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Study on the applications of some bis (hydroxyaryl) telluroxides as aldol catalyst

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ABSTRACT

Bis (p-hydroxyphenyl) telluroxide and bis (3-methyl-4-hydroxyphenyl) telluroxide have been synthesized by alkaline hydrolysis of corresponding bis (hydroxyaryl) tellurium (IV) dichloride which in turn were obtained by reactions of $TeCl_4$ with phenol and o-cresol respectively. These telluroxides have been investigated as aldol catalysts in the reactions of benzaldehyde / p-anisaldehyde with acetophenone, p-methyl-, p-chloro- and p-bromoacetophenones to yield the chalcones, which are known to be important class of medicinal compounds. It has been observed that the catalytic activity is more in case of bis (3-methyl-4-hydroxyphenyl) telluroxide as compared to bis (p-hydroxyphenyl) telluroxide, probably due to more basic nature of former.

Keywords: Bis(*p*-hydroxyphenyl) telluroxide, bis(3-methyl-4-hydroxyphenyl) telluroxide, aldol catalyst, chalcone.

INTRODUCTION

Organic derivatives of tellurium have attracted considerable interest in the field of organic synthesis [1-4]. Diaryl telluroxides, R_2TeO, are known to function as aldol catalyst for various organic substrates [5]. A number of aromatic telluroxides have been reported as aldol catalyst and their relative activity been determined [5]. High catalytic activity is associated with electron donating substituents on the aromatic ring which can increase the basicity of the telluroxide function by a resonance effect. We hereby report detailed studies of the reaction aimed at improving its efficiency by ascertaining the effect of structural variations of telluroxide catalyst, by taking bis(*p*-hydroxyphenyl) and bis (3-methyl-4-hydroxyphenyl) telluroxides as aldol catalysts.

MATERIALS AND METHODS

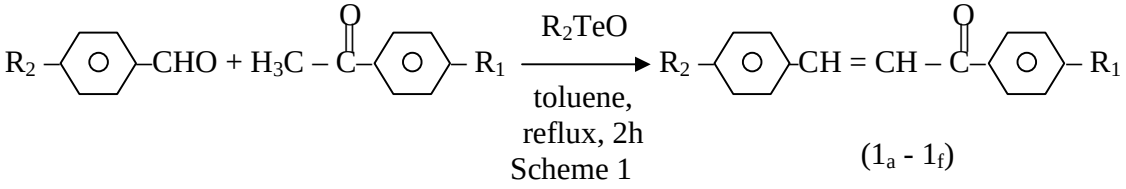
Melting points were determined in open capillary tube and are uncorrected. The IR spectra were recorded in KBr on F.T.I.R. Spectrometer Model RZX (Perkin Elmer) at SAIF, Panjab University, Chandigarh. The ^{1}H NMR were recorded in $CDCl_3$ on FT-NMR Cryomagnet Spectrometer 400 MHz (Bruker) using TMS as an internal standard. The purity of the compounds was checked by TLC using Silica gel-G (Merck). Column chromatography was performed on Silica gel (Merck, 60-120 mesh). Solvents for chromatography were distilled before use. The products were also characterized by comparison of their melting point with literature values.

Preparation of Telluroxides

Bis(*p*-hydroxyphenyl) telluroxide and bis (3-methyl-4-hydroxyphenyl) telluroxide have been synthesized by alkaline hydrolysis of corresponding bis (hydroxyaryl) tellurium (IV) dichloride which in turn were obtained by reactions of $TeCl_4$ with phenol [6,7] and *o*-cresol [6,8] respectively.

General Experimental Procedure for the Preparation of 1-(substituted phenyl)-3-(substituted phenyl) prop-2-en-1-ones (1_a – 1_f)

In a typical procedure, aldehyde (1 mmol), acetophenone (1 mmol) and toluene (10 mL) were refluxed under nitrogen atmosphere in presence of telluroxide (0.1 equivalent). The reaction was continued till the completion of the reaction, as monitored by the TLC. After the completion of reaction, the catalyst was removed by filtration and the filtrate was concentrated and kept in freeze overnight to obtained the chalcone derivatives. The products were identified by comparison with physical and spectral data.



Scheme 1

1_a : $R_1 = R_2 = H$
1_b : $R_1 = H$, $R_2 = OCH_3$
1_c : $R_1 = CH_3$, $R_2 = OCH_3$
1_d : $R_1 = Cl$, $R_2 = OCH_3$
1_e : $R_1 = Br$, $R_2 = OCH_3$
1_f : $R_1 = Br$, $R_2 = H$

1,3-Diphenyl prop-2-en-1-one (1_a)

IR (KBr, cm^{-1}): 1655 (C = O), 1602 (CH = CH); ^{1}H NMR ($CDCl_3$, δppm): 7.41 – 7.53 (m, 7H, H-3', H-5', H-2, H-3, H-5, H-6, H-β), 7.56 (m, 2H, H-4, H-4'), 8.01 (d, *J = 15 Hz*, IH, H-α), 8.13 (d, *J = 9.0 Hz*, 2H, H-2', H-6'), m.p. 55 – 57 ^{o}C (lit. [9] m.p. 56 ^{o}C).

3-(4-methoxyphenyl)-1-phenyl prop-2-en-1-one (1_b)
IR (KBr, cm^{-1}): 1657 (C=O), 1600 (CH=CH), 1262 (C-O-C); ^{1}H NMR ($CDCl_3$, δppm): 3.71 (s, 3H, OCH_3), 6.91 (d, *J=6.2 Hz*, 2H, H-3 and H-5), 7.41 (d, *J=15.0 Hz*, 1H, H-β), 7.46 – 7.60 (m, 5H, H-3', H-4', H-5', H-2, H-6), 7.81 (d, *J=15.5 Hz*, 1H, H-α), 8.0 (d, *J= 6.2 Hz*, 2H, H-2', H-6'), m.p. 79 – 80 ^oC (lit. [10] m.p. 80 ^oC).

3-(4-methoxyphenyl)-1-(4-methylphenyl) prop-2-en-1-one (1_c)
I.R. (KBr, cm^{-1}): 1653 (C=O) 1592 (CH=CH), 1170 (C-O-C); ^{1}H NMR ($CDCl_3$, δppm): 2.42 (s, 3H, CH_3), 3.83 (s, 3H, OCH_3), 6.91 – 6.93 (m, *J=8.76 Hz* & *J=1.92 Hz*, 2H, H-3 & H-5), 7.28 (d, *J=8.0 Hz*, 2H, H-2 & H-6), 7.41 (d, *J=15.6 Hz*, 1H, H-β), 7.57 (dd, *J=8.72 & J=1.88*, 2H, H-3' & H-5'), 7.77 (d, *J=15.6 Hz*, 1H, H-α), 7.92 (d, *J=8.2 Hz*, 2H, H-2' & H-6'); m.p. 96 – 97 ^oC (lit. [11] m.p. 96 ^0C).

1-(4-chlorophenyl)-3-(4-methoxyphenyl) prop-2-en-1-one (1_d)
I.R. (KBr, cm^{-1}): 1656 (C=O), 1594 (CH=CH), 1258 (C-O-C), 812 (C-Cl); ^{1}H NMR ($CDCl_3$, δppm): 3.86 (s, 3H, CH_3), 6.94 (dd, *J=6.84 Hz*, 2H, H-3 & H-5), 7.36 (d, *J=15.6 Hz*, 1H, H-β), 7.46 (d, *J=6.64 Hz*, 2H, H-2 & H-6), 7.60 (d, *J=6.0 Hz*, 2H, H-3' & H-5'), 7.79 (d, *J=15.56 Hz*, 1H, H-α), 7.95 (d, *J=6.2 Hz*, 2H, H-2' & H-6'); m.p. 123 – 125 ^oC (lit. [12] m.p. 124 ^oC).

1-(4-bromophenyl)-3-(4-methoxyphenyl) prop-2-en-1-one (1_e)
IR (KBr, cm^{-1}): 1655 (C=O), 1592 (CH=CH), 1256 (C-O-C), 818 (C-Br); ^{1}H NMR ($CDCl_3$, δppm): 3.85 (s, 3H, OCH_3), 6.93 (d, *J=6.8 Hz*, 2H, H-3 & H-5), 7.35 (d, *J=15.6 Hz*, 1H, H-β), 7.58 – 7.64 (m, 4H, H-2, H-6, H-3', H-5'), 7.78 (d, *J=15.6 Hz*, 1H, H-α), 7.87 (d, *J=8.0 Hz*, 2H, H-2' & H-6'); m.p. 143 – 144 ^oC (lit. [13] m.p. 142 ^oC).

1-(4-bromophenyl)-3-phenyl prop-2-en-1-one (1_f)
IR (KBr, cm^{-1}): 1745 (C=O), 1620 (CH=CH), 832 (C-Br); ^{1}H NMR ($CDCl_3$, δppm): 7.82 (1H, d, *J=16 Hz*, = CH-Ar), 7.40 (1H, d, -CO-CH=), 7.30 – 7.78 (9H, m, Ar-H); m.p. 103 – 104 ^oC (lit. [14] m.p. 102 ^oC).

RESULTS AND DISCUSSION

The formation of diaryltellurium (IV) dichlorides by the reactions of $TeCl_4$ with phenol [6,7] and *o*-cresol [6,8] involves the electrophilic substitution of the aromatic ring by a chlorotellurium group at a position *para* to the hydroxyl group;

$$2\ R - H + TeCl_4 \longrightarrow R_2TeCl_2 + 2\ HCl$$

The alkaline hydrolysis of these diaryl tellurium (IV) dichlorides yield the corresponding diaryl telluroxides [6,15].

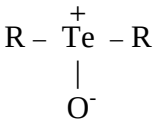
$$R_2TeCl_2 + 2\ NaOH \longrightarrow R_2Te(OH)_2 + 2\ NaCl$$

$$R_2Te(OH)_2 \xrightarrow{\Delta} R_2TeO + H_2O$$

The aldol condensation can be catalyzed by acid or base, the later being most frequently employed [16]. To our knowledge, however, neither sulphoxide nor selenoxides have ever been observed to function as aldol catalysts. Bis (*p*-methoxyphenyl) telluroxide is known as an efficient catalyst for aldol condensation under mild aprotic conditions [2,17]. Cava et al [5] determined the relative activities of a number of symmetrical and unsymmetrical aromatic telluroxides, where they reported that the efficacy of the telluroxide is very much dependent upon substituents effect.

During present course of work, we have attempted two telluroxides namely bis (*p*-hydroxyphenyl) telluroxide and bis (3-methyl-4-hydroxyphenyl) telluroxide as aldol catalysts in six such reactions which have been compiled in tables 1 and 2.

Telluroxides should exhibit a certain degree of basic character by virtue of the polar nature of tellurium-oxygen bond in telluroxide monomers.



Indeed, in 1977 a pKa of ~ 14.9 in acetonitrile was reported for telluroxide [18]. Apparently, the inherent basic nature of telluroxide as a dipole is responsible for the promotion of the aldol type reactions. The catalytic activity of the telluroxide can be attributed to the easy polarizability of the Te – O bond, furnishing a mild basic character [18].

The probable mechanism may be represented as below

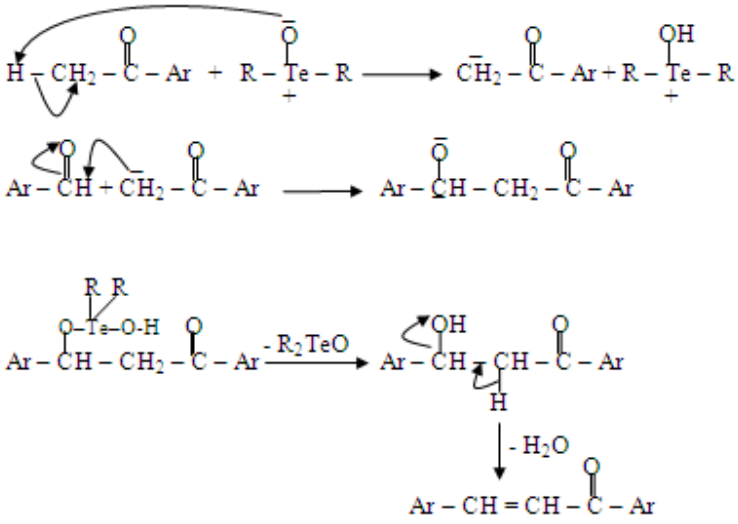


Table 1: Aldol Condensations Catalyzed by Bis (*p*-hydroxyphenyl) telluroxide

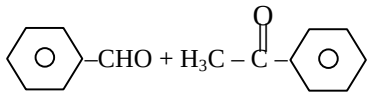
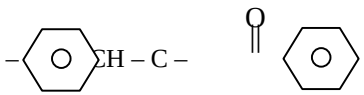
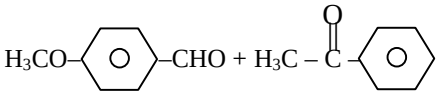
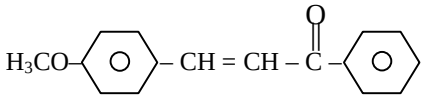
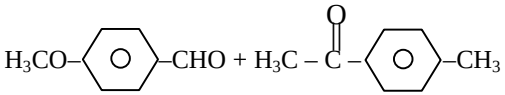
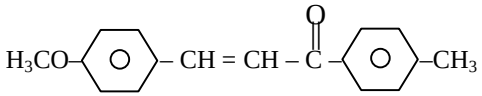
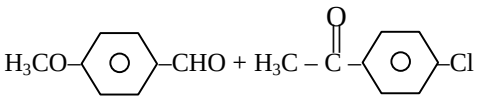
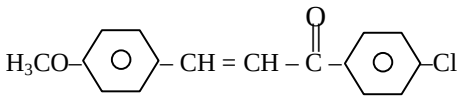
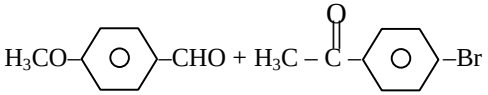
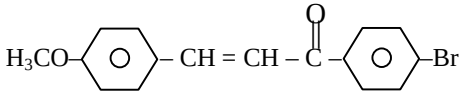
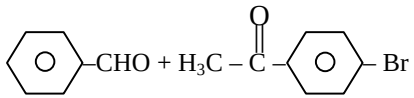
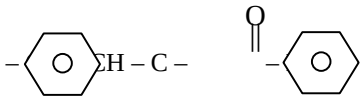
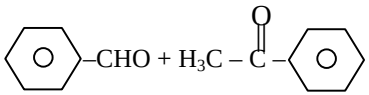
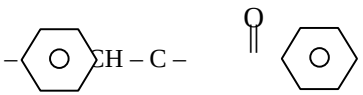
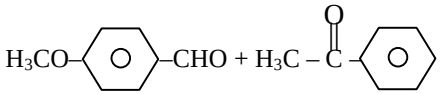
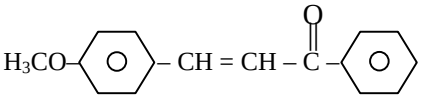
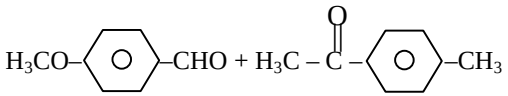
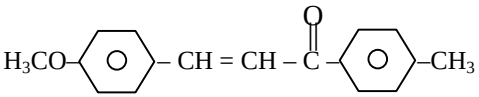
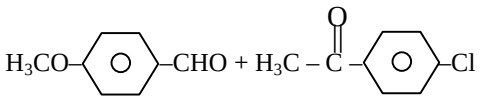
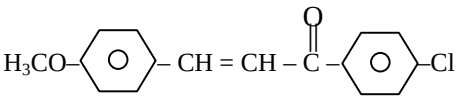
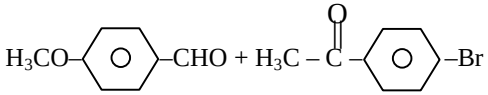
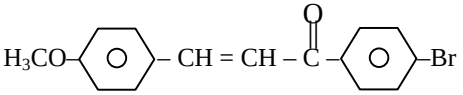
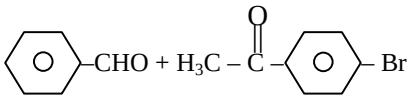
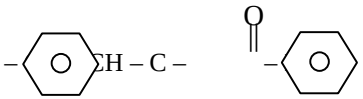
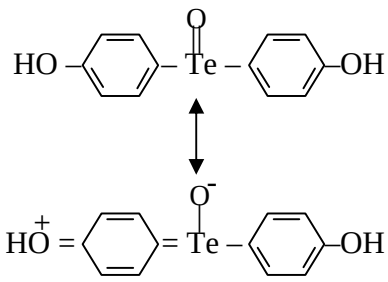
S. No.	Reagents	Product	Reaction time	Yield (%)	m.pt. °C
1.			3 h	65	55-57
2.			6 h	72	79-80
3.			6 h	70	96-97
4.			5 h	55	123-125
5.			7 h	62	143-144
6.			5 h	70	103-104

Table 2: Aldol Condensations Catalyzed by Bis (3-methyl-4-hydroxyphenyl) telluroxide

S. No.	Reagents	Product	Reaction time	Yield (%)	m.pt. ^{o}C
1.			2 h	85	55-57
2.			4 h	90	79-80
3.			4 h	85	96-97
4.			3 h	77	123-125
5.			5 h	85	143-144
6.			3 h	85	103-104

It has been observed that bis (3-methyl-4-hydroxyphenyl) telluroxide functions as a better aldol catalyst as compared to bis (*p*-hydroxyphenyl) telluroxide. Further, a comparison of this activity with earlier reported [17,5] telluroxides shows that bis (*p*-hydroxyphenyl) telluroxide is relatively weaker aldol catalyst as compared to bis (*p*-methoxyphenyl) telluroxide. This may be due to less basic character of bis (*p*-hydroxyphenyl) telluroxide.

The presence of an electron releasing groups on the aromatic ring of the telluroxide leads to an increase in basic character of the telluroxide and hence an increase in the catalytic activity. As a result of this, bis (3-methyl-4-hydroxyphenyl) telluroxide, which contains an additional electron donating methyl group, behaves as a better aldol catalyst.



This electron donating resonance effect [19] is directly responsible for the less or more activity of the diaryltelluroxides. It may further be added that diphenyl telluroxide, which does not contain any electron releasing group, does not function as an aldol catalyst [5].

CONCLUSION

The bis (*p*-hydroxyphenyl) and bis (3-methyl-4-hydroxyphenyl) telluroxides have been prepared by alkaline hydrolysis of corresponding diaryltellurium (IV) dichlorides, which in turn have been obtained by direct reactions of tellurium tetrachloride with phenol and *o*-cresol, respectively. These telluroxides have been investigated as efficient aldol catalysts in the reactions of benzaldehyde with acetophenone and *p*-bromoacetophenone; and *p*-anisaldehyde with acetophenone, *p*-methylacetophenone, *p*-chloroacetophenone and *p*-bromoacetophenone to yield the corresponding chalcones. It has been observed that bis (3-methyl-4-hydroxyphenyl) telluroxides is a better aldol catalysts as compared to bis (*p*-hydroxyphenyl) telluroxide, probably due to more basic nature of the former.

Acknowledgements
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