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RESEARCH ARTICLE

Telluride Catalyzed Pinacolization of Aromatic Aldehydes

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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 synthesis[1-2] . 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 compounds[3]. 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-MgI_2[4], Zn-$ZnCl_2$[5], a number of transition metals[6], lanthanides[6], actinides[6], Ti(II) and Ti(III) reagents have received much attention[7-8]. Olefin formation reaction is known to compete with these reagents[9]

Pinacolization of aromatic aldehydes using Zn/montmorillonite K 10-$ZnCl_2$ in aqueous THF under ultrasound[10], vanadium-catalysed[11], Te-KOH[12] and Al-KOH[13] has been reported. Tellurides find use in organic synthesis, both as a reagent for reductions[14] and as a source of Tellurium in the synthesis of organotellurium compounds[15]. 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. ^{1}H NMR spectra were recorded in DMSO-d_6 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, ^{1}H NMR spectral studies and identified by comparison of their properties with those of authentic samples.

Preparation of disodium telluride[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 ^{o}C stirred for 3 h, filtered and dried giving the white crystalline telluride, yield 0.688 g.

Preparation of bis(p-anisyl) telluride[17]

Anisyltellurium dichloride (8.3 g, 0.02 mol) suspended in EtOH/H_2O (150:15 mL) was heated under reflux and hydrazine (3.2 g, 0.1 mol) was added drop wise. Vigorous evolution of N_2 was observed. Addition of hydrazine was stopped when no further evolution of N_2 was observed. The mixture was then poured into H_2O (700 mL) and extracted with ether (2×300 mL). The extracts were washed with H_2O, dried and evaporated, giving the telluride in 6.2 g yield, m.p. 53-54 ˚C.

Preparation of bis(4-hydroxyphenyl) telluride[17]

Bis*(p*-hydroxyphenyl)tellurium dichloride (7.73 g, 0.02 mol) suspended in EtOH/H_2O (150:15 mL) was heated under reflux and hydrazine (3.2 g, 0.1 mol) was added drop wise (vigorous evolution of N_2).When further addition of hydrazine caused no evolution of N_2, the mixture is poured into H_2O (700 mL) and extracted with ether (2×300 mL). The extracts were washed with H_2O, dried and evaporated, giving the telluride in 5.9 g yield, m.p. 148-150 ˚C.

Preparation of di-3-methyl-4-hydroxyphenyl telluride[17]

Bis(3-methyl-4-hydroxyphenyl)tellurium dichloride (8.3 g, 0.02 mol) suspended in EtOH/H_2O (150:15 mL) was heated under reflux and hydrazine (3.2 g, 0.1 mol) was added drop wise till no further evolution of N_2. The mixture was poured into H_2O (700 mL) and extracted with ether (2×300 mL). The extracts were washed with H_2O, dried and evaporated giving telluride 6.4 g, m.p. 143-144 ˚C.

General procedure for Pinacolization of aromatic aldehydes using telluride (Na_2Te or Ar_2Te) - KOH as catalyst

Aldehyde (5 mmol) was dissolved in methanol (7.5 mL), 10 mmol of telluride (Na_2Te or Ar_2Te) 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 CH_2CI_2 (3×20 mL), drying with anhydrous Na_2SO_4 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: δ 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: δ 2.39(s, 2H, OH), 4.72(s, 2H, PhCH-), 6.37-7.19(m, 8H, Ar) IR (KBr): 3499, 1196, 1023, 747 cm^{-1}.

1, 2-Bis (2-chlorophenyl)-1, 2-ethanediol (**6**) (DMSO, 400MHz) ^{1}H NMR: δ 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: δ 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: δ 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: δ 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: δ 2.26(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: δ 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: δ 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: δ 2.10(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:

$$2ArCHO \xrightarrow[MeOH,\ r.t]{Na_2Tc\ /\ R_2Te,} Ar\text{-}HC(OH)\text{-}(OH)HC\text{-}Ar$$

(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 R_2Te/Na_2Te-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 R_2Te/Na_2Te-KOH the probable mechanism is:

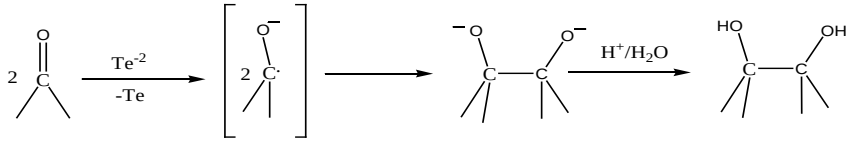

Figure. Probable mechanism of telluride catalyzed pinacolization

Table 1. Na_2Te-KOH catalyzed coupling of aromatic aldehyde in methanol.

Aldehyde	Reaction time*, min	Yield**, %	+/-: meso***
C_6H_5CHO	30	75	55:45
4-ClC_6H_4CHO	25	79	56:44
2, 4-$(Cl)_2 C_6H_3CHO$	20	75	53:47
2, 6-$(Cl)_2 C_6H_3CHO$	15	85	53:47
3-ClC_6H_4CHO	25	80	(-)#
2-ClC_6H_4CHO	25	82	(-)#
4-BrC_6H_4CHO	25	76	53:47
2-BrC_6H_4CHO	25	82	36:64
4-$CH_3OC_6H_4CHO$	40	70	83:17
4-$CH_3C_6H_4CHO$	35	72	41:59
3-$CH_3C_6H_4CHO$	35	75	37:63
2-$CH_3C_6H_4CHO$	35	79	41:59
4-OHC_6H_4CHO	35	79	41:59

**Monitored by complete disappearance of starting material using TLC. **Spectral data (IR, ^{1}H NMR) are in agreement with the structure. ***Ratio of +/- meso as calculated by ^{1}H 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. R_2Te-KOH catalysed of aromatic aldehydes in methanol

Aldehyde	R_2Te R=4-methoxyphenyl		R_2Te R=4-hydroxyphenyl		R_2Te R=3-methyl-4-hydroxyphenyl	
	Reaction Time*, min	Yield**, %	Reaction Time*, min	Yield**, %	Reaction Time*, min	Yield**, %
C_6H_5CHO	35	65	38	70	40	70
4-ClC_6H_4CHO	30	80	35	75	35	75
2,4-$(Cl)_2C_6H_3CHO$	25	85	30	69	30	80
2,6-$(Cl)_2C_6H_3CHO$	25	85	30	75	30	82
3-ClC_6H_4CHO	30	75	35	78	40	74
2-ClC_6H_4CHO	30	78	35	85	40	59
4-BrC_6H_4CHO	30	84	35	83	40	63
2-BrC_6H_4CHO	30	73	35	72	40	70
4-$CH_3OC_6H_4CHO$	40	78	45	75	50	72
4-$CH_3C_6H_4CHO$	35	81	40	80	45	70
3-$CH_3C_6H_4CHO$	35	60	40	70	45	65
2-$CH_3C_6H_4CHO$	35	72	40	70	50	68
4-OHC_6H_4CHO	45	70	45	75	55	75
C_6H_5CHO	35	65	38	70	40	70

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

Te^{2-} 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 α-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.

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