

## Study on Some Hydroxyaryltellurium(IV) Trichlorides Catalyzed Knoevenagel Reactions†

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Hydroxyaryltellurium trichlorides,  $R''TeCl_3$  (*p*-hydroxyphenyl and 3-methyl-4-hydroxyphenyl) have been prepared by condensation of tellurium tetrachloride with phenol or *o*-cresol respectively. These hydroxyaryltellurium trichlorides have been investigated as catalysts in Knoevenagel reactions between non-enolizable aldehydes and active methylene compounds to yield the corresponding olefinic products. This paper reports the reaction of ethylcyanoacetate, malononitrile and cyanoacetamide with aromatic aldehydes,  $ArCHO$  ( $Ar$  is  $C_6H_5$ , 4- $ClC_6H_4$ , 4- $CH_3OC_6H_4$  and  $C_6H_5-CH=CH$ ). The products are obtained in excellent yield and high purity and have been identified by comparison of their properties with those of authentic samples.

**Key Words:** *p*-Hydroxyaryltellurium trichlorides, Knoevenagel condensation, Non-enolizable aldehyde, Active methylene compounds.

### INTRODUCTION

Knoevenagel condensation is now a very well established method<sup>1</sup> 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<sup>2</sup> are ammonia and ammonium salts, primary and secondary amines and their salts. Subsequently the use of  $TiCl_4$  and base<sup>3</sup>, aluminium oxide<sup>4</sup>,  $AlPO_4-Al_2O_3$ <sup>5</sup> and doped xonolite<sup>6</sup> have been reported. Silica gel functionalized with amine groups has been used under heterogeneous catalysis conditions<sup>7</sup>. However, Lehnert's modification<sup>3</sup> of this method requires the equivalent of  $TiCl_4$  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<sup>8-11</sup>. Khan *et al.*<sup>12</sup> reported some tellurium tetrachloride catalyzed Knoevenagel reactions. *p*-Anisyltellurium trichloride<sup>13</sup> has been recently investigated as an efficient catalyst in Knoevenagel condensation. Here we report the use of hydroxyaryltellurium trichlorides as catalysts in similar reactions.

### EXPERIMENTAL

All products are known compounds and were characterized by melting points, IR and <sup>1</sup>H NMR spectral studies. <sup>1</sup>H NMR spectra were recorded on a Bruker AVANCE II-400 MHz NMR

spectro-meter using TMS as internal standard ( $CDCl_3$  solution). IR spectra were recorded from KBr disk on FT-IR Bruker Tensor 27. TLC plates of Silica Gel-G were used to monitor the reaction. All products were identified by comparison of their properties<sup>14,15</sup> with those of authentic samples.

**Preparation of *p*-hydroxyphenyltellurium trichloride<sup>16</sup>:** Phenol (10 g, 106.4 mmol) and  $TeCl_4$  (7.5 g, 27.8 mmol) in  $CCl_4$  (150 mL) were refluxed in an atmosphere of dry  $N_2$  for about 12 h until evolution of HCl ceased. The amount of HCl evolved corresponded to the loss of one equivalent of chlorine atom per mole of  $TeCl_4$ . The product was filtered, washed thoroughly with  $CCl_4$  to remove excess of phenol and then with benzene to remove any unreacted  $TeCl_4$ . It was recrystallized from acetonitrile to give a yellowish green solid.

**Preparation of 3-methyl-4-hydroxyphenyltellurium trichloride<sup>17</sup>:**  $TeCl_4$  (5.0 g, 18 mmol) and *o*-cresol (4.0 g, 37 mmol) in 100 mL of  $CCl_4$  were refluxed on a water bath under an atmosphere of dry  $N_2$  for about 12 h until the evolution of HCl ceased. The amount of HCl liberated corresponded to the loss of one equivalent of chlorine atom per mole of  $TeCl_4$ . The product was filtered and washed thoroughly with  $CCl_4$  and benzene to remove excess of *o*-cresol and  $TeCl_4$ , respectively. It was recrystallized from acetonitrile to give a yellow solid product.

**Knoevenagel condensation:** A mixture of carbonyl compound (**I**) (0.01 mol), the active methylene compound (**II**) (0.01 mol) and *p*-hydroxyaryltellurium(IV) trichloride (0.001 mol) was thoroughly mixed at room temperature. After being

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TABLE-1  
REACTION TIME, MELTING POINT AND YIELD OF THE PRODUCT (III) IN KNOEVENAGEL  
CONDENSATIONS OF (I) AND (II) IN THE ABSENCE OF SOLVENT

S. No.	Ar	R	R'= <i>p</i> -hydroxyphenyl		R'=3-methyl-4-hydroxy phenyl		Melting point (°C)
			Reaction time <sup>a</sup> (min)	Yield <sup>b</sup> (%)	Reaction time <sup>a</sup> (min)	Yield <sup>b</sup> (%)	
1.	C <sub>6</sub> H <sub>5</sub>	CONH <sub>2</sub>	60	78	58	70	75-78
2.	4-Cl-C <sub>6</sub> H <sub>4</sub>	CONH <sub>2</sub>	28	70	20	80	155-15
3.	C <sub>6</sub> H <sub>5</sub>	CN	32	79	60	75	80-83
4.	4-Cl-C <sub>6</sub> H <sub>4</sub>	CN	28	70	45	88	166-167
5.	4-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub>	CN	50	80	106	78	110-113
6.	(E)-C <sub>6</sub> H <sub>5</sub> -CH=CH	CN	90	72	125	78	115-116
7.	C <sub>6</sub> H <sub>5</sub>	COOEt	85	78	90	70	45-48
8.	4-Cl-C <sub>6</sub> H <sub>4</sub>	COOEt	58	75	55	72	89-92
9.	4-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub>	COOEt	90	78	105	78	85-86

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<sup>13</sup>, IR<sup>14</sup> and NMR<sup>13</sup> spectra with those of authentic samples

stirred for 5 min, the mixture was heated and continuously stirred at 90-100 °C at a magnetic stirrer with hot plate for specific time (Table-1). The reaction was cooled at room temperature and treated with a solution of 1 % aqueous ethyl alcohol. The product was extracted with methylene chloride, washed with water. After drying over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated to obtain the product(III) in high purity.

#### Physical data

**(E)-2-cyano-3-phenyl propenamide (1):** <sup>1</sup>H NMR: δ 8.20 (s, 1H, 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, ν<sub>max</sub>, cm<sup>-1</sup>): 3399, 3164, 2218, 1692, 1597, 1573, 1370 and 684.

**(E)-2-cyano-3-(4-chlorophenyl)-2-propenamide (2):** <sup>1</sup>H NMR: δ 8.19 (s, 1H, 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, ν<sub>max</sub>, cm<sup>-1</sup>): 3455, 3153, 2211, 1702, 1600, 1586, 1380, 1092, 852.

**2-(Phenylmethylene)malononitrile (3):** <sup>1</sup>H NMR: δ 7.86-7.98 (m, 2H, PhH), 7.79 (s, 1H, H-olefinic), 7.29-7.63 (m, 3H, PhH). IR (KBr, ν<sub>max</sub>, cm<sup>-1</sup>): 3184, 2222, 1592, 1693, 1383, 754, 679.

**2-[(4-Chlorophenyl)methylene]malononitrile (4):** <sup>1</sup>H NMR: δ 8.19 (s, 1H, H-olefinic), 7.90-7.97 (m, 2H, PhH), 7.40-7.50 (m, 2H, PhH). IR (KBr, ν<sub>max</sub>, cm<sup>-1</sup>): 3154, 2211, 1601, 1587, 1486, 1381, 1092, 825.

**2-[(4-Methoxyphenyl)methylene]malononitrile(5):** <sup>1</sup>H NMR: δ 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<sub>3</sub>). IR (KBr, ν<sub>max</sub>, cm<sup>-1</sup>): 3100, 2924, 2851, 2223, 1605, 1571, 1511, 1278, 1180, 833.

**2-[(E)-3-phenyl-2-propenylidene]malononitrile (6):** <sup>1</sup>H NMR: δ 8.50 (d, 1H H-olefinic), 7.50-7.80 (m, 2H, PhH), 7.30-7.49 (m, 2H, H-olefinic), 7.12-7.21 (m, 3H, PhH). IR (KBr, ν<sub>max</sub>, cm<sup>-1</sup>): 3029, 3057, 2223, 1671, 1577, 1607, 699, 752.

**Ethyl (E)-2-cyano-3-phenyl-2-propenoate (7):** <sup>1</sup>H NMR: δ 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<sub>2</sub>CH<sub>3</sub>), 1.37-1.41 (t, 3H, CH<sub>2</sub>CH<sub>3</sub>). IR (KBr, ν<sub>max</sub>, cm<sup>-1</sup>): 3064, 3030, 2981, 2939, 2224, 1724, 1606, 1574, 1449, 1264, 1204, 1091, 768, 686.

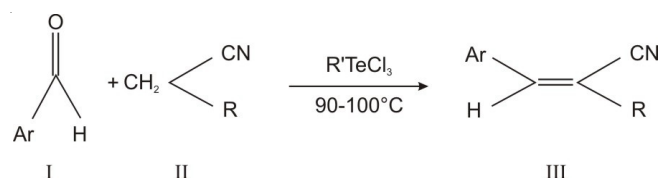
**Ethyl (E)-2-cyano-3-(4-chlorophenyl)-2-propenoate (8):** <sup>1</sup>H NMR: δ 8.25 (s, 1H, H-olefinic), 7.97-7.99 (t, 2H,

PhH) 7.47-7.57 (m, 3H, PhH), 4.38-4.40 (q, 2H, CH<sub>2</sub>CH<sub>3</sub>), 1.37-1.41 (t, 3H, CH<sub>2</sub>CH<sub>3</sub>). IR (KBr, ν<sub>max</sub>, cm<sup>-1</sup>): 3036, 2989, 2925 2854, 2211, 1723, 1612, 1589, 1491, 1262, 1199, 1080, 832.

**Ethyl (E)-2-cyano-3-(4-methoxyphenyl)-2-propenoate (9):** <sup>1</sup>H NMR: δ 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<sub>2</sub>CH<sub>3</sub>), 3.82 (s, 3H, OCH<sub>3</sub>), 1.36-1.40 (t, 3H, CH<sub>2</sub>CH<sub>3</sub>). IR (KBr, ν<sub>max</sub>, cm<sup>-1</sup>): 3194, 3073, 2980, 2937, 2841, 2221, 1716, 1591, 1566, 1512, 1463, 1263, 1175, 1090, 834.

## RESULTS AND DISCUSSION

Developments of new synthetic reactions utilizing characteristics of tellurium and its compounds has recently attracted much attention<sup>8-11</sup>. Tellurium(IV) chloride and *p*-methoxyphenyltellurium trichloride have been exploited as a catalyst<sup>12,13</sup> in Knoevenagel reaction. The potential of *p*-hydroxyaryl-tellurium(IV) trichlorides as catalyst in this reaction has not been reported so far.



where, Ar is C<sub>6</sub>H<sub>5</sub>, 4-Cl-C<sub>6</sub>H<sub>4</sub>, 4-CH<sub>3</sub>O-C<sub>6</sub>H<sub>4</sub>, (E)-C<sub>6</sub>H<sub>5</sub>-CH=CH, R is CN, CONH<sub>2</sub>, COO Et and R' is *p*-hydroxyphenyl, 3-methyl-4-hydroxyphenyl.

While exploring alternative methods for conversion I + II = III we discovered that *p*-hydroxyaryl-tellurium(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*-hydroxyaryl-tellurium (IV) trichloride (Table-1). Only (E) isomers were produced. However, the yields of products are low and reaction times are more as compared to TeCl<sub>4</sub> catalyzed<sup>12</sup> Knoevenagel condensation reactions. The catalytic activity of these hydroxy-aryl-tellurium trichlorides is more than that of anisyltellurium trichloride.

## Conclusion

The *p*-hydroxyphenyltellurium trichloride and 3-methyl-4-hydroxy tellurium trichloride have been prepared from phenol and *o*-cresol, respectively. These have been investigated as efficient catalyst in Knoevenagel condensation between non-enolizable aldehydes and active methylene compounds to yields the corresponding olefinic products in excellent yields and high purity.

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