Tetrahedron Vol. 40, No. 23, pp. 5001 to 5004, 1984
Printed in Great Britain.

0040-4020/84 $3.00 + .00
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BIS(2,2′-BIPYRIDYL)COPPER(II) PERMANGANATE (BBCP): A MILD AND VERSATILE OXIDANT IN ORGANIC SYNTHESIS

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(*Received in the U.K. 2 February* 1984)

Abstract—The preparation of bis(2,2′-bipyridyl)copper(II) permanganate (BBCP) is described. The reagent converts alcohols to the corresponding carbonyl compounds, α-hydroxy ketones to diketones, hydroquinone to *p*-benzoquinone, and compounds with benzylic double bonds to benzaldehyde in high yield. Benzophenone oxime, acetophenone oxime and various benzaldoximes are converted to the corresponding carbonyl compounds, aromatic amines to azo compounds, and benzylamine to benzaldehyde, usually in high yields, under mild condition.

Oxidation of organic compounds with aqueous potassium permanganate, a widely used oxidizing reagent, suffers from disadvantages which have been described.[1] To minimizing these, several reagents—potassium permanganate dicyclohexyl-18-crown-6,[2] benzyl (triethyl)ammonium permanganate,[3,4] tetrabutylammonium permanganate,[5] potassium permanganate with quaternary salts[6,7] and triphenylmethyl-phosphonium permanganate[8]—have been prepared and used in the oxidation of organic substrates in organic media. In spite of high yields, these reagents are very strong oxidants with no selectivity.

The oxidizing ability and the selectivity of the permanganate ion is quite dependent upon the nature of the counter ion.[6,7] With this in mind, we recently introduced bis(pyridine)silver permanganate[9,10] as a mild oxidant for alcohols, amines, and oximes. Although this reagent is very efficient it is relatively unstable and rather expensive. Therefore two other compounds, tetrakis(pyridine)copper-(II) permanganate, and tetrakis(pyridine)zinc permanganate,[11] were prepared and used in the oxidation of organic substrates. Unfortunately these two compounds are highly hygroscopic and the zinc permanganate is also highly flammable. These properties made these two compounds unsuitable reagents for clean reaction in organic synthesis.

Recently we have reported the use of bis(2,2′-bipyridyl)-copper(II) permanganate[12,13] as a practical reagent for the dimerization of thiols to disulfides. Its ease of handling encouraged us to extend our studies on the oxidation of organic compounds by this reagent and to compare the results with those obtained from the widely used reagent manganese dioxide.

With this reagent, benzylic alcohols, cinnamyl alcohol, α-hydroxy keto compounds and citronellol were converted to the corresponding carbonyl compounds very efficiently in high yields (Table 1). In one case, selective oxidation of a benzylic secondary alcohol group without attack on a secondary hydroxyl group was demonstrated (Table 1, entries 27, 28). Hydroquinone was also oxidized rapidly to *p*-benzoquinone in high yield, but 1,4-dihydroxyanthraquinone was quite resistant towards oxidation with the reagent.

The oxidation of compounds with benzylic and olefinic double bonds was also investigated. It was found that the reagent was ineffective in oxidizing double bonds in solvents like methylene chloride and benzene. In solvents such as acetone, benzylic double bond cleavage occured with high yields (Table 1). Compounds with olefinic double bonds were quite unreactive towards oxidation with this reagent under the same conditions.

Benzylamine, benzophenoneoxime, acetophenoneoxime and various substituted benzaldoximes were oxidized to the corresponding carbonyl compounds in high yields with this reagent (Table 2).

Aromatic amines such as *p*-chloroaniline, *p*-nitroaniline, *p*-toluidine, and 1-naphthylamine were converted into their corresponding azo compounds in from poor to good yields. In some of these cases manganese dioxide is reported to be quite unreactive (Table 3).

Having the following points in mind, oxidation with this reagent is advantageous over those obtained using manganese dioxide:[14] 1) reactions are usually faster (Table 2, 3)[9]; 2) higher yields are usually obtained (Table 2, 3)[9]; 3) the molar ratio of oxidant to reactant does not exceed 2, (Table 1, 2)[14]; 4) no special activation is required; 5) work up is simple and rapid.

EXPERIMENTAL

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

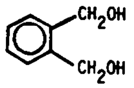
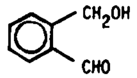
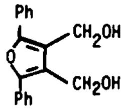
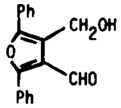
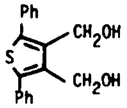
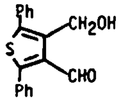
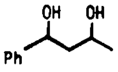
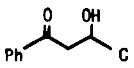
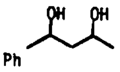
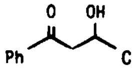
Bis(2,2′-bipyridyl)copper(II)chloride

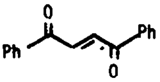
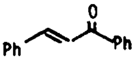
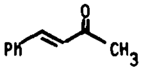
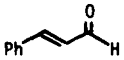
To 2,2′-bipyridyl (0.02 mol) in acetone-water (50/50), solution of copper(II) chloride (0.01 mol) in water (25 ml) was added with stirring. The dark blue solution was concentrated and cooled in an ice bath to produce crystals in quantitative yield, m.p. 250° (decomp.), (Anal: Found: Cu, 14.20 Calc for $C_{20}H_{16}Cl_2CuN_4$: Cu 14.31%), λ_{max} (H_2O) 290 (ϵ 17000), 296 (21000), 306 (20000).[13]

Bis(2,2′-bipyridyl)copper(II) permanganate

To bis(2,2′-bipyridyl)copper(II) chloride (0.02 mol) in water (25 ml), potassium permanganate (0.01 mol) in water was added with stirring. The dark purple solution was cooled and the crystalline compound was collected and dried in air;

Table 1. Oxidation of various organic compounds with BBCP

No	Substrate	Product	Reaction Time (hr)	Yield(%)	Oxidant/Reactant
1	Benzyl Alcohol	Benzaldehyde	0.25	95	0.5
2	Benzyl Alcohol	Benzaldehyde[a]	4	20-30	0.5
3	Benzhydrol	Benzophenone	0.5	100	0.5
4	Furfuril Alcohol	Furfural	0.3	90	0.5
5	9-Phenanthrene-methanol	9-Phenanthrene-carboxaldehyde	0.9	95	0.5
6	Citronellol	Citronellal	1	75-83	0.75
7	Cinnamyl Alcohol	Cinamaldehyde	1	95	1.5
8	Cinnamyl Alcohol	Benzaldehyde[a]	0.5	80	1.5
9	Cinnamyl Alcohol	Benzaldehyde[b]	0.5	90	1.5
10	Furfuril Alcohol	Furfural[b]	0.1	100	0.5
11	Mandelic Acid	Benzaldehyde[b]	0.5	90	0.5
12	p-Nitrobenzyl Alcohol	p-Nitrobenz-aldehyde	1.5	90-100	0.75
13	Furoin	Furil	0.5	90	1
14	Piperoin	Piperil	2	90-95	1
15	Benzoin	Benzil	2	90	1
16	Hydroquinone	p-Benzoquinone	0.25	100	0.5
17	Piperonol	Piperonal	0.5	100	0.5
18	1,4-Dihydroxy anthraquinone	----	4	---	0.5
19	Toluene	----	4	0	1
20	p-Xylene	----	4	0	2
21	Diphenylmethane	----	4	0	1
22	Styrene	Benzaldehyde[b]	2	4-8	0.5
23	Cyclohexene	----	2	0	0.5
24			0.2	100	1.5
25			0.3	100	0.5
26			0.3	75-80	1
27			0.3	90	0.5
28			0.3	90	1

29		---	3	0	1
30		Benzaldehyde[b]	0.25	85-90	1
31		Benzaldehyde[b]	0.25	80-90	1
32		Benzaldehyde[b]	0.1	80-85	1

[a] Reactions were performed in water.

[b] Reactions in acetone.

[c] Increasing the amount of the oxidant did not affect the second hydroxyl group.

yield 95%, m.p. 105–110° (decomp.) (Anal: Found: Cu 10.2; Mn 17.7, Calc for $C_{28}H_{16}Cl_2CuN$: Cu 10.35; Mn 17.90%), λ_{max} (H_2O) 290 (ϵ 32000), 296(39000), 306 (38000), 458 (1680), 474 (1900), 491 (2390), 510 (3090), 529 (3700), 552 (3470), 576 (2260).

General procedure for the conversion of hydorxy compounds to their carbonyl compounds

To the alcohol (0.01 mol) in dry CH_2Cl_2 (50 ml) in a round-bottomed flask equipped with a condenser and a magnetic stirrer, oxidizing reagent (0.005–0.015 mol) was added and stirred for $\frac{1}{4}$–3 h at room temp. The reaction mixture was filtered with suction and the solid material was washed with CH_2Cl_2 several times. The filtrates were combined and evaporated. The residue was chromatographed on silica gel, eluting with benzene. Evaporation of the solvent afforded the carbonyl compound in 75–100% yield (Table 1).

General procedure for the oxidation of benzylic double bonds

To a solution of the unsaturated compound (0.01 mol) in dry acetone (25 ml) in a round-bottomed flask (50 ml) equipped with a condenser and a magnetic stirrer, the oxidizing reagent (0.01 mol) was added and stirred for

Table 2. Oxidation of aromatic amines and oximes with BBCP

No	Substrate	Product	Reaction Time (hr)	Yield(%)	Oxidant / Reactant
1	p-Chloroaniline	4,4'-Dichloro-azobenzene	3	55-60	1.25
2	o-Nitroaniline	2,2'-Dinitro-azobenzene	1.5	0	1
3	p-Nitroaniline	4,4'-Dinitro-azobenzene	2	25	0.75
4	p-Toluidine	4,4'-Dimethyl-azobenzene	3	72-80	1
5	1-Naphthylamine	1,1'-Azonaphthalene	5-8	35-40	1.25
6	Benzylamine	Benzaldehyde	0.7	90	0.5
7	Benzophenone-oxime	Benzophenone	0.5	90-95	1
8	Acetophenone-oxime	Acetophenone	0.25	70-75	1
9	p-Chlorobenzal-doxime	p-Chlorobenz-aldehyde	0.15	80-90	1
10	Salicylaldoxime	Salicylaldehyde	0.5	100	1
11	m-Nitrobenzal-doxime	m-Nitrobenz-aldehyde	0.75	70-80	1
12	o-Nitrobenzal-doxime	o-Nitrobenz-aldehyde	0.5	90	1
13	p-Anisaldoxime	Anisaldehyde	0.6	90	1
14	Piperonaldoxime	Piperonal	0.15	70	1

Table 3. Comparison of oxidations of some organic compounds with BBCP and MnO_2

No	Substrate	Product	BBCP Reaction Time(hr)	BBCP Yield%	MnO_2 Reaction Time(hr)	MnO_2 Yield%
1	Benzhydrol	Benzophenone	0.5	100	2	87[15]
2	Benzyl Alcohol	Benzaldehyde	0.25	95	3	26.7[16]
3	Hydroquinone	p-Benzoquinone	0.25	100	0.5	38[15]
4	Furoin	Furil	0.5	90-95	250	87[17]
5	Benzenethiol	Phenyldisulfide	0.16	100[11]	---	92[18]
6	α-Toluenethiol	Benzyldisulfide	0.16	95[11]	---	82[18]
7	Diphenylmethane	---	4	---	2	49[15]
8	*p*-Nitroaniline	4,4'-Dinitro-azobenzene	2	25	24	0
9	1-Naphthylamine	1,1'-Azonaphthalene	5-8	35-40	24	0
10	*o*-Nitroaniline	2,2'-Dinitro-azobenzene	2	0	24	0

10 min. Work-up was as in the foregoing procedure, and afforded the carbonyl compound in 80–95% yield (Table 1).

General procedure for conversion of aromatic amines to azo compounds

Amine (0.001 mol) was dissolved in dry CH_2Cl_2 (10 ml) in a round-bottomed flask (25 ml), oxidizing reagent (0.0005–0.0125 mol) was added and refluxed for 0.7–8 hrs with stirring. The reaction mixture was filtered and the solid material was washed with CH_2Cl_2 (10 ml). The solvent was evaporated and the product purified by column chromatography (benzene, silica gel) to afford the desired azo compound in 0–90% yield (Table 2).

General procedure for the oxidation of oximes

To the oxime (0.001 mol) in dry CH_2Cl_2 (20 ml) in a round-bottomed flask (50 ml) the oxidizing reagent (0.001 mol) was added with stirring for 10–45 min. The mixture was filtered and the solid material was washed with CH_2Cl_2 chloride (10 ml). The solvent was evaporated and the product was purified by column chromatography (silica gel, benzene), to afford the desired compound in 70–100% yield (Table 2).

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