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RESEARCH ARTICLE

Phase Transfer Catalyzed Extraction of TeO_3^{2-} in Organic Media and use of Sodium Tellurite as an Oxidizing Agent

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Abstract: Sodium tellurite was used as effective oxidizing agent in organic-aqueous biphasic medium using phase transfer catalysis. TeO_3^{2-} ions get extracted in the organic phase in the presence of phase transfer catalyst, thus making the reaction to proceed in homogeneous manner.

Keywords: Phase transfer catalysis, Sodium tellurite, Benzoins, Chalcones

Introduction

Organometallic compounds of tellurium such as bis-aryltelluroxide, bis-aryltellurone, arenetellurium anhydride and tellurium oxide have been used in oxidation of variety of compounds[1]. Owing to non-availability of these compounds as such, these have the limitation of being used as general reagents. Survey of literature reveals that inexpensive and readily available sodium tellurite has hardly been used as oxidizing agent, perhaps due to its insolubility in the organic solvents, thus the reactions being of heterogeneous nature, are not effective. As sodium tellurite is freely soluble in water, the use of co-solvents such as THF, ethanol or dioxane could not make the reaction effective in our hands in an attempt to utilize sodium tellurite as oxidizing reagent in some reactions.

Extraction of anions including oxo ions and complex anions of metals[2-7] such as MnO_4^-, $Cr_2O_7^{2-}$, CrO_4^{2-}, $[Fe(CN)_6]^{3-}$ and $[Ce(NO_3)_6]^{2-}$ *etc.* in organic phase from aqueous phase using phase transfer catalysis is well documented process in the reactions when are carried in biphase medium.

In the present work we wish to report extraction of tellurite ion in the organic media using phase transfer catalysis thus making oxidation reactions with sodium tellurite in homogeneous manner.

Experimental

Oxidation of benzoin

A solution of benzoin (2.36 mmol) in benzene (10 mL), sodium tellurite (4.47 mmol), saturated aqueous potassium carbonate solution (10 mL) and tetra-*n*-butyl ammoniumhydrogensulphate (1 mmol) were stirred magnetically at 90 °C in an oil bath for 45 minutes. The completion of the reaction was checked by TLC. The organic layer was separated, washed with water and benzene removed by distillation under vacuum. The residue thus obtained was crystallized from methanol to give benzil.

Oxidation of benzaldehyde

A solution of benzaldehyde (4.9 mmol) in benzene (10 mL), sodium tellurite (4.47 mmol), saturated aqueous potassium carbonate solution (10 mL) and tetra-*n*-butylammonium hydrogen sulphate (1 mmol) were stirred magnetically at 90 °C in an oil bath for 1.5 h. The completion of the reaction was checked by TLC. The reaction mixture was acidified using conc. hydrochloric acid in an ice bath. The organic layer was separated, washed with water and benzene removed by distillation under vacuum. The residue thus obtained was crystallized from hot water to give benzoic acid.

Oxidation of chalcol

A solution of chalcol (1,3-diphenylprop-2-en-1-ol) (2.38 mmol) in benzene (10 mL), sodium tellurite (4.47 mmol), saturated aqueous potassium carbonate solution (10 mL) and tetra-*n*-butylammonium hydrogen sulphate (0.8 mmol) were stirred magnetically at 90 °C in an oil bath for 2.0 h. The completion of the reaction was checked by TLC. The organic layer was separated, washed with water and benzene removed by distillation under vacuum. The residue thus obtained was crystallized from methanol to give chalcone.

Oxidation of cinnamyl alcohol

A solution of cinnamyl alcohol (3.88 mmol) in benzene (10 mL), sodium tellurite (4.47 mmol), saturated aqueous potassium carbonate solution (10 mL) and tetra-*n*-butylammonium hydrogen sulphate (0.8 mmol) were stirred magnetically at 90 °C in an oil bath for 2.0 h. The completion of the reaction was checked by TLC. The reaction mixture was acidified using conc. hydrochloric acid in an ice bath. The organic layer was separated, washed with water and benzene removed by distillation under vacuum. The residue thus obtained was crystallized from aqueous methanol to give cinnamic acid.

Results and Discussion

Benzoin was taken as the initial example for the study and it was reacted with sodium tellurite in benzene-aqueous potassium carbonate biphasic medium in the presence of tetra-*n*-butyl ammonium hydrogen sulphate by stirring magnetically at 90 °C. The product obtained after working of reaction mixture was identified as benzil from its ^{1}H NMR spectra and by direct comparison with authentic samples (CO-IR) procured from Aldrich chemicals.

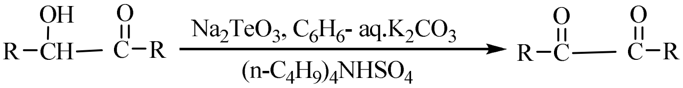
Smooth nature of the reaction indicates the extraction of TeO_3^{2-} into organic phase as ion pair with quaternary ammonium ion thus making the reaction homogeneous. At the end of the reaction separation of metallic tellurium as dark grey solid further confirmed the involvement of Te (+4) in the reaction. Differently substituted benzoins were oxidized into benzils.

$$2Q +_{(aq)} + TeO_3^{2-}{}_{(aq)} \rightleftharpoons Q^+{}_2TeO_3^{2-}{}_{(aq)}$$

$$Q^+{}_2TeO_3^{2-}{}_{(aq)} \rightleftharpoons Q^+{}_2TeO_3^{2-}{}_{(org)}$$

Encouraged by the results, scope of utility of the sodium tellurite was studied by carrying out oxidation of differently substituted benzoins to benzils (Scheme 1, Table 1), aromatic aldehydes to corresponding acids (Scheme 2, Table 2), 1,3-diarylprop-2-en-1-ol into corresponding *α, β*-unsaturated ketones (Scheme 3, Table 3) and primary alcohol to corresponding acids (Scheme 4, Table 4) in high yields.

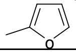
Sodium Tellurite has been used for the oxidation of various compounds such as benzoins to benzils, aldehydes to acids, chalcols to chalcones and aromatic alcohols to acids under phase transfer catalysed conditions. The reactions take place under milder conditions and compounds obtained in very high yield in shorter time.

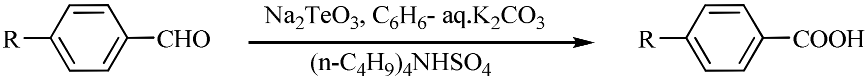


$$R-\underset{}{\overset{OH}{CH}}-\overset{O}{C}-R \xrightarrow[(n\text{-}C_4H_9)_4NHSO_4]{Na_2TeO_3,\ C_6H_6\text{- aq.}K_2CO_3} R-\overset{O}{C}-\overset{O}{C}-R$$

Scheme 1

Table 1. Oxidation of benzoins

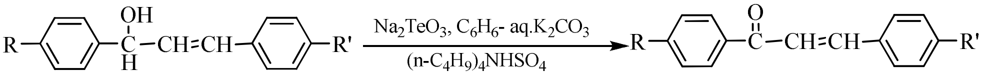
S.No.	R	Time, h	% Yield	m.p., ^{0}C	lit. m.p., °C
1	$-C_6H_5$	0.75	84	93-94	95-96 [8]
2	$-C_6H_4-OCH_3(p)$	1.0	90	130-31	134[8]
3	$-C_6H_4-CH_3(p)$	1.5	80	101-02	102[8]
4		1.0	80	163-64	165[9]



Scheme 2

Table 2. Oxidation of aldehydes

S.No.	R	Time, h	% Yield	m.p., °C	lit. [10] m.p., °C
1	4-H	1.5	94	121	121
2	$4-OCH_3$	2.0	85	180-82	184
3	$4-CH_3$	3.0	85	178-80	181
4	$2-NO_2$	1.5	90	145-46	146-48
5	$4-NO_2$	1.5	86	239-40	241

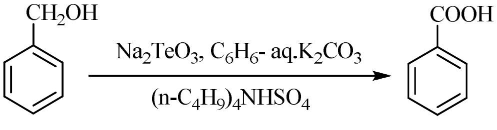


Scheme 3

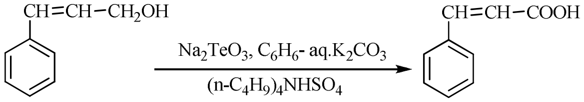
Table 3. Oxidation of *α,β*-unsaturated alcohols

S.No.	R	R'	Time, h	% Yield	m.p., °C	lit. m.p., °C
1	H	H	2.0	90	60-61	62[10]
2	H	OCH_3	2.0	84	78-79	79[11]
3	CH_3	OCH_3	2.0	80	95-97	96-97*

**Value of authentic sample procured from Aldrich chemicals*

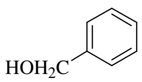
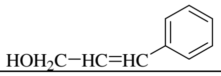


Scheme 4(a)



Scheme 4(b)

Table 4. Oxidation of primary alcohols

S.No.	R	Time, h	% Yield	m.p., °C	lit. [10] m.p., °C
1		2.0	65	120-21	121
2		2.0	60	131-32	134

Conclusion

In conclusion, it can be stated that sodium tellurite, an easily available and inexpensive compound can be used as effective oxidizing reagent under mild conditions using phase transfer catalysis.

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