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Barium Ferrate Monohydrate $BaFeO_4 \cdot H_2O$, a Useful Oxidant for the Oxidation of Organic Compounds under Aprotic Conditions

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Preparation of barium ferrate monohydrate with a slight modification is described. It is shown that this reagent is capable of oxidizing different organic compounds and could be used as a versatile reagent in organic synthesis. Primary and secondary alcohols are converted to their carbonyl compounds, α-hydroxy ketones to their diketones, and hydroquinones to their quinones. Aromatic amines are converted to their azo compounds, benzylamine to benzaldehyde, phenylhydrazones and oximes to their carbonyl compounds. Thiols are also converted to their disulfides in high yields. This reagent seems to be a non-toxic and a non-pollutant compound.

Oxidations of organic substrates have long been performed by manganese dioxide, potassium permanganate, chromium trioxide, and pottasium dichromate in organic synthesis.[1-3] The reaction conditions, special treatment for the activation of the reagent, and the lack of selectivity have restricted their use as oxidizing reagents in modern organic synthesis. Recently several chromium(VI) and manganese based oxidants have been prepared and reported in the literature,[4-35] in order to minimize the limitations encountered with mentioned reagents.

Reports are available which discuss manganese and chromium(VI) based oxidants and indicate that these reagents are toxic, pollutant, and are also corrosive and irritant to skin and mucous membrane.[26] Very recently it is reported that Cr(III), the product of the reduction of Cr(VI) is an animal carcinogen.[37]

Manganate, chromate, and ferrate anions are structurally similar species and as an oxidizing agent, organic chemists have long been familiar with potassium chromate. Recently attention has been paid to manganates as oxidizing agents and a few reports are also available in the literature.[30-32] Reports also exist which indicate that potassium ferrate has been used as an oxidizing reagent,[38-40] but the results reported are contradictory. Moreover, the reactions are performed in strongly basic aqueous media (pH 11.5—13.5) which limits drastically the use of this reagent as a versatile oxidizing agent in organic synthesis.

Ferrate anion decomposes in the presence of water according to the following equation;

$$2H_2O + 2FeO_4^{2-} \rightarrow Fe_2O_3 + 3/2O_2 + 4OH^-$$

The products obtained are unlikely to be toxic and pollutant. It is also reported that ferrate anion is a strong oxidant.[41] Unfortunately very little attention has been paid to these properties in preparative organic chemistry.

Very recently we have reported that silver ferrate[42] could be a good substitute for the potassium ferrate phase-transfer catalysis oxidation,[40] where a neutral, nonaqueous, and aprotic medium is of importance. However, silver ferrate is an expensive and a moderately stable reagent, therefore, these findings limit the use of this compound as a versatile agent.

The purpose of this investigation was to find a ferrate compound which would be stable and cheap, and could be used as a versatile oxidant in organic synthesis. The preparation of Co^{2+}, Pb^{2+}, Hg^{2+}, Fe^{3+}, and Zn^{2+} ferrate have been examined. Unfortunately it was found that all of these compounds were highly unstable and liberate their oxygen immediately after their formation in the reaction media.

Lately in a communication we introduced barium ferrate monohydrate[43] as an oxidizing agent for the oxidation of alcohols, and its advantages over potassium ferrate and manganese dioxide were indicated. Here we discuss with a slight modification, the preparation of pure barium ferrate monohydrate. We have extended our studies upon the oxidation of different classes of organic compounds with this reagent. Most of the results obtained are also extensively compared with barium manganate, a new and commercially available reagent.[31,32]

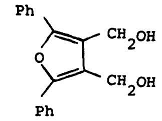
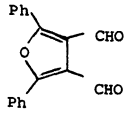
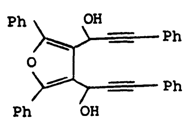
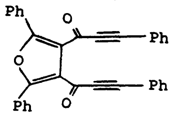
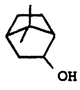
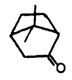
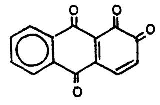
Results and Discussion

First sodium ferrate was prepared according to the procedure described by Thompson et al.[44]

In the previous report, barium ferrate monohydrate[45] has been prepared from potassium ferrate which in turn was made from sodium ferrate. In the present report we have used directly the solution of sodium ferrate as the precurser for the preparation of the barium salt, which improves drastically the yield of the desired product. By the addition of saturated solution of barium nitrate to the solution of sodium ferrate, barium ferrate monohydrate was precipitated immediately. In this preparation carbon dioxide-free distilled water was important, in order to avoid the formation of the corresponding carbonate. The precipitated barium ferrate monohydrate was washed with a weakly acidic solution (pH=5) until the filtrates pH reached 7, and was dried overnight in a vacuum desiccator under a dynamic vacuum.

Oxidation of organic substrates with barium ferrate monohydrate gives reproducible results and activation of the reagent is not necessary. In contrast, oxidation with manganese dioxide usually does not give reproducible results.[20] Barium ferrate monohydrate is a very stable compound and could be stored for months without losing its oxidizing potential. This compound is a dark purple powder, which is very slightly soluble in water. Barium ferrate monohydrate does not irritate mucous membrane and skin, whereas barium manganate seriously does irritate mucous membrane. According to our findings, barium ferrate monohydrate is a good oxidizing reagent in organic synthesis and may replace toxic and pollutant reagents. This reagent is a good substitute for manganese dioxide in many respects; 1) it does not need special treatment for its activation, 2) the ratio of substrate to manganese dioxide can range from 1:5 to 1:50, this ratio for barium ferrate monohydrate in this study ranged from 1:1 to 1:10, which makes the isolation of the oxidation product from the reaction mixture easier and more practical, 3) the rate of the reaction and 4)

Table 1. Comparison of Oxidation of Some Organic Compounds with $BaFeO_4 \cdot H_2O$ and $BaMnO_4$, MnO_2

No.	Substrate	Product	Mp θ_m/ °C[32,49] (n_D^{20})	$BaFeO_4 \cdot H_2O$			$BaMnO_4$[32]		MnO_2	
				Reaction time/h	Yield %	Oxidant/Reactant	Reaction time/h	Yield %	Reaction time/h	Yield %
1			126—128	4	80—85	10	4	90	17	20—40[50]
2	Benzhydrol	Benzophenone	58	0.5	100	2	0.5	100	2	87[45]
3	Benzyl alcohol	Benzaldehyde	(1.5455)	0.8	95—100	1	1.5	90	3	26.7[45]
4	Hydroquinone	*p*-Benzoquinone	—	0.25	100	2	0.3	75	0.5	38[45]
5	Aniline	Azobenzene	66—68	0.25	>95	3	0.5	90	6	87[45]
6	*p*-Toluidine	4,4′-Dimethylazobenzene	67	2	40	5	1.5	67	6	87[45]
7	*m*-Nitroaniline	3,3′-Dinitroazobenzene	148—150	4.5	25	5	2.5	55	24	04[45]
8	*o*-Nitroaniline	2,2′-Dinitroazobenzene	—	4.5	0	5	24	0	24	0[45]
9	*p*-Nitroaniline	4,4′-Dinitroazobenzene	220—222	4.5	27	5	2.5	30	24	0[45]
10	Benzylamine	Benzaldehyde	(1.5454)	1	100	2	1	95	24	34[45]
11	1-Naphthylamine	1,1′-Azonaphthalene	187—189	4.5	15	5	4.5	25	24	0[45]
12	*p*-Chloroaniline	4,4′-Dichloroazobenzene	220—221	2	50	5	1.5	80	6	87[45]
13	2,4-Dinitrophenylhydrazine	*m*-Dinitrobenzene	86—88	1	60	5	1.5	50	5	50[45]
14	Cinnamyl alcohol	Cinnamaldehyde	(1.6220)	1	100	4	0.75	100		
15	Cyclohexanol	Cyclohexanone	(1.4500)	24	70	2	24	56—60		
16			165	4	70	10	4	70		
17			170—173	24	80	5	15	90		
18	Furfuryl alcohol	Furfural	(1.5244)	0.15	40	2	0.15	75		
19	Citronellol	Citronellal	(1.5490)	24	40	10	24	85—90		
20	*p*-Nitrobenzyl alcohol	*p*-Nitrobenzaldehyde	106	2	85	2	4.5	60		
21	1-Phenylethanol	Acetoplenone	(1.5352)	1	100	3				
22	Benzoin	Benzil	43—45	6	95	6				
23	Furoin	Furil	162—163	1.5	100	6				
24	Catechol	*o*-Benzoquinone	113—115	0.7	100	6				
25	Alizarin		—	5	0	6				
26	1-Heptanol	Heptanal	(1.4217)	48	60	10				

the yields are usually higher with barium ferrate monohydrate than those reported for active manganese dioxide (Table 1). The results obtained with this reagent are also very comparable with those obtained with barium manganate (Table 1). Barium ferrate monohydrate is a mild oxidizing agent and oxidizes different organic substrates in benzene, heptane, and toluene under reflux conditions.

Benzylic alcohols were converted to the corresponding carbonyl compounds in high yields. Cinnamyl alcohol was converted to cinnamaldehyde almost quantitatively. Saturated primary and secondary alcohols were also converted to their carbonyl compounds in good yields. α-Hydroxyketones, such as benzoin and furoin were converted to benzil and furil in excellent yields (Table 1).

The mildness of this reagent is demonstrated by the oxidation of different thiols to their corresponding disulfides in excellent yields (Table 2).

Coupling reaction of aromatic amines to their corresponding azo compounds were also investigated. 1-Naphthylamine and aromatic amines with nitro groups substituted on the aromatic ring gave low yields of their corresponding azo compounds. The same oxidations with manganese dioxide is reported to be quite unreactive.[46] Other amines such as benzylamine were converted to benzaldehyde quantitatively. Aniline, *m*- and *p*-chloroanilines, and *m*-toluidines were converted to their azo compounds in moderate yields (Table 3). Phenylhydrazine was converted to biphenyl in good yield. Oxidation of *p*-nitrophenylhydrazine and 2,4-dinitrophenylhydrazine produced nitrobenzene and *m*-dinitrobenzene respectively in good yields (Table 3). Oxidation of several oximes were also investigated. Benzophenone oxime, benzaldehyde oxime, and 2-naphthaldehyde oxime produced their corresponding carbonyl compounds from low to good yield. Anisaldehyde phenylhydrazone produced anisaldehyde in good yield. Benzophenone phenylhydrazone produced benzophenone in high yields and also biphenyl as a by-product (Table 3).

Catechol and hydroquinone were converted their

Table 2. Oxidation of Thiols with $BaFeO_4 \cdot H_2O$

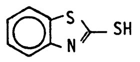
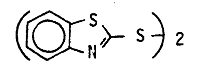
No.	Substrate	Product	Mp θ_m/°C[32,49) (n_D^{20})	$BaFeO_4 \cdot H_2O$		Oxidant
				Reaction time/h	Yield/%	Reactant
1			182—183.5	0.33	100	2
2	Thiophenol	Diphenyl disulfide	60—61	0.25	100	2
3	α-Toluenethiol	Dibenzyl disulfide	70—71	1	100	2
4	1-Butanethiol	Dibutyl disulfide	116—118/20	0.5	85—90	2
5	Cyclohexanethiol	Dicyclohexyl disulfide	—	0.5	85—90	2
6	*m*-Thiocresol	Di-*m*-tolyl disulfide	—	1	90	2

Table 3. Oxidation of Nitrogen-Containing Organic Compounds with $BaFeO_4 \cdot H_2O$

No.	Substrate	Product	Mp θ_m/°C[32,49) (n_D^{20})	$BaFeO_4 \cdot H_2O$		Oxidant
				Reaction time/h	Yield/%	Reactant
1	Benzylamine	Benzaldehyde	1.5454	1	100	2
2	1-Naphthylamine	1,1′-Azonaphthalene	187—188	4.5	15	2
3	Aniline	Azobenzene	66—68	0.25	100	3
4	*m*-Nitroaniline	3,3′-Dinitroazobenzene	146—149	4.5	23	5
5	*p*-Nitroaniline	4,4′-Dinitroazobenzene	138—140	4.5	27	5
6	o-Nitroaniline	2,2′-Dinitroazobenzene	—	4.5	0	5
7	*m*-Chloroaniline	3,3′-Dichloroazobenzene	98—100	2	40	5
8	*p*-Chloroaniline	4,4′-Dichloroazobenzene	219—221	2	50	5
9	Phenylhydrazine	Biphenyl	70—72	0.1	70	5
10	p-Nitrophenylhydrazine	Nitrobenzene	1.5511	0.25	94	5
11	2,4-Dinitrophenylhydrazine	*m*-Dinitrobenzene	86—88	1	60	5
12	Benzophenone phenylhydrazone	Benzophenone + Biphenyl	58 70—72	6	85 + 10	6
13	*p*-Anisaldehyde phenylhydrazone	*p*-Anistaldehyde	1.5715	6	70	6
14	Benzophenone oxime	Benzophenone	58	0.5	90	5
15	*p*-Chlorobenzaldehyde oxime	*p*-Chlorobenzaldehyde	42—43	0.5	30	5
16	2-Naphthaldehyde oxime	2-Naphthaldehyde	59—62	1	18	6

quinones in excellent yields. Alizarin was quite resistant towards oxidation with this oxidant (Table 1).

Experimental

General. All yields refer to isolated products. Products were characterized by comparison with authentic sample (IR spectrum, thin-layer and gas chromatography, melting point, and refractive index). Most reaction proceeded in dry benzene, unless otherwise indicated.

Preparation of Barium Ferrate Monohydrate. Sodium hydroxide (30 g) was dissolved in 75 ml of carbon dioxide-free distilled water and the solution was cooled to 20 °C. Chlorine gas was slowly bubbled through this solution, while being stirred vigorously, until a total weight gain of 20 g was achieved. The resulting hypochlorite solution was made strongly basic with the slow addition of 70 g of sodium hydroxide while the solution was being stirred vigorously and the temperature was permitted to rise to 30 °C. The resulting reaction mixture was cooled to 20 °C and the precipitated sodium chloride was removed by filtration. To the stirred solution of the resulting sodium hypochlorite at 25—30 °C, 25 g of iron(III) nitrate was added slowly, and this solution was saturated with sodium hydroxide at 30 °C with stirring. The reaction mixture was filtered with suction and to the resulting filtrate a sufficient amount of saturated solution of barium nitrate was added with stirring. The precipitated barium ferrate monohydrate was filtered rapidly and washed with a weakly acidic solution (pH=5) until the filtrates pH reached 7. The precipitate was dried overnight in a vacuum desiccator under a dynamic vacuum. The yield, based on sodium ferrate was almost quantitative. The analytical data were consistent with the proposed structure.

Oxidation of Benzhydrol to Benzophenone, Typical Procedure. To a solution of benzhydrol (194 mg, 0.001 mol) in dry benzene (30 ml), in a 100 ml round-bottomed flask, equipped with a condenser and magnetic stirrer, barium ferrate (1188 mg, 0.003 mol) was added and refluxed for 50 min. The reaction mixture was filtered with suction and the solid material was washed with benzene for several times. The filtrates were added together and evaporated. The resulting material was chromatographed on a silica-gel column eluted with benzene. Evaporation of the solvent afforded benzophenone (176 mg, 97%) (Table 1).

Oxidation of *p*-Chloroaniline to Its Corresponding Azo Compound, Typical Procedure. In a round-bottomed flask (100 ml), equipped with a condenser and a magnetic stirrer, *p*-chloroaniline (101 mg, 0.01 mol) in dry benzene (30 ml) was mixed with barium ferrate (1375 mg, 0.005 mol) and refluxed for 1.5 h. The reaction mixture was filtered with suction. The solid material was washed with acetone (15 ml). The filtrates were added together and evaporated. The resulting material was chromatographed on a silica-gel column eluted with benzene. Evaporation of the solvent afforded the desired azo compound (22.5 mg, 50% yield) (Table 3).

Conversion of Cyclohexanethiol to Dicyclohexyl Disulfide, Typical Procedure. To a solution of cyclohexanethiol (116 mg, 0.001 mol) in dry benzene (20 ml) in a 50 ml round-bottomed flask, equipped with a condenser and a magnetic stirrer, the oxidant (550 mg, 0.002 mol) was added. The resulting mixture was refluxed for 30 min. The reaction mixture was filtered, the solid material was washed with acetone (10 ml). The filtrates were added together and evaporated. The resulting material was chromatographed on a silica-gel column eluted with benzene. Evaporation of the solvent afforded the desired disulfide quantitatively (Table 2).

Conversion of Phenylhydrazine to Biphenyl, Typical Procedure. In a round-bottomed flask (50 ml), equipped with a condenser, and a magnetic stirrer, the oxidant (1375 mg, 0.005 mol) was added to a solution of phenylhydrazine (108 mg, 0.001 mol) in dry benzene (30 ml). The resulting mixture was refluxed for 6 min. The reaction mixture was filtered and the filter cake was washed with acetone (10 ml). The filtrates were added together and evaporated. The resulting material was chromatographed on a silica-gel column eluted with benzene. Evaporation of the solvent afforded biphenyl (54 mg, 70%) (Table 3).

Oxidation of Benzophenone Phenylhydrazone, Typical Procedure. In a round-bottomed flask (50 ml), equipped with a condenser and a magnetic stirrer, benzophenone phenylhydrazone (81 mg, 0.0003 mol) in dry benzene (30 ml) was mixed with the oxidant (495 mg, 0.00018 mol) and refluxed for 6 h. The reaction mixture was filtered with suction. The solid material was washed with acetone (10 ml). The filtrates were added together and evaporated. The resulting material was chromatographed on a silica-gel column eluted with benzene. Two fractions were isolated; benzophenone (47 mg, 85%) and biphenyl (4.5 mg, 10%) (Table 3).

Deoximation of Benzophenone Oxime, Typical Procedure. Barium ferrate monohydrate (171 mg, 0.0006 mol) was added to a solution of benzophenone oxime (24 mg, 0.00012 mol) in dry benzene (31 ml) in a round-bottomed flask (50 ml) equipped with a condenser and a magnetic stirrer. The resulting mixture was refluxed for 30 min. The reaction mixture was filtered and the filter-cake was washed with benzene (10 ml). The filtrates were added together and evaporated. The resulting material was chromatographed on a silica-gel column eluted with benzene. Evaporation of the solvent afforded benzophenone (20 mg, 91%) (Table 3).

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