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Zinc Bismuthate $Zn(BiO_3)_2$. I. A Useful Oxidizing Agent for the Efficient Oxidation of Organic Compounds

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Zinc bismuthate is an easily prepared and a stable compound. It could be used as an oxidant in organic solvents under aprotic or in the presence of a catalytic amount of a protic solvent. Primary and secondary saturated, allylic, and benzylic alcohols are converted to their carbonyl compounds in high yields. Mildness of the reagent is shown by the oxidation of thiols to their disulfides in excellent yields. Thioethers are also oxidized to their corresponding sulfoxides in good yields.

Oxidation is one of the most important classes of organic reactions from the academic, industrial, and pharmaceutical points of views. Traditional oxidants, such as potassium permanganate, manganese dioxide, potassium chromate and dichromate, chromium trioxide, and etc., encounter problems which are described.[1—7]

Oxidations in aprotic organic solvents have found valuable applications in modern organic synthesis and their mechanistic studies are of importance. Along this line, new reagents have been introduced in the literature. Their uses, advantages, and their drawbacks are discussed.[7—10] We have also studied and reported new oxidants which have been effective for the important functional group transformations in a variety of aprotic solvents. These oxidants show also drawbacks and advantages, which are described.[7—10]

Oxidation ability and the mode of reaction of oxoanions is partly dependent upon the type of cations they carry. Most of the time, either a very unstable compound is produced or the compound becomes so unreactive which will not be a practical oxidant for the synthetic purposes.[7,8] Therefore, development of the new and a practical reagent is still a trial and error process.

Bismuthate anion BiO_3^- is a strong oxidant, but little attention has been paid to this potential in organic synthesis. To the best of our knowledge, only one report is available in the literature in which sodium bismuthate has been used for the carbon–carbon bond cleavage of vic. diols under acidic conditions.[11] We have tried the other functional group transformations by this reagent under aprotic conditions in organic solvents. It is noticed that sodium bismuthate is a rather sluggish reagent under aprotic conditions. Therefore, the other bismuthates with cations; Ba^{2+}, $(n\text{-}Bu)_4N^+$ and Cu^{2+} are prepared and tried for the oxidation of alcohols in organic solvents. Barium bismuthate and tetrabutylammonium bismuthate are recognized to be more reactive than their copper (II) analogue, but they are not efficient enough, as being considered as practical bench top oxidants.

In connection with our work in oxidation, we have observed that zinc permanganate, and tetrakis(pyridine)-zinc permanganate are highly reactive and unstable reagents,[7] whereas zinc dichromate trihydrate is an effective and a stable oxidant for the oxidation of different classes of organic compounds.[7] Having these points in mind and the drastic effects of zinc cation upon the reactivity and stability of permanganate and dichromate anions, we tried the synthesis of zinc bismuthate and investigated its ability for the oxidation of different classes of organic compounds. We have found that zinc bismuthate could be considered as an efficient and a mild oxidant. In this paper we report the effective conversion of hydroxyl groups to their carbonyl groups, thiols to their disulfides, and sulfides to their sulfoxides. Most of the results obtained are also extensively compared with the recently reported oxidizing agents; barium manganate,[10] barium ferrate monohydrate,[8] barium permanganate,[9] tetrabutylammonium chlorochromate,[12] and sodium perborate.[13,14]

Results and Discussion

Zinc bismuthate was easily prepared from sodium bismuthate and hydrated zinc chloride in water in a quantitative yield. This reagent may be used for the medium to large-scale operations.

Oxidation of organic compounds with zinc bismuthate proceeds well in refluxing toluene and the results are reproducible. Substrates which are not soluble in toluene may be oxidized in the mixture of toluene–acetonitrile very easily.

Primary and secondary saturated, allylic, and benzylic alcohols were converted to their corresponding aldehydes and ketones in high yields (Table 1). Further oxidation of aldehydes to their carboxylic acids were not observed. Zinc bismuthate has also been successfully applied to the oxidation of α-hydroxy ketones, such as benzoin and furoin to convert them to their diketones in excellent yields (Table 1). Carbon–carbon bond cleavage was not observed in the above oxidations. Catechol and hydroquinone were also converted to their quinones effectively in excellent yields (Table 1).

Table 1. Oxidation of Some Hydroxy Compounds with $Zn(BiO_3)_2$ and Comparison with $BaMnO_4$,[10] $Ba(MnO_4)_2$,[9] and $BaFeO_4 \cdot H_2O$[8]

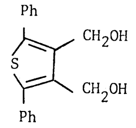
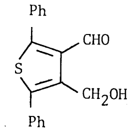
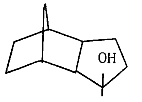
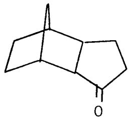
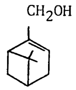
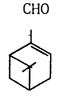
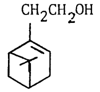
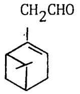
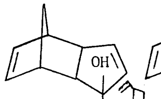
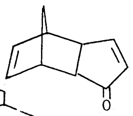
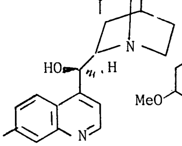
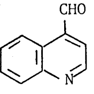
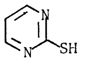
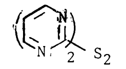
Entry no.	Substrate	Product	Mp or bp[8,10,15]	$Zn(BiO_3)_2$			$BaMnO_4$[10]		$Ba(MnO_4)_2$[9]		$BaFeO_4 \cdot H_2O$[8]	
				Reaction time	Oxid. / React.	Yield	Reaction time	Yield	Reaction time	Yield	Reaction time	Yield
			°C	h		%	h	%	h	%	h	%
1	Benzyl alcohol	Benzaldehyde	175—178	0.3	2	95	1.5	90	0.4	90	0.8	95—100
2	Benzhydrol	Benzophenone	48—50	0.3	2	100	0.5	100	1	99	0.5	100
3	*p*-Nitrobenzyl alcohol	*p*-Nitrobenzaldehyde	103—106	3	2.5	90	4.5	60	0.5	90	2	85
4	Benzoin	Benzil	93—96	0.7	1	97	—	—	0.25	96	6	95
5	Furoin	Furil	161—164	0.3	1.5	95	—	—	4	80	1.5	100
6	*p*-Methoxybenzyl alcohol	*p*-Methoxybenzaldehyde	245—248	0.7	1.5	95	—	—	3.5	90	—	—
7	9-Anthracenemethanol	9-Anthraldehyde	100—103	1	2	90	—	—	—	—	—	—
8	1-Phenylethanol	Acetophenone	—	1	2	90	—	—	0.25	94	1	100
9	*p*-Bromobenzyl alcohol	*p*-Bromobenzaldehyde	53—56	0.5	2	96	—	—	—	—	—	—
10	*p*-Chlorobenzyl alcohol	*p*-Chlorobenzaldehyde	42—45	0.5	2	93	—	—	—	—	—	—
11			131—134	0.7	4	80	—	—	2	80	—	—
12	1-Heptanol	Heptanal	150	4.5	6	80	—	—	—	—	48	60
13			101	4.5	6	90	—	—	—	—	—	—
14	Cyclohexanol	Cyclohexanone	153	5	6	85	24	56—60	2.25	60	24	70
15	2-Phenylethanol	Phenylacetaldehyde	192	1.5	4	90	—	—	—	—	—	—
16			218	4	4	85	—	—	—	—	—	—
17			—	2.5	4	90	—	—	—	—	—	—
18			—	4	5	70	—	—	—	—	—	—
19			—	4	5	60	—	—	—	—	—	—
20	Catechol	*o*-Benzoquinone	—	0.1	1	100	—	—	—	—	0.7	100
21	Hydroquinone	*p*-Benzoquinone	113	0.1	1	93	0.3	75	0.5	90	0.25	100
22	Benzilic aid	Benzophenone	48	0.5	1	95	—	—	1.25	95	—	—

Table 2. Oxidation of Thiols with $Zn(BiO_3)_2$ and Comparison with $BaFeO_4 \cdot H_2O$,[8] Sodium Perborate (SPB),[13,14] and Tetrabutylammonium Chlorochromate (TBACC)[12]

Entry no.	Substrate	Product	Mp[15]	$Zn(BiO_3)_2$			$BaFeO_4 \cdot H_2O$		SPB[13,14]		TBACC[12]	
			°C	Reaction time	Yield	Oxid. React.	Reaction time	Yield	Reaction time	Yield	Reaction time	Yield
				h	%		h	%	h	%	h	%
1	2-Pyridinethiol	$(2\text{-Py})_2S_2$	54—57	0.5	98	2	—	—	2	75	—	—
2			141—145	1	90	2	—	—	—	—	—	—
3	Thiophenol	Diphenyl disulfide	58—61	0.25	97	2	0.25	100	2	92	1	87
4	*m*-Thiocresol	Di-*m*-tolyl disulfide	45	0.2	97	2	1	90	2	86	—	—
5	2-Furylmethanethiol	Furfuryl disulfide	—	0.25	86	2	—	—	—	—	—	—
6	Cyclohexanethiol	Dicyclohexyl disulfide	—	0.25	99	2	0.5	90	—	—	—	—
7	α-Toluenethiol	Dibenzyl disulfide	65—68	0.2	93	2	1	100	2	93	1	80

Oxidation of the hydroxyl group of quinine was occurred in parallel with the cleavage of carbon–carbon bond and produced the aromatic aldehyde (Entry 19, Table 1) the NMR spectrum in deuterated chloroform shows absorption bands; $\delta=3.95$ (3H, s) for a -OMe group, $\delta=10.5$ (1H, s) for a -CHO group, and $\delta=7.2$—9.1 (5H, m) for aromatic protons, which are all consistent with the proposed structure. Benzaldehyde was obtained in a 10% yield as a side product of the partial benzylic double bond cleavage of cinnamyl alcohol.

The mildness of the reagent is demonstrated by the oxidation of different thiols to their disulfides in excellent yields (Table 2). α-Toluenethiol, in addition to dibenzyl disulfide, produces also benzaldehyde in a 7% yield.

Oxidation of thioethers with zinc bismuthate was also proceeded well in toluene in the presence of a catalytic amount of acetic acid, and their corresponding sulfoxides were isolated in good yields.

Experimental

General: All yields refer to isolated products. Reactions proceeded in toluene, or in the mixture of toluene–acetonitrile, or in toluene in the presence of a catalytic amount of acetic acid. Products were characterized by comparison with authentic samples (IR spectrum, thin-layer, gas chromatography, NMR spectrum, melting point). Melting points are not corrected.

Preparation of Zinc Bismuthate $Zn(BiO_3)_2$: To a suspension of sodium bismuthate (20 g, 34.54 mmol) in water (30 ml) a solution of (15% by weight) zinc chloride hexahydrate (300 ml) was added and the resulting mixture was refluxed for 1.5 h. The reaction mixture was filtered and the solid material was isolated. The solid brown material was washed first with hot water (100 ml) and then with acetone (100 ml) and was dried further over calcium chloride in a dessicator to afford zinc bismuthate; yield 20.5 g (99%); the analytical data were consistent with the proposed structure.

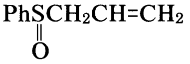
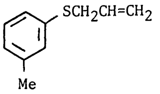
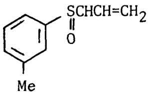
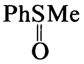
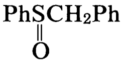
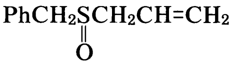
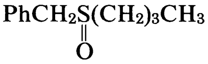
Oxidation of Benzoin to Benzil. A Typical Procedure for the Hydroxyl Group Oxidation. In a round-bottomed flask (100 ml), equipped with a condenser, a solution of benzoin (1 g, 4.71 mmol) in toluene (50 ml) was prepared and zinc bismuthate (2.72 g, 471 mmol) was added to this solution. The reaction mixture was stirred magnetically under reflux condition for 0.7 h. The progress of the reaction was followed by TLC (eluent: $CCl_4/Et_2O=3/1$).

The reaction mixture was filtered and the solid material was washed with acetonitrile (50 ml) and carbon tetrachloride (50 ml). The filterates were combined and evaporated. The resulting crude material was purified on a silica-gel column with an appropriate eluent. After evaporation of the solvent, benzil was obtained as a white crystalline material in 0.96 g (97%), mp 93—96 °C (lit,[15] mp 94—95 °C) (Table 1).

Oxidation of Hydroquinone to *p*-Benzoquinone. A Typical Procedure. In a round-bottomed flask (200 ml) equipped with a condenser and a magnetic stirrer, a solution of hydroquinone (2 g, 8.18 mmol) in toluene (100 ml) was prepared. Zinc bismuthate (10.52 g, 18.16 mmol) was added to the solution and the reaction mixture was stirred magnetically under reflux conditions for 0.1 h. The progress of the reaction was followed by TLC. The reaction mixture was filtered and the solid material was washed with acetonitrile (300 ml) and then with carbon tetrachloride. The filterates were combined together and evaporated. The resulting crude material was purified by column chromatography (silica gel, eluent; $CCl_4/Et_2O=3/1$). Evaporation of the solvent afforded *p*-benzoquinone in 0.9 g (93%), mp 112—115 °C (lit,[15] mp 113—115 °C). (Table 1).

Conversion of α-Toluenethiol to Dibenzyl Disulfide. A Typical Procedure. In a round-bottomed flask (200 ml), equipped with a condenser and a magnetic stirrer, a solution of thiol (1.25 g, 10 mmol) in toluene (100 ml) was prepared. Zinc bismuthate (11.58 g, 20 mmol) was added to the solution and the resulting mixture was refluxed for 0.2 h and filtered and the solid material was washed with acetonitrile (30 ml) and carbon tetrachloride (30 ml). The filtrates were combined together and the resulting crude material was purified on a silica-gel column eluted with (benzene/$Et_2O=4/1$). Evaporation of the solvent afforded pure dibenzyl disulfide in 1.16 g

Table 3. Oxidation of Sulfides with $Zn(BiO_3)_2$ and Comparison with $Ba(MnO_4)_2$

Entry no.	Substrate	Product	Mp or bp[15]	$Zn(BiO_3)_2$			$Ba(MnO_4)_2$[16]	
				Reaction time	Oxid./React.	Yield	Reaction time	Yield
			°C	h		%	h	%
1	$PhSCH_2CH=CH_2$	 $Ph\underset{O}{\underset{\|}{S}}CH_2CH=CH_2$	—	1.5	1.25	65	6	60
2			—	2	1.5	69	4	60
3	PhSMe	 $Ph\underset{O}{\underset{\|}{S}}Me$	139—141/14 mm Hg[a)]	0.8	1.5	78	—	—
4	$PhSCH_2Ph$	 $Ph\underset{O}{\underset{\|}{S}}CH_2Ph$	121—125	1.25	1.5	75	4	88
5	$PhCH_2SCH_2CH=CH_2$	 $PhCH_2\underset{O}{\underset{\|}{S}}CH_2CH=CH_2$	62—64	0.8	1.5	70	5	70
6	$PhCH_2S(CH_2)_3CH_3$	 $PhCH_2\underset{O}{\underset{\|}{S}}(CH_2)_3CH_3$	62—64	0.8	1.5	70	5	70

a) 1 mm Hg=133.322 Pa.

(93%), mp 66—69 °C, (lit,[8] mp 70—71 °C). (Table 2).

Oxidation of Benzyl Phenyl Sulfide to Its Corresponding Sulfoxide. A Typical Procedure. To a solution of the thioether (2 g, 10 mmol) in toluene (50 ml) and acetic acid (5 ml) in a 100 ml round-bottomed flask which was equipped with a condenser and a magnetic stirrer, zinc bismuthate (8.68 g, 15 mmol) was added. The reaction mixture was refluxed for 1.25 h. The progress of the reaction was monitored by TLC. The reaction mixture was filtered and the solid material was washed with acetonitrile (50 ml) and then with carbon tetrachloride (50 ml). The filtrates were combined together and evaporated. The resulting crude material was purified by column chromatography (silica gel, eluent; benzene/CH_2Cl_2=3/1). Evaporation of the solvent afforded pure benzyl phenyl sulfoxide in 1.62 g (75%), mp 122—125 °C, (lit,[15] mp 122—125 °C) (Table 3).

Conclusions

In this paper we have introduced zinc bismuthate as an efficient oxidizing agent which could be used for medium to large-scale operations. We have explored the utility of this compound as an oxidant for a number of synthetically important oxidations. The ease of preparation of the reagent, reproducibility of the reaction, ease of the work-up, stability and the mildness of the reagent, and also good yields of the products make this compound an attractive oxidant and a useful bench top reagent for organic synthesis.

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