

OXIDATION OF ALCOHOLS TO CARBONYL COMPOUNDS  
WITH CHROMIUM(V) REAGENTS

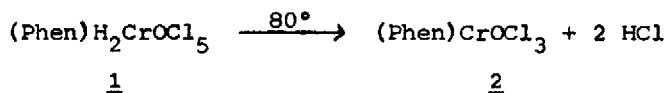
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Abstract: Two pentavalent chromium complexes have been used effectively for the oxidation of alcohols to carbonyl compounds.

Oxidation of primary and secondary alcohols to carbonyl compounds are usually carried out with chromium(VI) reagents.<sup>1-6</sup> Chromium(V) is postulated as an intermediate in all the oxidations with chromium(VI). Only a few pentavalent chromium complexes have been reported and all are moisture sensitive<sup>7-12</sup> and as such no chromium(V) reagent has been studied systematically for the oxidation of alcohols to carbonyl compounds.

We report, herein, two stable complexes of oxochromium(V),<sup>13</sup> (phen)H<sub>2</sub>-CrOCl<sub>5</sub> 1 and (phen)CrOCl<sub>3</sub> 2 (phen = 1,10-phenanthroline) which we have conveniently used for the oxidation of some primary, and secondary alcohols and diols.

The complex, (phen)H<sub>2</sub>CrOCl<sub>5</sub> 1 was obtained as brown crystals, stable in dry air from the reaction of chromium trioxide with 1,10-phenanthrolinehydrochloride in concentrated HCl at 0° and the complex (phen)CrOCl<sub>3</sub> 2 by dehydrochlorination of complex 1 in dry CO<sub>2</sub> or N<sub>2</sub> at 80° as reported earlier.<sup>13</sup>

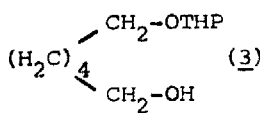
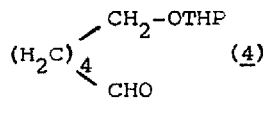
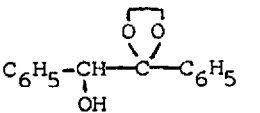
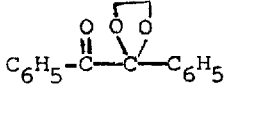


The pentavalent chromium complex 1 is comparable to pyridinium chlorochromate<sup>3</sup> in its oxidising power and the yield of aldehydes and ketones with two molar equivalents of the reagent is usually high. In contrast to the slightly acidic nature of the complex 1, the dehydrochlorinated complex 2 is essentially neutral. Oxidation with pentavalent chromium complex 2 is rela-

tively slower but the yields are still high and even acid labile groups such as ethylene ketals and tetrahydropyranyl ethers survive the reaction conditions. On the basis of these results obtained thus far, these two pentavalent chromium reagents obviously qualify as important additions to the present methodology.

In a typical small scale experiment complex 1 or complex 2 (2 mmol) was rapidly added to the solution of the alcohol (1 mmol) in 2-3 ml of  $\text{CH}_2\text{Cl}_2$  at room temperature under inert atmosphere. The reaction followed by thin layer chromatography was generally complete in 0.5-3 hr. in the case of complex 1 (5-10 hr. in the case of complex 2). The reaction mixture was then diluted with dry ether (10 ml) and filtered through celite and the solvent was evaporated to isolate the product. Oxidation of 1,4-butane diol with 5 equivalents of the complex 1 led to the formation of  $\gamma$ -butyrolactone in 95% yield. The results of these oxidations are summarised in the TABLE.

TABLE<sup>a</sup>

Alcohol	Molar ratio	Time (hr)	Product <sup>b</sup>	% Yield <sup>c</sup>
<u>I. Oxidations with Complex (Phen)<math>\text{H}_2\text{CrOCl}_5</math> <u>1</u></u>				
Benzyl alcohol	1:2	2	Benzaldehyde	92
Cyclohexanol	1:2	2	Cyclohexanone	94
Benzoin	1:2	2	Benzil	92
Cinnamyl alcohol	1:2	0.5	Cinnamaldehyde	96
Benzhydrol	1:2	1.5	Benzophenone	96
1,4-Butane diol	1:5	8	$\gamma$ -Butyrolactone	95
<u>II. Oxidations with Complex (Phen)<math>\text{CrOCl}_3</math> <u>2</u></u>				
 (3)	1:2	7	 (4)	85
	1:2.5	12		55 <sup>d</sup>
Cinnamyl alcohol	1:2	6	Cinnamaldehyde	96
Benzoin	1:2	9	Benzil	95

<sup>a</sup>Oxidations were carried out at room temperature (25°) in  $\text{CH}_2\text{Cl}_2$ ;

<sup>b</sup>Products were characterised by comparison with authentic material (NMR and IR

spectra, TLC and m.p.);

<sup>c</sup>All yields refer to isolated yields;

<sup>d</sup>Yield based on recovered starting material.

The following experimental procedure was used for the preparation of reagents 1 and 2.<sup>13</sup>

(Phen)H<sub>2</sub>CrOCl<sub>5</sub> 1. A solution of 1,10-phenanthroline (5.4 g; 30 mmol) in conc. HCl (25 ml) kept at 0°C was added to a solution of chromium trioxide (3.0 g; 30 mmol) in conc. HCl (25 ml) and the mixture was stirred for 15 min. at 0°. The resulting dark brown precipitate was filtered through a sintered glass funnel and washed twice with 10 ml portions of cold conc. HCl and dried under vacuum. The dark brown free flowing powder (12 g; 90%) can be stored under vacuum.

(Phen)CrOCl<sub>3</sub> 2. Complex 1 (4.4 g, 10 mmol) was heated under a current of dry N<sub>2</sub> or CO<sub>2</sub> at 80° for two hours. The colour changed from darkbrown to brownish black. The resulting complex 2 (3.7 g) was stored under vacuum.

#### Oxidation of Benzoin to Benzil with Complex 1

In a 25 ml round bottomed flask was taken benzoin (0.212 g, 1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 ml) and to the stirred solution under N<sub>2</sub> atmosphere was added the complex 1 (0.887 g, 2 mmol) at room temperature (25°C). After stirring for 2 hr, dry ether (15 ml) was added to the reaction mixture and passed through a short pad of celite and washed twice with 10 ml portions of dry ether. Combined ether extract was evaporated and benzil (0.193 g, 92%) was obtained as a crystalline material, m.p. 93-94°; ir and nmr spectra identical with authentic material.

#### Oxidation of Alcohol 3 Containing THP Ether with Complex 2

To a solution of the alcohol 3 (0.101 g, 0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 ml) kept under N<sub>2</sub> atmosphere was added rapidly the complex 2 (0.444 g, 1 mmol) at room temperature and stirred for 7 hr. Dry ether (15 ml) was then added to the dark reaction mixture and worked up as above to yield 0.096 g of crude material. Column chromatography on silica gel gave the aldehyde 4 as an oil (0.085 g, 85%); ir, nmr and tlc identical with the authentic sample.

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