MHz) $^1$H NMR: $\delta$ 2.24(s, 3H, OH), 4.69(s, dl) and 5.39(s, meso) (2H, PhCH-), 6.67-7.21(m, 8H, Ar). IR (KBr): 3498, 3393, 1196, 1023 cm$^{-1}$.

1, 2-Bis (2-methylphenyl)-1, 2-ethanediol (12) (DMSO, 400MHz) $^1$H NMR: $\delta$ 2.25(s, 3H, OH), 3.4(s, 2H, OH), 4.65(s, dl) and 5.65(s, meso) (2H, PhCH-), 6.58-7.21(m, 8H, Ar). IR (KBr): 3498, 3387, 1174, 1107 cm$^{-1}$.

1, 2-Bis (4-hydroxyphenyl)-1, 2-ethanediol (13) (DMSO, 400MHz) $^1$H NMR: $\delta$ 2.1(s, 2H, OH), 2.52(s, 2H, PhOH), 4.57(s, dl) and 4.98(s, meso) (2H, PhCH-), 7.07-7.88(m, 8H, Ar). IR (KBr): 3366, 1247, 1172, 1033, 1006 cm$^{-1}$.

**Results and Discussion**

The coupling of aromatic aldehydes to yield the pinacoles can be represented by following equation:

$$2\text{ArCHO} \xrightarrow{\text{Na}_2\text{Te} / \text{R}_2\text{Te}, \text{MeOH, r.t}} \text{Ar-CH(OH)-(OH)HC-Ar}$$

(Where R is 4-methoxyphenyl, 4-hydroxyphenyl and 3-methoxy-4-hydroxyphenyl)

As shown in Tables 1 and 2, the coupling of some aromatic aldehydes gives pinacols in good yield in the presence of $\text{R}_2\text{Te/Na}_2\text{Te-KOH}$ in methanol. It is reported that the reaction proceed via a single electron transfer mechanism with Te powder supplying the electrons.$^{11}$ In case of $\text{R}_2\text{Te/Na}_2\text{Te-KOH}$ the probable mechanism is:

**Figure.** Probable mechanism of telluride catalyzed pinacolization
Table 1. Na₂Te-KOH catalyzed coupling of aromatic aldehyde in methanol.

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>Reaction time*, min</th>
<th>Yield**, %</th>
<th>+/-: meso***</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅CHO</td>
<td>30</td>
<td>75</td>
<td>55:45</td>
</tr>
<tr>
<td>4-ClC₂H₄CHO</td>
<td>25</td>
<td>79</td>
<td>56:44</td>
</tr>
<tr>
<td>2, 4-(Cl)₂C₆H₅CHO</td>
<td>20</td>
<td>75</td>
<td>53:47</td>
</tr>
<tr>
<td>2, 6-(Cl)₂C₆H₅CHO</td>
<td>15</td>
<td>85</td>
<td>53:47</td>
</tr>
<tr>
<td>3-ClC₂H₄CHO</td>
<td>25</td>
<td>80</td>
<td>(-)</td>
</tr>
<tr>
<td>2-ClC₂H₄CHO</td>
<td>25</td>
<td>82</td>
<td>(-)</td>
</tr>
<tr>
<td>4-BrC₂H₄CHO</td>
<td>25</td>
<td>76</td>
<td>53:47</td>
</tr>
<tr>
<td>2-BrC₂H₄CHO</td>
<td>25</td>
<td>82</td>
<td>36:64</td>
</tr>
<tr>
<td>2,4-(Cl)₂C₂H₅CHO</td>
<td>30</td>
<td>70</td>
<td>83:17</td>
</tr>
<tr>
<td>3-ClC₂H₄CHO</td>
<td>35</td>
<td>72</td>
<td>41:59</td>
</tr>
<tr>
<td>2-ClC₂H₄CHO</td>
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<td>75</td>
<td>37:63</td>
</tr>
<tr>
<td>4-CH₃OC₂H₅CHO</td>
<td>40</td>
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<td>83:17</td>
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<tr>
<td>4-CH₃C₂H₅CHO</td>
<td>35</td>
<td>72</td>
<td>41:59</td>
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<tr>
<td>3-CH₃C₂H₅CHO</td>
<td>35</td>
<td>75</td>
<td>37:63</td>
</tr>
<tr>
<td>2-CH₂C₂H₅CHO</td>
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<td>79</td>
<td>41:59</td>
</tr>
<tr>
<td>4-OHC₆H₅CHO</td>
<td>35</td>
<td>79</td>
<td>41:59</td>
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</tbody>
</table>

*Monitored by complete disappearance of starting material using TLC. **Spectral data (IR, ¹H NMR) are in agreement with the structure. ***Ratio of +/- meso as calculated by ¹H NMR. # dl or meso was not determined. No alcohol or carboxylic acid (due to competing cannizaro reaction) was observed to have been formed in these reactions.

Table 2. R₂Te-KOH catalysed of aromatic aldehydes in methanol

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>R₂Te R=4-methoxyphenyl</th>
<th>Reaction Time*, min</th>
<th>Yield**, %</th>
<th>R₂Te R=4-hydroxypbenyl</th>
<th>Reaction Time*, min</th>
<th>Yield**, %</th>
<th>R₂Te R=3-methyl-4-hydroxyphenyl</th>
<th>Reaction Time*, min</th>
<th>Yield**, %</th>
</tr>
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<tbody>
<tr>
<td>C₆H₅CHO</td>
<td>35</td>
<td>65</td>
<td>38</td>
<td>70</td>
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<td>25</td>
<td>85</td>
<td>30</td>
<td>69</td>
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<td>2,6-(Cl)₂C₂H₅CHO</td>
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<td>30</td>
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<td>73</td>
<td>35</td>
<td>72</td>
<td>40</td>
<td>70</td>
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<tr>
<td>4-CH₃OC₂H₅CHO</td>
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<td></td>
</tr>
</tbody>
</table>

*Monitored by complete disappearance of starting material using TLC. **Spectral data (IR, ¹H NMR) are in agreement with the structure.

Te² donates electron to the ketone to generate a radical anion, which dimerizes, yielding the vicinal diol with both hydroxyl group deprotonated. Addition of water gives the diol. KOH makes these tellurides more active. The effect of the substituent of the aromatic ring on the reaction time is clear. The aromatic aldehydes with electron donating group show less reactivity. In contrast, electron withdrawing group in the aromatic ring of aromatic
aldehydes increase the reactivity. The steric hindrance around the carbonyl group inhibits the coupling reaction. When aromatic ketones such as acetophenone and \( p \)-chloroacetophenone were used as a substrate, no pinacol was obtained. The effect of the substituent of the aromatic ring on the dl/meso ratio is not clear.

**Conclusion**

The coupling reaction of aldehyde leading to pinacols was carried out by using disodium telluride and diaryl tellurides in presence of potassium hydroxide in methanol solution at room temperature. These tellurides catalyze the pinacolization reactions to form \( \alpha \)-glycols in considerable yield. It has been observed that disodium telluride is better catalyst as compared to diaryl tellurides and bis(\( p \)-methoxyphenyl) telluride is better catalyst as compared to bis(hydroxyaryl) tellurides.

**Acknowledgement**

The authors are thankful to Maharshi Dayanand University, Rohtak for providing necessary facilities. One of the authors (Rimpi) is thankful to CSIR, New Delhi for providing SRF.

**References**

Fig. 3.2: $^1$H NMR Spectrum of 2-Cyano-3-phenyl-2-propenamide in CDCl$_3$
Fig. 3.3: IR Spectrum of 2-[(4-Methoxyphenyl)methylene]malononitrile
Fig. 3.6: $^1$H NMR Spectrum of 2-[(E)-3-Phenyl-2-propenylidene]malononitrile in CDCl$_3$
Fig. 3.7: IR Spectrum of Ethyl(E)-2-cyano-3-phenyl-2-propenoate
Fig. 3.8: $^1$HNMR Spectrum of Ethyl(E)-2-cyano -3-phenyl-2-propenoate in CDCl$_3$
Fig. 3.9: IR Spectrum of Ethyl(E)-2-cyano-3-(4-chlorophenyl)-2-propenoate
**Fig. 3.10:** $^1$H NMR Spectrum of Ethyl(E)-2-cyano-3-(4-chlorophenyl)-2-propenoate in CDCl$_3$
Fig. 4.1 IR Spectrum of 1, 2-bis(2, 6-dichlorophenyl)-1, 2-ethanediol
Fig. 4.2 $^1$HMR Spectrum of 1, 2-bis(2, 6-dichlorophenyl)-1, 2-ethanediol in DMSO-$d_6$
Fig. 4.3: IR Spectrum of 1, 2-bis(3-chlorophenyl)-1, 2-ethanediol
Fig. 4.4: $^1$H NMR Spectrum of 1, 2-bis(3-chlorophenyl)-1, 2-ethanediol in CDCl$_3$
Fig. 4.5: IR Spectrum of 1, 2-bis(4-bromophenyl)-1, 2-ethanediol
Fig. 4.6: $^1$H NMR Spectrum of 1, 2-bis(4-bromophenyl)-1, 2-ethanediol in CDCl$_3$
Fig. 4.7: IR Spectrum of 1, 2-bis(4-methoxyphenyl)-1, 2-ethanediol
Fig. 4.8: $^1$H NMR Spectrum of 1, 2-bis(4-methoxyphenyl)-1, 2-ethanediol in CDCl$_3$
Fig. 4.9: IR Spectrum of 1, 2-bis(4-methylphenyl)-1,2-ethanediol
Fig. 4.10: $^1$H NMR Spectrum of 1, 2-bis(4-methylphenyl)-1, 2-ethanediol in CDCl$_3$
Fig. 5.1: IR Spectrum of Diethyl chlorophosphate
Fig. 5.2: $^1$H NMR Spectrum of Diethyl chlorophosphate in CDCl$_3$
Fig. 5.3: IR Spectrum of Di-n-propyl chlorophosphate
Fig. 5.4: $^1$H NMR Spectrum of Di-n-propyl chlorophosphate in CDCl$_3$
Fig. 5.5: IR spectrum of Di-iso-butyl chlorophosphate
Fig. 5.6: $^1$H NMR Spectrum of Di-iso-butyl chlorophosphate in CDCl$_3$
Fig. 5.7: IR Spectrum of Diphenyl chlorophosphate
Fig. 5.8: $^1$H NMR Spectrum of Diphenyl chlorophosphate in CDCl$_3$
Fig. 5.9: IR Spectrum of Ditolyl chlorophosphate
Fig. 5.10: $^1$H NMR Spectrum of Ditolyl chlorophosphate in CDCl$_3$