



STUDY ON THE REDUCING PROPERTIES OF SOME DIARYL DITELLURIDES

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ABSTRACT

Bis (*p*-hydroxyphenyl) ditelluride and bis (3-methyl-4-hydroxyphenyl) ditelluride have been synthesized by reduction of corresponding hydroxyaryl tellurium (IV) trichloride with hydrazine hydrate. These ditellurides have been investigated as catalytic reducing agents in presence of sodium borohydride and sodium hydroxide in ethanol. They reduce nitrobenzene to azoxybenzene and azobenzene, *p*-chloronitrobenzene to 4,4'-dichloroazobenzene and *p*-nitroanisole to 4,4'-dimethoxyazobenzene. The catalytic reducing property is found to be more in case of bis (3-methyl-4-hydroxyphenyl) ditelluride as compared to bis (*p*-hydroxyphenyl) ditelluride.

Key words: Bis (*p*-hydroxyphenyl) ditelluride, Bis (3-methyl-4-hydroxyphenyl) ditelluride, Reducing properties.

INTRODUCTION

Diaryl ditellurides, R₂Te₂, are orange to red solids. Only the methyl and trifluoromethyl derivatives are liquids at room temperature. While the aromatic compounds are well represented, only a few aliphatic derivatives have been described. The aromatic derivatives are more stable and are much easier to handle than the aliphatic members, which in addition to their relative instability possess an abnoxious, persistent odor.

These reducing agents, the most familiar being sodium telluride, aryltellurols, ditellurides, exhibit peculiar, and frequently unique properties such as mild reaction conditions and high selectivity.

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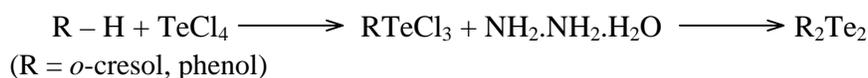
EXPERIMENTAL

Materials and methods

Melting point 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 ^1H 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 diaryl ditelluride

Bis (*p*-hydroxyphenyl) ditelluride and bis (3-methyl-4-hydroxyphenyl) ditelluride have been synthesized by reduction of corresponding hydroxyaryl tellurium (IV) trichloride with hydrazine hydrate. The trichlorides in turn were obtained by the reactions of TeCl_4 with phenol and *o*-cresol¹⁻³.



General experimental procedure for the reduction reactions

To a mixture of diarylditellurides (1 mmol) and NaBH_4 (10 mmol) ethyl alcohol (10 mL) and 5 M aqueous NaOH (3 mL) were added successively during reflux or room temperature under an N_2 atmosphere. The reaction was continued till the completion of the reaction, as monitored by the TLC. After the completion of reaction, the mixtures are concentrated by evaporation and subjected to column chromatography to isolate the products. All the products were identified by comparison with physical and spectral data.

(1) Azoxybenzene

IR (KBr, cm^{-1}): 1571 (N = N), ^1H NMR (CDCl_3 , δ ppm): 8.45 (m, 4H), 7.65-7.25 (m, 6H), m.p. 33-37°C (lit. m.p. 33°C)⁴.

(2) Azobenzene

IR (KBr, cm^{-1}): 1582 (N = N), ^1H NMR (CDCl_3 , δ ppm): 7.92 (d, 4H), 7.49 (m, 4H), 7.43 (d, 2H), m.p. 66-69°C (lit. m.p. 68°C)⁵.

(3) 4,4'-Dichloroazobenzene

IR (KBr, cm^{-1}): 1568 (N = N), ^1H NMR (CDCl_3 , δ ppm): 7.78 (d, 4H), 7.62 (d, 4H), m.p. 183-185°C (lit. m.p. 185°C)⁵.

(4) 4,4'-Dimethoxyazobenzene

IR (KBr, cm^{-1}): 1600 (N = N), ^1H NMR (CDCl_3 , δ ppm): 3.86 (s, 6H, 2OCH₃), 7.10 (d, 4H), 7.86 (d, 4H), m.p. 140 – 141°C (lit. m.p. 140°C)⁵.

RESULTS AND DISCUSSION

Tellurium tetrachloride when reacted with phenol and *o*-cresol gives *p*-hydroxyphenyl tellurium trichloride and 3-methyl-4-hydroxyphenyl tellurium trichloride, respectively. These trichlorides upon reduction with hydrazine hydrate yield the corresponding ditellurides, R_2Te_2 .

These two diarylditellurides have been investigated as catalytic reducing agents by treating the organic substrates with R_2Te_2 in presence of sodium borohydride and sodium hydroxide in ethanol (Method⁶⁻⁸ C). Nitrobenzene have been reduced to azoxybenzene (room temperature) and azobenzene (reflux). *p*-chloronitrobenzene and *p*-nitroanisole are reduced to 4,4'-dichloroazobenzene and 4,4'-dimethoxyazobenzene, respectively and are described in Tables 1 and 2.

The reduction of nitroarenes is probably by the reagent aryl tellurol, which is generated *in situ* by the reactions of diarylditellurides with NaBH_4 ^{7,9}. Since the ditellurides is continuously reformed during the reactions, a catalytic amount of ditelluride is sufficient.

It has also been suggested that the effective reagents formed by this method is probably the complex sodium triethyl (aryl telluro) borate $[\text{Na}^+ \text{Ar TeB} (\text{OEt})_3]^-$, as in the similar reaction of Ph_2Se_2 with NaBH_4 in ethanol¹⁰. The complex sodium triethyl (aryl telluro) borate $[\text{Na}^+ \text{Ar TeB} (\text{OEt})_3]^-$ may further be converted to sodiumaryl tellurolate (ArTeNa) in the presence of NaOH which effects the reduction of azoxy to azo compounds⁶.

A comparison of catalytic reducing property of these ditellurides with themselves and with already reported ditellurides indicates that bis (3-methyl-4-hydroxyphenyl) ditelluride is a better reducing agent than bis (*p*-hydroxyphenyl) ditelluride, which in turn is better than diphenylditelluride⁸.

Table 1: Reductive Reactions with Bis (*p*-hydroxyphenyl) ditelluride

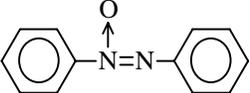
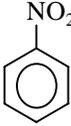
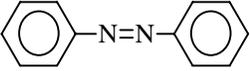
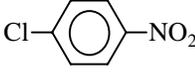
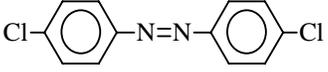
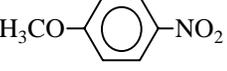
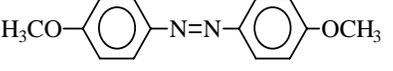
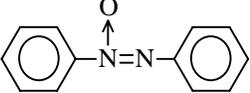
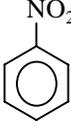
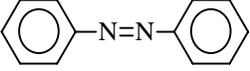
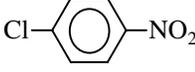
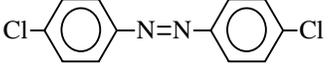
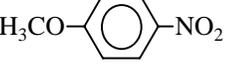
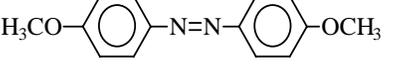
S. No.	Substrate	Solvent	Temp.	Time	Product	Yield (%)
1.		Ethyl alcohol	r.t.	9 h		72
2.		Ethyl alcohol	Reflux	14 h		65
3.		Ethyl alcohol	Reflux	8 h		75
4.		Ethyl alcohol	Reflux	10 h		80

Table 2: Reductive Reactions with Bis (3-methyl-4-hydroxyphenyl) ditelluride

S. No.	Substrate	Solvent	Temp.	Time	Product	Yield (%)
1.		Ethyl alcohol	r.t.	6 h		92
2.		Ethyl alcohol	Reflux	10 h		85
3.		Ethyl alcohol	Reflux	6 h		90
4.		Ethyl alcohol	Reflux	7 h		95

CONCLUSION

Bis (4-hydroxyphenyl) and bis (3-methyl-4-hydroxyphenyl) ditellurides have been synthesized by the reduction of corresponding hydroxyaryl tellurium (IV) trichlorides with hydrazine hydrate. These ditellurides have been investigated as catalytic reducing agents in presence of sodium borohydride and sodium hydroxide in ethanol. They reduce nitrobenzene to azoxybenzene and azobenzene, *p*-chloronitrobenzene to 4, 4'-dichloroazobenzene and *p*-nitroanisole to 4, 4'-dimethoxyazobenzene. A probable mechanism for their catalytic reducing property has also been suggested.

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