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Barium Manganate. A Versatile Oxidant in Organic Synthesis

Habib FIROUZABADI* and Zohreh MOSTAFAVIPOOR
Chemistry Department, Shiraz University, Shiraz, Iran

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Preparation of barium manganate in large-scale is discussed. It is also shown that this reagent is capable of oxidizing organic substrates, converting alcohols to their corresponding carbonyl compounds, aromatic amines to their corresponding azo compounds, hydroquinone to *p*-benzoquinone, benzylamine to benzaldehyde, and triphenylphosphine to its oxide in good yields. Saturated hydrocarbons, unsaturated hydrocarbons, unsaturated ketones, and saturated amines are not affected by this reagent in a reasonable reaction time.

Among many oxides and oxoanions of manganese, only manganese dioxide[1] and potassium permanganate[2] have extensively studied in the oxidation of organic compounds. Recently several permanganates; potassium permanganate "dicyclohexyl-18-crown-6",[3] benzyltriethylammonium permanganate,[4] tetrabutylammonium permanganate,[5,6] bis(pyridine)silver permanganate[7] have been prepared and used in the oxidations of organic substrates in organic solvents. Manganates are also of interest in the oxidation of organic compounds but, very little attention has been paid to their properties in organic oxidation reactions. There have been few reports available in the literature in which potassium manganate is used as an oxidant.[8,9] Very recently basic strontium manganic manganate[10] has also been used in the oxidation of alcohols to their corresponding carbonyl compounds in organic media.

Lately in a communication we introduced barium manganate in heterogeneous system as a good oxidizing agent for the oxidation of alcohols and indicated its advantages over manganese dioxide.[11] Here we discuss the large-scale preparation of this reagent with some modification to our previously reported procedure.[11] We have also extended our studies to the oxidation of different groups of organic compounds.

Results and Discussion

Barium manganate was prepared as following: 1) 2 mol of potassium hydroxide were fused with 1 mol of manganese dioxide at 350 °C to produce dark green potassium manganate.[12] 2) 1 mol of potassium manganate was added while being stirred to a warm solution of 1 mol of barium hydroxide at pH=7. The dark blue crystals of barium manganate[13] were collected and dried at 100 °C for 24 h.

Oxidation with barium manganate, prepared by this method, gives reproducible results without requiring

TABLE 1. COMPARISON OF OXIDATION OF SOME ORGANIC COMPOUNDS WITH $BaMnO_4$ AND MnO_2

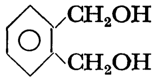
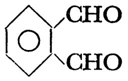
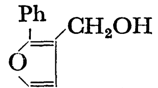
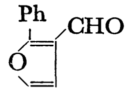
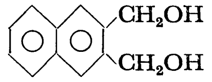
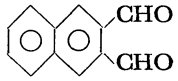
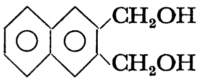
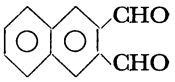
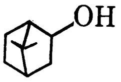
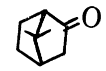
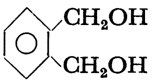
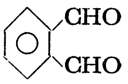
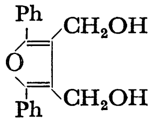
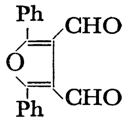
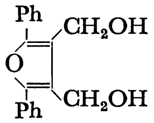
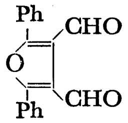
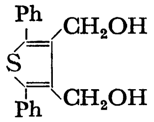
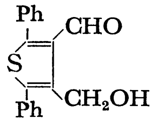
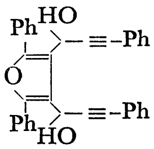
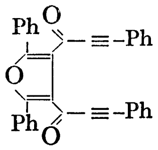
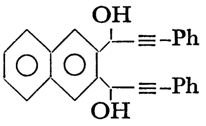
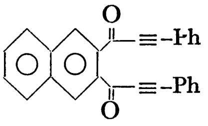
No.	Substrate	Product	$BaMnO_4$		MnO_2	
			Reaction time/h	Yield/%	Reaction time/h	Yield/%
1	Aniline	Azobenzene	0.5	90	6	87[14]
2	*p*-Toluidine	4,4′-Dimethylazobenzene	1.5	67	6	87[14]
3	*m*-Nitroaniline	3,3′-Dinitroazobenzene	2.5	55	24	0[14]
4	*o*-Nitroaniline	2,2′-Dinitroazobenzene	24	0	24	0[14]
5	Benzyl alcohol	Benzaldehyde	1.5	90	3	26.7[15]
6	Benzhydrol	Benzophenone	0.5	100	2	87[14]
7	*p*-Nitroaniline	4,4′-Dinitroazobenzene	2.5	30	24	0[14]
8	1-Naphthylamine	1,1′-Azonaphthalene	4.5	25	24	0[14]
9	*p*-Chloroaniline	4,4′-Dichloroazobenzene	1.5	80	6	87[14]
10	*o*-Phenylenediamine	2,2′-Diaminoazobenzene	0.5	60	4	50[18]
11	Benzylamine	Benzaldehyde	1	95	24	34[19]
12	Hydroquinone	*p*-benzoquinone	0.3	75	0.5	38[14]
13	Diphenylmethane	Tetraphenylethane	3	0	2	49[14]
14	Triphenylphosphine	Triphenylphosphine oxide	2	100	5	75[14]
15	2,4-Dinitrophenylhydrazine	*m*-Dinitrobenzene	1.5	50	5	50[14]
16			3	80	5	45[16]
17			4	90	17	20—40[16,17]
18			12	87	8	50[16]

TABLE 2. OXIDATION OF ALCOHOLS WITH $BaMnO_4$

No.	Substrate	Product	Mp θ_m/°C (n_D^{20})	$BaMnO_4$		
				Reaction time/h	Yield/%	Oxidant/Reactant
1	Citronellol	Citronellal	(1.4590)	24	85—90	5
2	PhCH: CHCH$_2$OH	PhCH: CHCHO	(1.6220)	0.75	100	4
3	PhCH: CHCHOHCH$_3$	PhCH: CHCOCH$_3$	36—40	3	50	5
4	PhCH: CHCHOHCH$_3$	PhCH: CHCOCH$_3$	36—40	0.75	80	10
5	1-Pentanol	1-Pentanal	(1.3945)	24	50	10
6	Cyclohexanol	Cyclohexanone	(1.4500)	24	50—60	10
7	1-Tetradecylol	1-Tetradecylal	—	6	30	5
8	Benzyl alcohol	Benzaldehyde	(1.5455)	0.15	90	1
9	Furfuryl alcohol	Furfural	(1.5244)	0.15	75	2
10	Piperonol	Piperonal	35—38	1.5	60	5
11	*p*-Nitrobenzylalcohol	*p*-Nitrobenzaldehyde	106	4.5	60	2
12	Benzhydrol	Benzophenone	58	0.5	100	2
13			112—115	12	87a)	10
14			170—173	15	90a)	5
15			54	3	80	10
16			126—128	4	90	10
17			126—128	16	80a)	10
18			114—116	3	85	10
19	PhCHOHC≡CPh	PhCOC≡CPh	110—113	4	80	10
20			165—166	4	70	10
21			119—120	5	80a)	10

a) In dichloromethylene.

further activation, while oxidation reaction with manganese dioxide is not reproducible in many aspects.1) This reagent is indefinitely stable, active, and could be stored for months under dried condition. According to our finding barium manganate is a good reagent in organic synthesis whenever both the rate and the selectivity of the reaction are concerned. To our view this reagent is a good substitute for manganese dioxide in many respects. First, its preparation and isolation is much easier than of active manganese dioxide. Second, the ratio of substrates to manganese dioxide can range from 1 : 5 to 1 : 50.1) This ratio for barium manganate in our investigation ranged from 1 : 1 to 1 : 10, which makes the isolation of the oxidation product from the solid oxidizing material easier and more practical. Third, the oxidation reactions of organic compounds under investigation with barium manganate were usually faster and resulting higher yields than those obtained from manganese dioxide. The results obtained are summarized in Table 1. Barium manganate reacts very mildly and selectively in dry organic solvents, *e.g.* dichloromethane and benzene, either at room temperature, or under reflux conditions. The rate of reaction under reflux conditions

Table 3. Oxidation of amines with $BaMnO_4$

No.	Substrate	Product	Mp θ_m/°C (n_D^{20})	$BaMnO_4$		
				Reaction time/h	Yield/%	Oxidant/Reactant
1	2-Nitro-4-chloroaniline	2,2′-Dinitro-4,4′-dichloroazobenzene	220—221	2	8	5
2	Aniline	Azobenzene	66—68	0.5	90	3
3	*m*-Toluidine	3,3′-Dimethylazobenzene	49—50	1.5	46	5
4	*p*-Toluidine	4,4′-Dimethylazobenzene	138—140	1.5	67	5
5	*o*-Toluidine	2,2′-Dimethylazobenzene	52—54	1.5	66	5
6	*m*-Nitroaniline	3,3′-Dinitroazobenzene	148—150	2.5	55	5
7	*o*-Nitroaniline	—	—	24	0	5
8	*p*-Nitroaniline	4,4′-Dinitroazobenzene	220—222	2.5	30	5
9	1-Naphthylamine	1,1′-Azonaphthalene	187—189	4.5	25	5
10	*m*-Chloroaniline	3,3′-Dichloroazobenzene	99—100	2	67	5
11	*p*-Chloroaniline	4,4′-Dichloroazobenzene	220—221	1.5	80	5
12	*m*-Methoxyaniline	3,3′-Dimethoxyazobenzene	73—75	2	50	5
13	*o*-Phenylenediamine	2,2′-Diaminoazobenzene	132—133	0.5	60	5
14	Benzylamine	Benzaldehyde	(1.5454)	1	95	2
15	2,4-Dinitrophenylhydrazine	*m*-Dinitrobenzene	86—88	1.5	50	5

Table 4. Miscellaneous oxidation with $BaMnO_4$

No.	Substrate	Product	Mp θ_m/°C	$BaMnO_4$		
				Reaction time/h	Yield/%	Oxidant/Reactant
1	Hydroquinone	*p*-Benzoquinone	112—114	0.3	75	2
2	Diphenylmethane	—	—	3	0	2
3	Styrene	—	—	2	0	2
4	Toluene	—	—	3	0	5
5	Triphenylphosphine	Triphenylphosphine oxide	150—154	2	100	5
6	1-Heptylamine	—	—	3	0	4
7	$PhCH{:}\,CHCOCH_3$	—	—	4	0	4
8	$PhCH{:}\,CHCOH$	—	—	3	0	4

is much faster.

Benzylic alcohols were converted to the corresponding carbonyl compounds without further oxidation. In the oxidation of diols; (16 and 18) in Table 2 in addition to the isolation of corresponding aldehydes a small amount of the corresponding lactone was also isolated. Allyl alcohols were also very reactive and produced their carbonyl compounds in good yields. 2-Alkyn-1-ols were very reactive and were oxidized very easily to their corresponding carbonyl compounds in good yields. Saturated alcohols were oxidized rather slowly with difficulty. In some cases even after 24 h only fifty percent conversion were observed (Table 2).

Aromatic amines with nitro groups substituted on the aromatic ring and 1-naphthylamine gave none to low yields of their corresponding azo compounds. In these cases manganese dioxide is reported to be quite unreactive.[14] The other aromatic amines were quite reactive and their corresponding azo compounds were produced very easily. Benzylamine was converted to benzaldehyde very rapidly (Table 3).

Triphenylphosphine was converted very easily and rapidly to triphenylphosphine oxide, 2,4-dinitrophenylhydrazine to *m*-dinitrobenzene, and hydroquinone to *p*-benzoquinone. The oxidation of a few hydrocarbons, unsaturated ketones, and saturated amines were also investigated. They were unreactive towards this reagent (Table 4).

Experimental

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

Preparation of Potassium Manganate. Potassium hydroxide (2 mol) were thoroughly mixed with manganese dioxide (1 mol) and left in an oven at 350 °C for 3 h. The fused green potassium manganate was discharged and used for the preparation of barium manganate.

Preparation of Barium Manganate. In a (500 ml) flask, barium hydroxide (7 g, 0.041 mol) was added to distilled water (100 ml) and pH was adjusted to 7 with dilute hydrochloric acid. To the resulting warm solution, 8.6 g (0.043 mol) of potassium manganate was added with stirring. The colour of the reaction mixture immediately changed to dark purple. The reaction mixture was filtered with suction and the dark blue crystals were washed for several times with distilled water. The resulting crystals were put in an oven at 100 °C for 24 h, to produce active barium manganate in 60% yield. Found: Ba, 52.85%. Calcd for $BaMnO_4$: Ba, 53.58%.

General Procedure for the Conversion of Alcohols to Their Aldehydes and Ketones. To a solution of alcohol (0.01 mol) in dry benzene (30 ml), in a (100 ml) round-bottomed flask, equipped with a condenser and magnetic stirrer, barium manganate (0.05—0.1 mol) was added and refluxed for 1/2-24 h the reaction mixture was filltered with suction and the solid material was washed with dichloromethane for several times. The filterates were added together and evaporated. The resulting material was chromatographed on silica-gel column eluted with benzene. Evaporation of the solvent afforded pure carbonyl compound in 50—100% yield (Table 2).

General Procedure for the Conversion of Aromatic Amines to Their Corresponding Azo Compounds. In a round-bottomed flask (100 ml), equipped with a condenser and magnetic stirrer, amine (0.01 mol) in dry benzene (30 ml) was mixed with barium manganate (0.03—0.05 mol) and refluxed for 0.5 to 4.5 h. The reaction mixture was filtered with suction. The solid material was washed with dichloromethane for several times. The filterates were added together and evaporated. The resulting material was chromatographed on either silica gel or neutral alumina column eluted with benzene. Evaporation of the solvent afforded the azo compound in 0—90% yield (Table 3).

Conversion of 2,4-Dinitrophenylhydrazine to m*-Dinitrobenzene.* In a round-bottomed flask (100 ml) equipped with a condenser and magnetic stirrer, 2,4-dinitrophenylhydrazine (0.01 mol) in dry benzene (30 ml) was mixed with barium manganate (0.05 mol) and refluxed for 1.5 h. The reaction mixture was filtered with suction and the solid material was washed with dichloromethane for several times. The filterates were added together and evaporated. The resulting material was chromatographed on neutral alumina column eluted with benzene. Evaporation of the solvent afforded *m*-dinitrobenzene in 50% yield (Table 4).

Conversion of Benzylamine to Benzaldehyde. In a round-bottomed flask (100 ml) equipped with a condenser and magnetic stirrer, benzylamine (0.01 mol) in dry benzene (30 ml) was mixed with barium manganate (0.02 mol) and refluxed for 1 h. The reaction mixture was filtered with suction. The solid material was washed with dichloromethane for several times. The filterates were added together and evaporated. The resulting material was chromatographed on silica-gel column eluted with benzene. Evaporation of the solvent afforded benzaldehyde in 95% yield (Table 4).

Conversion of Hydroquinone to p*-Benzoquinone.* In a round-bottomed flask (100 ml) equipped with a condenser and magnetic stirrer, hydroquinone (0.01 mol) in dry benzene (30 ml) was mixed with barium manganate (0.02 mol) and refluxed for 20 min. The reaction mixture was filtered with suction. The solid material was washed with dichloromethane for several times. The filterates were added together and evaporated. The resulting material was chromatographed on silica-gel column eluted with benzene. Evaporation of the solvent afforded *p*-benzoquinone in 75% yield (Table 4).

Conversion of Triphenylphosphine to Triphenylphophine Oxide. In a round-bottomed flask (100 ml) equipped with a condenser and magnetic stirrer, triphenylphosphine (0.01 mol) in dry benzene (30 ml) was mixed with barium manganate (0.05 mol) and refluxed for 2 h. The reaction mixture was filtered with suction. The solid material was washed with dichloromethane for several times. The filterates were added together and evaporated. The resulting material was chromatographed on silica-gel column eluted with benzene. Evaporation of the solvent afforded triphenylphosphine oxide in 100% yield (Table 4).

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