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CHROMIUM(VI) BASED OXIDANTS—1

CHROMIUM PEROXIDE COMPLEXES AS VERSATILE, MILD, AND EFFICIENT OXIDANTS IN ORGANIC SYNTHESIS

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Abstract—The preparation of 2,2'-bipyridylchromium peroxide, pyridinechromium peroxide, and chromium peroxide etherate is described. 2,2'-Bipyridylchromium peroxide converts different classes of alcohols to the carbonyl compounds. In 1,2-diols C—C bond cleavage occurs extensively. α-Hydroxy acids are decarboxylated quantitatively. Oximes are converted to their carbonyl compounds and thiols to their disulfides, dihydroxy phenolic compounds to quinones, benzyl amine to benzaldehyde, aromatic amines to their azo compounds, anthracene and phenanthrene to their quinones. Pyridinechromium peroxide converts different classes of alcohols efficiently to the carbonyl compounds, thiols to their disulfides, anthracene to anthraquinone. Mandelic and benzilic acids are decarboxylated very efficiently. Chromium peroxide etherate is an efficient reagent for the oxidation of different classes of alcohols to their carbonyl compounds.

Oxidation of organic substrates in aprotic solvents, under mild, and neutral conditions is important in modern organic synthesis. Therefore, a search for new oxidizing reagents is of interest to synthetic organic chemists. For this purpose reagents have been developed in recent years with some success.[1] Among several Cr(VI) based oxidants which are reported in the literature none show the utility of chromium peroxide complexes as general oxidants in organic synthesis.[1-17]

In this paper we have investigated the possibility of using chromium peroxide etherate, pyridinechromium peroxide, and 2,2'-bipyridylchromium peroxide[18-22] in the oxidation of organic compounds.

Chromium peroxide was prepared easily and safely by the addition of concentrated hydrogen peroxide solution to a quite acidic solution of potassium dichromate at $-10°$ in the presence of ether. The deep-blue ethereal solution of chromium peroxide which was produced could be stored in a refrigerator for a few hours. The amount of available peroxide in the ethereal solution was determined by the quantitative precipitation with 2,2'-bipyridyl which produced blue crystals of 2,2'-bipyridylchromium peroxide. This complex is sparingly soluble in methylene chloride, chloroform, and benzene and can be stored at room temperature for months without observable change. This compound is decomposed at 153° without detonation and is quite stable towards hammer blows.

Pyridinechromium peroxide was prepared by the addition of pyridine to the ethereal solution of chromium peroxide. This complex is stable and could be stored, preferentially in a refrigerator, for weeks without observable change. Pyridinechromium peroxide is quite soluble in methylene chloride, chloroform, and benzene and decomposes at 102° without detonation and is also quite stable towards hammer blows.

Oxidation of different classes of organic compounds with 2,2'-bipyridylchromium peroxide was performed in refluxing benzene. Benzylic alcohols were converted to the corresponding carbonyl compounds in excellent yields (Table 1). Oxidation of cinnamyl alcohol and the other two allyl alcohols (entries 15 and 16, Table 1) to their carbonyl compounds proceeded well in high yields.

Primary and secondary alcohols were also oxidized with this reagent and they afforded carbonyl compounds in excellent yields (Table 1). Benzilic and mandelic acids were decarboxylated to benzaldehyde and benzophenone, respectively, in almost quantitative yields (Table 1). Oxidation of 1,2-diphenylethylene glycol and 1-phenylethylene glycol was accompanied both with the extensive C—C bond cleavage and the oxidation of OH groups. 1,2-Diphenylethylene glycol produced benzaldehyde as a major product, and benzoin, and benzil as by-products. 1-Phenylethylene glycol produced only benzaldehyde in excellent yield (Table 1). 1,3-Diphenyl-1,3-propane diol was effected with this reagent without C—C bond cleavage and the diketone was isolated in high yield (Table 1). Benzoin and furoin were converted to benzil and furil, respectively, in high yields (Table 1).

Oxidation of two sterols (entries 12 and 13, Table 1) with this reagent proceeded well and several carbonyl compounds[23] were isolated in reasonable yields (Table 1). Deoximation of different oximes with this reagent afforded the corresponding carbonyl compounds and several thiols were also converted to their corresponding disulfides in high yields (Table 1).

Hydroquinone, catechol, and 1,4-dihydroxy naphthalene were oxidized very easily to their quinones in almost quantitative yields (Table 1).

Benzylamine was converted to benzaldehyde quantitatively. *p*-Toluidine, aniline, and α-naphthylamine produced their azo compounds in poor yields plus unidentified red–orange materials (Table 1).

Anthracene and phenanthrene were converted to their corresponding quinones in good yields (Table 1).

Oxidation of different classes of organic substrates with pyridinechromium peroxide proceeded very well in methylene chloride at room temperature or in benzene under reflux conditions. Primary and secondary alcohols were quite reactive and produced their carbonyl compounds in high yields (Table 2). 1-Phenyl-1,3-butane diol produced 1-phenyl-1,3-butanedione in poor yield. 1,2-Diphenylethylene glycol

Table 1. Oxidation of different organic compounds with 2,2'-bipyridylchromium peroxide (BPCP)

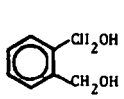
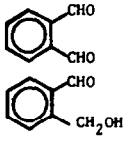
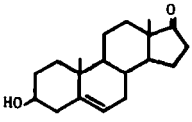
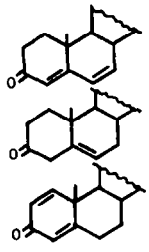
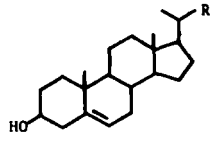
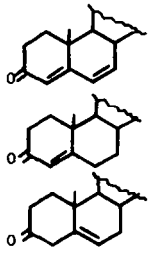
No.	Substrate	Product	(BPCP) Reaction time (h)	(BPCP) Oxidant / Reactant	Yield (%)
1	Benzyl alcohol	Benzaldehyde	1	2	95
2	Benzhydrol	Benzophenone	1	2	95
3	Ethylphenyl carbinol	Ethylphenyl ketone	0.8	2	95
4	Piperonol	Piperonal	1.25	2	100
5	*p*-Nitrobenzyl alcohol	*p*-Nitrobenzaldehyde	4	2	0
6	*p*-Ainsyl alcohol	*p*-Anisaldehyde	0.8	2	100
7			0.8	8	90 10
8	Citronellol	Citronellal	4	2	80
9	Cyclohexanol	Cyclohexanone	3	2	85
10	2-Octanol	2-Octanone	4	2	90
11	1-Heptanol	1-Heptanal	4	2	90
12			3	3	35–40 10 8
13			3	2	33 22 3
14	Cinnamyl alcohol	Cinnamaldehyde	1.25	2	100
15			4	2.5	60
16			2	2.5	80
17	Benzilic acid	Benzaldehyde	0.7	2	100
18	Mandelic acid	Benzophenone	0.3	2	100
19	1,2-Diphenyl glycol	Benzaldehyde Benzoin	0.8	2	90 10
20	1-Phenylethylene glycol	Benzaldehyde	1.25	2	95
21	1,3-Diphenyl-1,3-propanediol	1,3-Diphenyl-1,3-propanedione	1	2	75
22	Benzoin	Benzil	3	2	90
23	Furoin	Furil	2	2	90
24	Acetophenone oxime	Acetophenone	0.25	2	100
25	Benzaldoxime	Benzaldehyde	0.5	2	80
26	Benzylmethylketoxime	Benzylmethyl ketone	1	2	100
27	*p*-Chlorobenzaldoxime	*p*-Chlorobenzaldehyde	1	2	85
28	Salycilaldoxime	Salycilaldehyde	1	2	70
29	Cyclohexylthiol	Cyclohexyldisulfide	0.7	2	100
30	n-Butylthiol	n-Butyldisulfide	1	2	80

Table 1—*continued*

No.	Substrate	Product	(BPCP) Reaction time (h)	Oxidant / Reactant	Yield (%)
31	α-Toluenethiol	Benzyldisulfide	0.25	2	100
32	Hydroquinone	*p*-Benzoquinone	0.2	2	95
33	Catechol	*o*-Benzoquinone	0.5	2	100 (conversion yield not determined)
34	1,4-Dihydroxynaphthalene	1,4-Naphthoquinone	0.5	2	100
35	Benzylamine	Benzaldehyde	0.4	2	100
36	Aniline	Azobenzene	1.25	2	30
37	1-Naphthylamine	1,1'-Azonaphthalene	1	2	20
38	Anthracene	Anthraquinone	7	8	60
39	Phenanthrene	Phenanthroquinone	7	6	60

Table 2. Oxidation of different organic compounds with pyridinechromium peroxide (PCP)

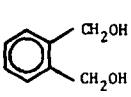
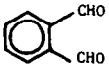
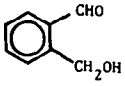
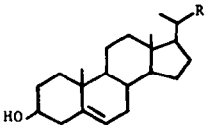
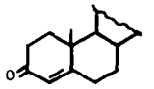
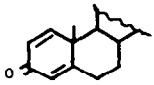
No.	Substrate	Product	(PCP) Reaction time (h)	Oxidant / Reactant	Yield (%)
1	Cyclohexanol	Cyclohexanone	1.5	2	95
2	2-Octanol	2-Octanone	1.25	2	90
3	1-Heptanol	1-Heptanal	1.25	2	99
4	Citronellol	Citronellal	1.25	2	99
5	1-Phenyl-1,3-butanediol	1-Phenyl-1,3-butanedione	4	4	15
6	Benzhydrol	Benzophenone	0.5	2	65
7	Piperonol	Piperonal	0.3	2	100
8	*p*-Nitrobenzyl alcohol	*p*-Nitrobenzaldehyde	0.2	2	100[a]
9	Benzyl alcohol	Benzaldehyde	0.5	2	100
10	*p*-Anisyl alcohol	*p*-Anisaldehyde	0.3	2	100
11			3	2	50
					trace
12	Cinnamyl alcohol	Cinnamaldehyde	2	2	90
13			1	2	80
14			0.6	2	90
15	n-Butylthiol	n-Butyldisulfide	0.1	2	80
16	α-Toluenethiol	Benzyldisulfide	0.02	2	100
17	Thiophenol	Phenyldisulfide	0.1	2	100
18	Acetophenone oxime	Acetophenone	1.25	2	70
19			5		17
					35–40

Table 2—*continued*

No.	Substrate	Product	(PCP) Reaction time (h)	(PCP) Oxidant / Reactant	(PCP) Yield (%)
20	Benzoin	Benzil	0.1	2	100[a]
21	Furoin	Furil	0.2	2	50[a]
22	Mandelic acid	Benzophenone	0.25	2	100
23	Benzilic acid	Benzaldehyde	0.3	2	100
24	*p*-Toluidine	4,4'-Dimethylazobenzene	0.5	2	20
25	Anthracene	Anthraquinone	5	4	50
26	Benzylamine	Benzaldehyde	2.5	2	30
		Benzaldehyde			50
27	1,2-Diphenylethylene glycol	Benzoin	1.5	2	15–20

[a] Reactions were conducted in refluxing benzene.

produced benzaldehyde and a trace amount of benzil (Table 2). Oxidation of benzylic alcohols proceeded very well and their carbonyl compounds were produced in high yields. *p*-Nitrobenzaldehyde which was quite resistant towards oxidation with 2,2'-bipyridylchromium peroxide, with this reagent produced *p*-nitrobenzaldehyde quantitatively. Allylic alcohols produced their carbonyl compounds in high yields (Table 2). Oximes under investigation afforded their carbonyl compounds in 0–70% yields (Table 2). Cholesterol produced several products in reasonable yields (entry 19, Table 2). Oxidation of benzoin to benzil performed well in refluxing benzene but furoin was resistant and furil was produced in poor yield (Table 2). Decarboxylation of mandelic and benzilic acids afforded benzophenone and benzaldehyde in quantitative yields, respectively (Table 2). *p*-Toluidine produced the azo compound in poor yield, plus an unidentified orange–red compound. Anthracene afforded anthraquinone in fair yield (Table 2). Thiols dissolved in methylene chloride were oxidized with this reagent to afford their disulfides in excellent yields.

Violent explosion accompanied with firing was observed when pure liquids of α-toluenethiol and thiophenol were mixed with solid pyridinechromium peroxide.

At room temperature chromium peroxide etherate is liquid and unstable and should be prepared freshly for a

Table 3. Oxidation of some classes of organic compounds with chromium peroxide etherate (CPE)

No.	Substrate	Product	(CPE) Reaction time (h)	(CPE) Oxidant / Reactant	(CPE) Yield (%)
1	Benzhydrol	Benzophenone	0.7	2	90
2	Benzyl alcohol	Benzaldehyde	1	2	85
3	Benzylphenyl carbinol	Benzylphenyl ketone	1.25	2	75–80
4	Cyclohexanol	Cyclohexanone	1	2	85
5	1-Heptanol	1-Heptanal	1	2	80
		Cinnamaldehyde			30
6	Cinnamyl alcohol		1.5	2	+ unreacted material
		Benzaldehyde			15
7	2-Mercaptobenzothiazol	2-Mercaptobenzothiazolyl-disulfide	1	2	30
8	α-Toluenethiol	Benzyldisulfide	1	2	20
9	Acetophenone oxime	Acetophenone	1	2	20
10	Benzilic acid	Benzaldehyde	0.5	2	90
11			1	2	80–85
12			1	2	45–50

Table 4. Comparison of 2,2'-bipyCrO$_5$ (BPCP) and pyCrO$_5$ (PCP) with Py$_2$CrO$_3$ (DPCO) in the oxidation of organic compounds

No.	Substrate	Product	(BPCP) Reaction time (h)	(BPCP) Yield (%)	(PCP) Reaction time (h)	(PCP) Yield (%)	(DPCO) Reaction time (h)	(DPCO) Yield (%)
1	2-Octanol	2-Octanone	4	90	1.25	90	0.2	97[3]
2	Cyclohexanol	Cyclohexanone	3	85	1.5	95	0.2	98[3]
3	1-Heptanol	1-Heptanone	4	90	1.25	99	0.2	93[3]
4	Benzhydrol	Benzophenone	1	95	0.5	65	0.2	96[3]
5	Benzyl alcohol	Benzaldehyde	1	95	0.5	100	0.2	95[3]
6	4-Nitrobenzyl alcohol	4-Nitrobenz-aldehyde	4	0	0.2	100	0.2	97[3]
7	Cinnamyl alcohol	Cinnamaldehyde	1.25	100	2	90	15–22	81[25]
8	*p*-Anisyl alcohol	*p*-Anisaldehyde	0.8	100	0.3	100	15–22	76[25]
9	Piperonol	Piperonal	1.25	100	0.3	100	15–22	85[25]
10	Citronellol	Citronellal	4	80	1.25	99	15–22	25[25]

successful oxidation. This reagent was useful for the oxidation of primary, secondary, allylic, and benzylic alcohols to their carbonyl compounds. The decarboxylation of benzylic and mandelic acids also proceeded well in high yields (Table 3).

The cheap and commercially available dipyridinechromium(VI) oxide[3] has several disadvantages:[5]

(1) it must be used in large excess (molar ratio five or six),
(2) it is unstable,
(3) it is highly hygroscopic,
(4) it is prepared by a dangerous procedure and can ignite spontaneously,
(5) it shows poor selectivity in the oxidation of primary alcohols to aldehydes.[5]

Pyridinium chlorochromate[6] another widely used oxidant and commercially available reagent also presents a number of difficulties:[5]

(1) its acidity is not suitable for the acid sensitive compounds and consequently buffering of the reaction mixture is essential,
(2) it is hygroscopic,
(3) in the oxidation of some classes of organic compounds either a long reaction time[14] is required or it will not be effective at all,[24]
(4) photochemically it is not so stable.[5]

According to our findings, 2,2'-bipyridylchromium peroxide and pyridinechromium peroxide are versatile oxidants in organic synthesis due to the following:

(1) reaction time is reasonable,
(2) usually high yields are obtained,

Table 5. Comparison of 2,2'-bipyCrO$_5$ (BPCP) and pyCrO$_5$ (PCP) with pyCrO$_3$·HCl (PCC) in the oxidation of organic compounds

No.	Substrate	Product	(BPCP) Reaction time (h)	(BPCP) Yield (%)	(PCP) Reaction time (h)	(PCP) Yield (%)	(PCC) Reaction time (h)	(PCC) Yield (%)
1	1-Heptanol	1-Heptanal	4	90	1.25	90–100	1–2	78(PCC)[6]
2	Benzhydrol	Benzophenone	1	95	0.5	85	1–2	100(PCC)[6]
3	Citronellol	Citronellal	0.5	80	1.25	98	1–2	82(PCC)[6]
4	Piperonol	Piperonal	1.25	100	0.3	100	1.23	90(PCC)[26]
5	Benzyl alcohol	Benzaldehyde	1	95	0.5	100	0.5	100(PCC)[26]
6	*p*-Nitrobenzyl alcohol	*p*-Nitrobenzaldehyde	4	0	0.2	100	1	80(PCC)[26]
7	Cinnamyl alcohol	Cinnamaldehyde	1.25	100	2	90		10(PCC)[26]
8	Acetophenone oxime	Acetophenone	0.25	100	1.2	70	15	61(PCC)[14]
9	Benzaldoxime	Benzaldehyde	0.5	80	—	—	15	56(PCC)[14]
10	α-Toluenethiol	Benzyldisulfide	0.25	100	0.02	100	0.025	75(PCC)[24]†
11	n-Butylthiol	n-Butyldisulfide	1	75–80	0.1	80	2	0(PCC)[24]
12			2	80	1	80	3	80(PCC)[27]

† Reagent did not survive more than the time indicated.

(3) over-oxidation of the products is not observed,
(4) they are not hygroscopic,
(5) reaction medium is neutral which is suitable for the oxidation of acid labile compounds,
(6) usually the molar ratio of oxidant to reactant does not exceed 2 per functional group,
(7) work up is easy and rapid,
(8) the preparation of the reagents is neither difficult nor dangerous.

For comparison, some of the results obtained from the oxidation of organic compounds with 2,2'-bipyridylchromium peroxide and pyridinechromium peroxide, and some of those obtained from dipyridinechromium(VI) oxide, and pyridinium chlorochromate are tabulated in Tables 4 and 5.

EXPERIMENTAL

Products were isolated by different chromatography techniques (column, PLC and GLC). Products were characterized by comparison with authentic samples (IR, UV spectra, thin layer, gas chromatography and m.p.). Reactions were conducted in diethyl ether, CH_2Cl_2 and benzene.

Chromium peroxide etherate (CPE).[18–20] Conc H_2SO_4 (0.6 ml), and diethyl ether (100 ml) were added to a soln of potassium dichromate (2.94 g) in distilled water (50 ml), at $-10°$. To the resulting mixture, conc H_2O_2 (6 ml) was added with vigorous stirring to produce a deep-blue soln of chromium peroxide, which was extracted into the ethereal phase. The ethereal phase was dried on Na_2SO_4 and filtered. The resulting filtrate was concentrated and stored in a refrigerator. The amount of chromium peroxide in the ethereal soln (48–57% yield) was determined by quantitative precipitation with 2,2'-bipyridyl.

Bipyridylchromium peroxide (BPCP).[18,20,22] To the same deep-blue ethereal soln obtained from the previous experiment, 2,2'-bipyridyl (3.12 g) in diethyl ether (20 ml) was added, which resulted in immediate precipitation. The blue ppts were filtered and washed several times with diethyl ether and were dried at room temp. 3–4.2 g, 48–57% yield, m.p. 153° (dec).

Pyridinechromium peroxide (PCP).[18,20,21] To the same ethereal soln of the deep-blue chromium peroxide which was used in the previous experiment, a soln of pyridine (2.0 g) in diethyl ether (3 ml) was added. The mixture was cooled to 0° and after 5 hr the deep-blue crystals were filtered under N_2 and stored in a cold place. 1.4–1.8 g, 33–43% yield, m.p. 102° (dec).

General procedure for the conversion of hydroxy compounds to their carbonyl compounds with (BPCP). To the soln of the hydroxy compound (0.001 mol) in dry benzene (20 ml), the oxidant (0.008 mol) was added and then the mixture was refluxed with stirring for 0.2–4 hr. The colour change was observed from deep blue to dark green, while reaction proceeded. The mixture was filtered and the filter cake was washed several times with benzene. The resulting mixture was evaporated and chromatographed on a silica gel column and eluted with benzene. The oxidized compound was obtained in 0–100% yield and was identified by comparison with authentic samples. GLC analysis of the liquid products thus obtained indicated a purity of greater than 99% (Table 1).

General procedure for the oxidation of sterols with (BPCP). A soln of the sterol (0.001 mol) and the oxidant (0.002 mol) in dry benzene (30 ml) was stirred under reflux conditions for 3 hr. The mixture was worked up according to the previous experiment. Separation and purification of the product obtained was achieved by silica gel (PLC) and developed in the mixture of n-hexane and MeOH. Products were identified by the comparison of their UV and IR spectra with authentic samples (Table 1).

General procedure for the conversion of oximes to their aldehydes and ketones with (BPCP). In a round-bottomed flask (20 ml), the oxime (0.001 mol) was dissolved in dry benzene (10 ml) and an oxidizing agent (0.002 mol) was added while the mixture was being stirred for 0.3–1 hr under reflux conditions. The mixture was worked up as previous experiments and chromatographed on a silica gel column using benzene as eluent. Evaporation of the solvent afforded the oxidized product in 70–100% yield. The products were identified by comparison with authentic samples. GLC analysis of the liquid products showed greater than 95% purity.

General procedure for the conversion of thiols to their disulfides with (BPCP). To a soln of thiol (0.001 mol) in dry benzene (10 ml), the oxidant (0.002 mol) was added and the mixture was refluxed with stirring for 0.25–1 hr. The mixture was filtered and the filtrate evaporated. Purification of the resulting mixture proceeded by column chromatography on silica gel and elution with benzene to afford pure disulfide (80–100% yield, Table 1).

Oxidation of anthracene and phenanthrene to their quinones with (BPCP). A mixture of the hydrocarbon (0.001 mol) and the oxidant (0.006–0.008 mol) in dry benzene (20 ml) was refluxed for 7 hr. The mixture was filtered and the filtrate evaporated. The resulting mixture was chromatographed on silica gel and eluted with benzene–MeOH to afford the oxidized product in 60% yield (Table 1).

General procedure for the oxidation of hydroxy compounds with (PCP). To a soln of hydroxy compound (0.001 mol) in CH_2Cl_2 (20 ml), the oxidant (0.002 mol) was added and the mixture was stirred for 0.3–4 hr. The colour change of the mixture was observed from deep-blue to brown, while the reaction proceeded. To the resulting mixture, diethyl ether (10 ml) was added and filtered. The resulting mixture was evaporated and the residue was chromatographed on a silica gel column and eluted with non-polar solvents to afford the oxidized compound in 15–100% yield (Table 2). GLC analysis of the liquid products thus obtained showed them to be greater than 99% pure.

Oxidation of cholesterol with (PCP). To the soln of oxidant (0.002 mol) in CH_2Cl_2 (20 ml), cholesterol (0.001 mol) was added and the mixture was stirred for 5 hr at room temp. Filtration of the mixture and evaporation of the solvent afforded a brown residue. Purification of this residue proceeded by PLC (silica gel) and developed by benzene and MeOH mixture afforded carbonyl compounds in reasonable yields (Table 2). Products were identified by comparison of their UV and IR spectra with authentic samples.

Oxidation of anthracene with (PCP). To a soln of anthracene (0.001 mol) in CH_2Cl_2 (20 ml) the oxidant (0.004 mol) was added and the mixture was stirred at room temp for 5 hr. Filtration of the mixture followed by column chromatography on a silica gel column and elution with a benzene–MeOH mixture afforded anthraquinone in 50% yield (Table 2).

General procedure for the oxidation of hydroxy compounds with (CPE). To the ethereal soln of chromium peroxide (0.002 mol), the hydroxy compound (0.001 mol) was added and then the mixture was stirred under reflux conditions for 0.7–1.25 hr. The mixture was evaporated and the resulting mixture was purified by column chromatography on a silica gel column and eluted with benzene to afford the oxidized compound in 75–90% yield (Table 3). GLC analysis of the liquid products thus obtained showed them to be greater than 99% pure.

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