Barium Permanganate, $Ba(MnO_4)_2$, A Versatile and Mild Oxidizing Agent for Use Under Aprotic and Non-Aqueous Conditions

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Abstract: Barium Permanganate is an easily prepared, stable, and a versatile oxidation reagent. With this reagent different types of primary and secondary hydroxy compounds are converted to their carbonyl derivatives. Aldehydes could be transformed to their carboxylic acids. Benzylic chloride and bromides are converted to their aldehydes and carboxylic acids. Semicarbazide and 2,4-dinitrophenylhydrazine derivatives of benzylic carbonyl compounds undergo carbon-nitrogen bond cleavage selectively and yield the expected carbonyl compounds. p-Hydroquinone is converted to p-benzoquinone and aromatic amines to their azo compounds. Anthracene and phenanthrene produce their 9,10-quinones. Diphenyl acetylene and trans stilbene give benzil, and styrene produces benzaldehyde. Selective oxidations of secondary benzylic carbon-hydrogen bonds occur and the corresponding carbonyl compounds are produced in good yields.

INTRODUCTION

Introduction of the new reagents has always been rewarding to synthetic organic chemists and beneficial in organic synthesis.

In recent years several modified permanganate based-oxidants are reported in the literature¹ and their drawbacks and advantages are also discussed¹. Very recently we

have reported that barium permanganate could be considered as a new variant in this category of oxidants with some advantages over the reported ones. We have reported that oxidations of allylic and benzylic alcohols, benzylic oximes, and thiols performed well with this oxidant and produce carbonyl compounds and disulfides respectively^{2,3}. Barium permanganate is a cheap and an easily prepared reagent. It is stable towards heat, light, shocks , and could be stored for months without loosing its oxidation ability. This reagent does not need special treatment for its activation. These observations prompted us to extend our studies on the oxidation ability of this reagent towards varieties of substrates and compare the results with some of those reported in the literature⁴⁻⁹.¹¹

RESULTS AND DISCUSSIONS

Oxidations are performed well in acetonitrile, t-butanol, and tetrahydrofuran under reflux conditions. Saturated and unsaturated primary and secondary alcohols, sterols, and hydroxy derivatives of organosilicon compounds undergo oxidations and give the corresponding carbonyl compounds in 40-95% yields (Table 1). p-Hydroquinone is converted to p-benzoquinone in 90% yield; benzylchloride, benzylbromide, and p-methoxybenzylbromide are converted to benzaldehyde and anisaldehyde respectively in good yields. Benzoic acid and anisic acid are also isolated from the reaction mixtures in 10-15% yields(Table 1). Phenylethyleneglycol undergoes carbon-carbon bond cleavage and produces benzoic acid quantitatively (Table 1). Different types of aldehydes are also oxidized with this reagent and their corresponding carboxylic acids are isolated in 15-100% yields (Table 2). Diphenylacetylene produces benzilin 80% yield. Terminal benzylic carbon-carbon double bond cleavage occurs in styrene and produces benzaldehyde in good yield (Table 1) whereas, carbon-carbon double bond in trans stilbene undergoes another type of transformation and produces benzil (Table 1). Polycyclic arenes such as phenanthrene and anthracene produce their respective 9,10-quinones in good yields.

Barium permanganate shows high selectivity for the oxidation of secondary benzylic carbon-hydrogen bonds; ethylbenzene and diphenylmethane both produce acetophenone and benzophenone in good yields in the presence of toluene which remains intact in the reaction mixture.

Barium permanganate is also effective for the oxidation of benzylic and arylamines. Benzylic amines are converted to their carbonyl compounds in good yields (Table 4). Arylamines are transformed to their corresponding azo compounds. In some cases under study, a good enhancement of the yields of azo compounds are also observed in comparison with some of those reported with the other methods⁴,⁷.

Selective oxidative cleavage of benzylic carbon-nitrogen double bond occurs with this reagent. 2,4-Dinitrophenyl hydrazene and semicarbazide derivatives of arylearbonyl

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compounds are oxidized and their parent carbonyl compounds are recovered from the reaction mixtures in 35-85% yields (Table 4). The same derivatives of benzaldehyde and cyclohexanone remain intact in the reaction mixture under the same reaction conditions. This reagent seems to be also suitable for the conversion of benzylic alcohols to their carboxylic acids. For this purpose benzyl alcohol was converted to benzoic acid quantitatively, 1-methylhydroxynaphthalene, p-nitrobenzyl alcohol, and piperonol to the corresponding carboxylic acids in 70-95% yields (Table 1). Primary alcohols such as 3-phenylpropanol and 1-octanol seems to be rather resistant towards this type of oxidation (Table 1).

CONCLUSION

Barium permanganate is a mild oxidant which could be used under non-aqueous and aprotic conditions. This reagent reacts selectively and its selectivity could be controlled by the ratio of the oxidant towards substrates. The ease of preparation, reasonably short reaction time, neutrality of the reaction media, ease of work-up, stability of the reagent, mildness of the reaction condition, comparatively small ratio of the oxidant towards substrates and also the reasonable yields of the products, make this compound a practical bench top oxidant in organic synthesis and could be considered as a new variant and a useful addition to the present methodologies¹⁰.

EXPERIMENTAL

Products were characterized by comparison with authentic sample (IR, ¹H-NMR spectra, thin layer or gas chromatography, melting point). All reactions proceeded in acetonitrile. All yields refer to isolated products. Barium permanganate was prepared according to the procedure described².

<u>General procedure for the conversion of hydroxy compounds to their carbonyl</u> <u>compounds</u>. Barium permanganate (0.03-0.08 mol) was added to a solution of hydroxy compound (0.01 mol) in acetonitrile (30 ml). The reaction mixture was refluxed for 2-6 hrs with stirring (the progress of the reaction may be monitored by TLC) and filtered and the solid material was washed with CH_3CN several times (30 ml). The combined filtrates were evaporated and the residue was chromatographed on a silica gel column eluting with benzene or benzene/ CH_2CI_2 . Evaporation of the solvent afforded the carbonyl compound in 30-100% yield (Table 1).

General procedure for the oxidation of benzylic halides to their carbonyl compounds. To a solution of benzyl halide (0.01 mol) in acetonitrile (25 ml) the oxidizing agent (0.03 mol) was added and the mixture was refluxed with stirring for 5-6 hrs. Work-up was proceeded as described in the foregoing procedure. The carbonyl compound was isolated in 55-75% yield. The corresponding carboxylic acid was also isolated in 10-15% yield. (Table 1).

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General procedure for the oxidation of alcohols to their carboxylic acids. Alcohol (0.01 mol) was dissolved in CH_3CN (30 ml) and the oxidant (0.1 mol) was added to the mixture and refluxed with stirring for 4-10 hrs. The reaction mixture was filtered and the solid material was washed with warm CH_3CN (30 ml). The combined filtrates were evaporated and the residue was chromatographed on a silica gel column (eluted first with benzene and then with CH_3OH/CCl_4 : 25/75) to afford carboxylic acid in 25-100% yield (Table 1). It is also possible to extract acids with a basic solution which on acidification affords the corresponding carboxylic acids.

General procedure for the oxidation of polycyclic arenes, acetylenic, ethylenic, and sec. benzylic C-H bonds. To a solution of the hydrocarbon (0.01 mol) in CH_3CN (20 ml), barium permanganate (0.02-0.05 mol) was added. The reaction mixture was stirred under reflux for 1.5-4.5 hrs. The progress of the reaction was monitored by TLC. The mixture was filtered and the filtrate was evaporated. The resulting product was purified by column chromatography on silica gel using n-hexane, benzene, and the mixture of benzene/ CH_2Cl_2 as eluents. Evaporation of the benzene fraction or benzene/ CH_2Cl_2 fraction afforded the desired oxidized product in 30-90% yield (Table 3).

<u>General procedure for the oxidation of benzylic amines to their carbonyl compounds</u>. Barium permanganate (0.02-0.03 mol) was added to a solution of amine (0.01 mol) in CH₃CN (20 ml) and refluxed with stirring for 2-3 hrs. The progress of the reaction was monitored by TLC. The reaction mixture was filtered and the solid material was washed with CH₃CN (20 ml). The filtrates were combined and evaporated. The resulting material was chromatographed on silica gel column and eluted with benzene. Evaporation of the solvent afforded carbonyl compound in 75-80% yield (Table 4).

<u>General procedure for the conversion of aromatic amines to their corresponding azo</u> <u>compounds</u>. A solution of aromatic amine (0.01 mol) in CH_3CN (20 ml) was prepared. To the resulting solution the oxidant (0.02-0.05 mol) was added and the reaction mixture was refluxed for 0.25-7 hrs. The reaction mixture was filtered and the solid material was washed with CH_3CN (20 ml). The filtrates were combined together and evaporated. The resulting material was chromatographed on either silica gel or neutral alumina column, and eluted with benzene. Evaporation of the solvent afforded the azo compound in 0-85% yield (Table 4).

<u>General procedure for the cleavage of carbon-nitrogen double bond of the carbonyl</u> <u>derivatives of 2,4-dinitrophenylhydrazine and semicarbazide</u>. Barium permanganate (0.03 mol) was added to the solution of hydrazone or semicarbazone (0.01 mol) in Cl_3CN (25 ml) and the mixture was refluxed for 2-16 hrs. The reaction mixture was filtered and the solid material was washed with CH_3CN (20 ml). The filtrates were combined together and evaporated. The resulting material was purified by column chromatography (silica gel, eluted with benzene) to afford the expected carbonyl compound in 0-85% yield (Table 4).

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No.	Substrate	Product	Rxn Time (hr)	Yield (°)	Oxid/Reac.
1	2-Ethyl-1-hexanol	2-Ethy1-1-hexanone	3	35-40	3
2	2-Octanol	2-Octanone	2.5	50-55	3
3	Cyclohexanol	Cyclohexanone	2.25	55-60	4
4	Isopropanol	Acetone	2	70-75	3
5	1-Octanol	Octanal	2.5	30-40	4
6	1,4-Cyclohexane- diol	1,4-Cyclohexane- dione	3	75	3
7			3.25	85	3
8 HO			3	70	3
9 He			4	60	4.5
10 H			3	90	3

Table 1. Oxidation of Hydroxy Organic Compounds and Benzyl Halides with $Ba(MnO_4)_2$.



























18	p-Hydroquinone	p-Benzoquinone	0.5	90	1
19	1-Phenylethylene glycol	Benzoic Acid	0.5	100	3

Table 1 Continued

20	Benzyl Alcohol	Benzoic Acid	4	100	8
21	^a -Hydroxymethyl naphthalene	a-Naphthyl- carboxylic Acid	10	70	8
22	3-Phenvlpropyl Alconol	2- PhenylPropanoic Acid	8	25	8
23	n-Octanol	n-Octanoic Acid	10	10	8
24	p-Nitrobenzyl Alcohol	p-Nitrobenzoic Acid	24	45	10
25	Piperonol	Piperonic Acid	18	95	10
26	Benzyl Chloride	Benzaldehyde Benzoic Acid	6	55 12	3
27	Benzyl Bronide	Benzaldehyde Benzoic Acid	6	66 15	3
28	p-Methoxybenzyl Bromide	Anisaldehyde Anisic Acid	5	75 10	3

Table 2. Oxidation of Aldehydes to Carboxylic Acids with $Ba(MnO_4)_2$.

No.	Substrate	Product	Rxn Time (hr)	Yield (%)	Oxidant Reactant
1	Benzaldehyde	Benzoic Acid	3.5	90	6
2	Anisaldehyde	Anisic Acid	4	75	3
3	p-Bromobenz- aldehyde	p-Bromobenzoic Acid	2	90	3
4	p-Chlorobenz- aldehyde	p-Chlorobenzoic Acid	3	90	3
5	Naphthalene-9- carboxaldehyde	Naphathalene-9- carboxylic Acid	2	75	3
6	Phenylacetaldehyde	Phenylacetic Acid	4	75	3
7	Cinnama1dehyde	Cinnamic Acid	15	52	10
8	m-Nitrobenzla- dehyde	m-Nitrobenzoic Acid	5	100	3
9	p-Nitrobenzal- dehyde	p-Nitrobenzoic Acid	15	92	10
10	Piperonal	Piperonic Acid	15	81	10

Table 3. Oxidation of Polycyclic Arenes, Acetylenic, Ethylenic, and sec-Benzylic C-H Bonds with ${\rm Ba\,(MnO}_4)_2$

No.	Substrate	Product	Rxn Time (hr)	Yield (%)	Oxidant Product
1	Naphthalene	1, 4-Naphtho- quinone	3	0	4
2	Phenanthrene	9,10-Phenanthro- quinonc	4.5	50-60	4

3	Anthracene	9,10-Anthraquinone	1.5	85-90	2
4	Diphenylmethane	Benzophenone	3.5	75	4
5	1,2-Diphenyl- ethane	Benzil Benzylphenyl Ketone	3.5	70 20	4
6	Phenylethane	Acetophenone	4	75	4
7	Diphenylacetylene	Benzil	3.25	75-80	3
8	trans-Stil b ene	Benzil	2.5	30-40	4
9	Styrene	Benzaldehyde	2	65	3
10	Toluene	Benzaldehyde	12	0	5

Table 4. Oxidation of Nitrogen Containing Organic Compounds with $Ba(MnO_4)_2$.

No.	Substrate	Product	Rxn Time (hr)	Yield (%)	Oxidant Reactant
Ме(1			2	75-80	2
2	Benzyl Amine	Benzaldehyde	3	75	3
3	p-Toluidine	4,4'-Azobenzene	0.25	86	2
4	p-Chloroaniline	4,4'-Dichloro- azobenzene	3	60	3
5	p-Nitroaniline	4,4'-Dinitro- azobenzene	7	50-60	3
6	a -Naphthyl Amine	Azonaphthalene	6	40-45	2
7	m-Toluidine	3,3'-Dimethyl- azobenzene	0.5	80	2
8	o-Phenylene- diamine	1,1'-Diamino- azohenzene	2	70	3
9	o-Nitroaniline	1,1'-Dinitroazo- benzene	15	0	5
10	Acetophenone-2,4- DNPH ^a	Acetophenone	6	52	3
11	Benzophenone-2,4- DNPH ^a	Benzophenone	6	58	3
Ме 12	-Mer 2,4-DNPH ^a		2	47	3

Table 4.	Continued				
13	Anisaldehyde- 2,4-DNPH ^a	Anisaldehyde	4	60	3
14	Anthrone-2,4- DNPH ^a	Anthrone	2	85	3
15	Benzaldehyde-2,4- DNPH ^a	Benzaldehyde	12	0	3
16	Phenanthrene-9- carboxyaldehyde- 2,4-DNPH ^a	Phenanthrene-9- carboxaldehyde	2	75	3
17	Cyclohexanone-2,4- DNPH ^a	Cyclohexanone	16	0	3
18	Anthronesemicarbazone	Anthrone	4	51	3
19	Phenanthrene-9- carboxaldehydesemi- carbazone	Phenanthro-9- carboxaldehyde	2	75	3
20	Anisaldehydesemi- carbazone	Anisaldehyde	3	70	3
21	Benzophenonesemi- carbazone	Benzophenone	6	65	3
22	Acetophenonesemi- carbazone	Acetophenone	6	45	3
23	Benzaldehydesemi- carbazone	Benzaldehyde	12	0	3

a: 2,4-DNPH stands for 2,4-dinitrophenylhydrazine

Table 5. Comparison of Oxidations of Some Organic Compounds with $Ba(MnO_4)_2$ with Some of those Reported with the Other Oxidants.

No.	Substrate	Product	$Ba(MnO_4)_2^2$	$BaMnO_4$ 7,9,	$\frac{1}{(\text{bipy})_2 \text{Cu}(\text{MnO}_4)_2^{8,1}}$	Mn02 ^{4,6}
			Yield (%)	Yield(%)	Yield(%)	Yield(%)
1	Benzyl Alcohol	Benzaldehyde	90	90	95	26.7
2	Benzhydrol	Benzophenone	99	95	100	87
3	Cyclohexanol	Cyclohexanone	55-60	50-60	-	-
4	Diphenyl- methane	Benzophenone	75	0	0	49
5	P-Nitro- aniline	4,4'-Dinitroazo- benzene	50-60	30	25	0
6	Naphthyl Amine	Azonaph- thalene	40-45	25	35-40	0
7	Benzyl Amine	Benzaldehyde	75	95	90	34
8	Benzophenone Oxime	Benzophenone	80	-	90-95	-

Table	5	Cont	in	ied
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9	Salicylaldoxime	Salicylaldehyde	60	•	100	-
10	p-Hydroquinone	p-Benzoquinone	75	75	100	38
11	Styrene	Benzaldehyde	65	0	4-8	-
12	Furoin	Furi1	80	-	90-95	8- 7
13	Benzoin	Benzil	96	-	90	-
14	Benzaldehyde	Benzoic Acid	90	92	-	-
15	p-Methoxybenzaldehyde	p-Methoxy- benzoic Acid	75	77	-	-
16	Cinnamaldehyde	Cinnamic Acid	52	30	-	-
17	m-Nitrobenzaldehyde	m-Nitrobenzoic Acid	100	92	-	-
18	p-Nitrobenzaldehyde	p-Nitrobenzoic Acid	92	88	-	-
19	Piperonal	Piperonic Acid	81	61	-	-
20	Phenanthrene	9,10-Phenanthro- quinone	50-60	trace	70	-
21	Anthracene	9,10-Anthra- quinone	85-90	trace	80	-
22	Diphenylmethane	Benzophenone	75	0	0	49
23	Phenylethane	Acetophenone	75	0	0	-
24	Diphenylacetylene	Benzil	75-80	0	.9 5	-
25	1,2-Diphenyl ethane	Benzil	70	0	0	-
26	Styrene	Benzaldehyde	65	0	4-8	-

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