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

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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, 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.*

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 $TiCl_4$ and base [3], aluminium oxide [4], $AlPO_4$-Al_2O_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 $TiCl_4$ 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_2SO_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: δ 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: δ 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: δ 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: δ 8.19 (s, 1H, H-olefinic), 7.90-7.97 (m, 2H, PhH), 7.40-7.50 (m, 2H, PhH); IR (KBr):

3154, 2211, 1601, 1587, 1486, 1381, 1092, 825 cm^{-1}.

2-[(4-Methoxypheyl)methylene] malononitrile (5)
^{1}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$_3$); IR (KBr): 3100, 2924, 2851, 2223, 1605, 1571, 1511, 1278, 1180, 833 cm^{-1}.

2-[(E)-3-Phenyl-2-propenylidene] malononitrile (6)
^{1}H NMR: δ 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}.

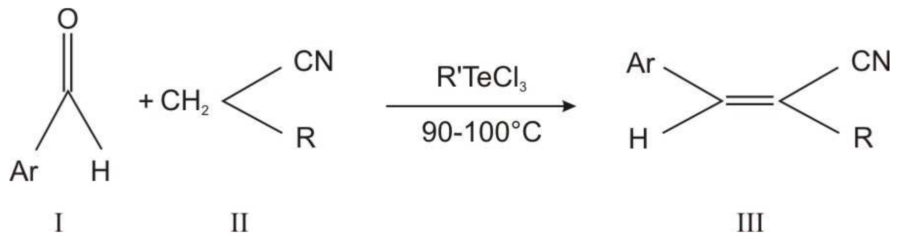
Ethyl (E)-2-cyano-3-phenyl-2-propenoate (7)
^{1}H NMR: δ 8.25 (s, 1H, H-Olefinic), 7.97-7.99 (t, 2H, PhH), 7.47-7.57 (m, 3H, PhH), 4.35-4.40 (q, 2H, C$\underline{H}_2$CH$_3$), 1.37-1.41 (t, 3H, CH$_2$C$\underline{H}_3$); IR (KBr): 3064, 3030, 2981, 2939, 2224, 1724, 1606, 1574, 1449, 1264, 1204, 1091, 768, 686 cm^{-1}.

Ethyl (E)-2-cyano-3-(4-chlorophenyl)-2-propenoate (8)
^{1}H NMR: 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, C$\underline{H}_2$CH$_3$), 1.37-1.41 (t, 3H, CH$_2$C$\underline{H}_3$); 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: 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, C$\underline{H}_2$CH$_3$), 3.82 (s, 3H, OCH$_3$), 1.36-1.40 (t, 3H, CH$_2$C$\underline{H}_3$); 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.



Where, Ar is C_6H_5, 4-Cl-C_6H_4, 4-CH_3O-C_6H_4, (E)-C_6H_5-CH=CH, R is CN , $CONH_2$, COOEt and R' is p-*methoxylphenyl*

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 $TeCl_4$ 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

Sr. No.	Ar	R	Reaction time[a] (min)	Yield[b] (%)	Melting point (°C)
1.	C_6H_5	$CONH_2$	65	85	75-78
2.	4-Cl-C_6H_4	$CONH_2$	30	80	155-15
3.	C_6H_5	CN	55	80	80-83
4.	4-Cl-C_6H_4	CN	50	70	166-167
5.	4-CH_3O-C_6H_4	CN	120	85	110-113
6.	(E)-C_6H_5-CH=CH	CN	125	82	115-116
7.	C_6H_5	COOEt	120	78	45-48
8.	4-Cl-C_6H_4	COOEt	60	75	89-92
9.	4-CH_3O-C_6H_4	COOEt	130	85	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 [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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