

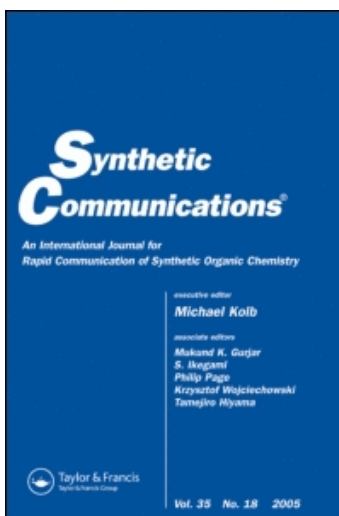
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**FACILE OXIDATION OF ALDEHYDES TO CARBOXYLIC ACIDS
WITH CHROMIUM(V) REAGENTS**

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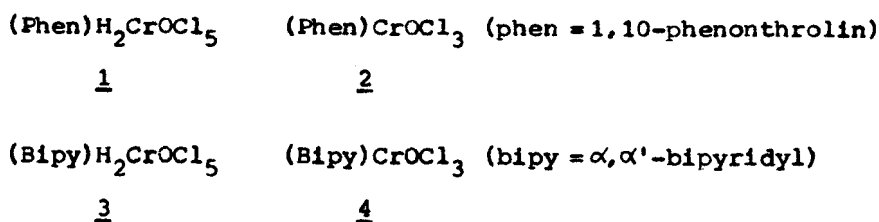
Recently we reported a convenient method of oxidation of alcohols to carbonyl compounds using chromium(V) reagents.¹ Although a variety of reagents are available for effecting this transformation, there are only a few reagents which have been successfully used for the oxidation of aldehydes to carboxylic acids. Chromic acid, silver oxide and potassium permanganate are commonly employed for this purpose and reactions are performed in protic media under conditions which are not that mild.² The "non-aqueous" chromium(VI) reagent, pyridinium dichromate, recently reported by Corey³ oxidises alcohols and aldehydes to carboxylic acids in DMF at room temperature. Although Cr(V) species is postulated as an intermediate in all oxidations with Cr(VI), no systematic oxidation studies have been reported with

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these reagents. This note reports the results of some fruitful investigations on aldehyde \rightarrow carboxylic acid conversion involving some "non-aqueous" chromium(V) complexes 1, 2, 3 and 4 under anhydrous conditions.

As reported previously, oxidation of primary alcohols with two equivalents of either 1 or 2 gave the aldehydes in good yield, with very little overoxidation, if any.¹ On the other hand when excess reagent was used and reaction mixture stirred for longer period, partial oxidation to carboxylic acids took place. This prompted us to study the oxidation of aldehydes with these reagents.

Although direct oxidation of primary alcohols to carboxylic acids with excess Cr(V) reagent 1 was not very clean, it has now been found that a variety of aldehydes can be oxidised conveniently to carboxylic acids in very good yields with our "non-aqueous" chromium(V) complexes 1 and 2. Herein, we also report the behaviour of yet another set of closely related chromium(V) reagents 3 and 4 which are similar in their reactivity to complexes 1 and 2 respectively, but are more economical for large scale reactions.⁴ Complex 3 is prepared essentially in the same manner as reported for complex 1.¹ Dehydrochlorination of 3 around 80° under a current of dry N₂ yields complex 4.⁴



The oxidation of aldehydes with any of these Cr(V) complexes takes place very readily at room temperature in CH_2Cl_2 under anhydrous conditions. Oxidation of aliphatic aldehydes in general are more facile than aromatic aldehydes. Aromatic aldehyde like *p*-nitrobenzaldehyde containing electron withdrawing group reacts with ease to give *p*-nitrobenzoic acid in 96% yield.

In a typical small scale experiment complex 1 or 3 (2 mmol) was rapidly added to a solution of the aldehyde (1 mmol) in 2-3 ml of CH_2Cl_2 with stirring at room temperature under inert atmosphere. The reaction followed by thin layer chromatography was generally complete in 0.5 hr. The reaction mixture was then diluted with CH_2Cl_2 or CHCl_3 (10 ml) and filtered through a small pad of celite and silica gel and washed two or three times with 10 ml portions of CHCl_3 . The combined organic layer was then evaporated to isolate the product. The results of these oxidations are summarized in the TABLE.

TABLE^a

Aldehyde	Molar ratio	Time (hr)	Product ^b	% Yield ^c
<u>I. Oxidations with the complex (bipy)H₂CrOCl₅, <u>3</u></u>				
n-Butyraldehyde	1:2	0.5	n-Butyric acid	92
n-Heptaldehyde	1:2	0.5	n-Heptanoic acid	85
Crotonaldehyde	1:2	0.25	Crotonic acid	90
2-Furaldehyde	1:2	0.5	2-Furoic acid	85
p-Tolualdehyde	1:2	3.0	p-Toluic acid ^d	80
9-Anthraldehyde	1:3	12.0	Anthracene-9-carboxylic acid	95
p-Nitrobenzaldehyde	1:2	0.5	p-Nitrobenzoic acid	96
<u>II. Oxidations with the complex (phen)H₂CrOCl₅, <u>1</u></u>				
n-Butyraldehyde	1:2	0.5	n-Butyric acid	90
2-Furaldehyde	1:2	0.5	2-Furoic acid	85
p-Tolualdehyde	1:2	3.0	p-toluic acid ^d	80
<u>III. Oxidation with the complex (bipy)CrOCl₅, <u>4</u></u>				
p-Nitrobenzaldehyde	1:2	3.0	p-Nitrobenzoic acid	96

- Oxidations were carried out at room temperature 28-30° in CH₂Cl₂.
- Products were characterized by comparison with authentic samples (spectra, TLC and m.p.).
- All yields refer to isolated products.
- Trace amount of starting material remains unreacted even after 4-5 hr.

From the data presented in the table, it is evident that the chromium(V) complexes we have reported are important additions to the present methodology of aldehyde \rightarrow carboxylic acid transformation under mild and anhydrous conditions.

Preparation of complex $(bipy)_2CrOCl_5$, 3⁴

A solution of α, α' -bipyridyl (4.68 g, 30 mmol) in conc. HCl (25 ml) kept at 0° was added to a solution of CrO_3 (3.0 g, 30 mmol) in conc. HCl (25 ml) and the mixture was stirred for 15 min. at 0°. The resulting brown precipitate was filtered through a sintered glass funnel and washed twice with 10 ml portions of cold (0°) conc. HCl and dried under vacuum. The dark brown free flowing powder (11.0 g, 92%) can be stored under vacuum for a few days.

Oxidation of p-nitrobenzaldehyde to p-nitrobenzoic acid with complex 3

In a 25 ml round bottomed flask was taken p-nitrobenzaldehyde (0.151 g, 1 mmol) in CH_2Cl_2 (5 ml) and to the magnetically stirred solution at room temperature (28°C) under N_2 atmosphere was added to the complex 3 (0.803 g, 2 mmol). After stirring for 0.5 hr, chloroform (15 ml) was added to the reaction mixture and passed through a short pad of celite and silica gel and washed 2-3 times with 10 ml portions of chloroform. Combined organic filtrate was evaporated to get p-nitro-

benzoic acid as a crystalline solid (0.160 g, 96%),
m.p. 240°.

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