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OXIDATION OF ALCOHOLS BY HETEROCYCLIC COMPLEXES OF OXODIPEROXYCHROMIUM(VI), CrO_5

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Although many chromium (VI) compounds have been used as organic reagents,[1] there have been few studies on the reaction of complexes of CrO_5 with organic compounds.[2] Pyridine oxodiperoxychromium(VI), $C_5H_5N:CrO_5$, is a deep blue solid, readily soluble in organic solvents[3]. The dry complex is spontaneously explosive;[4] however, the damp complex is safe to handle and its preparation has been used as an undergraduate experiment.[5]

A solution of the pyridine complex was prepared as follows: pyridine (9 ml) was added to a solution of chromium trioxide (4 g) dissolved in ice-water (70 ml). Hydrogen peroxide (100 vol, 4 ml) in water (16 ml) was then added to the reaction mixture; a dark blue precipitate formed immediately, was collected by filtration, washed with water (100 ml) and, while still damp, was dissolved in dichloromethane (90 ml). The dichloromethane solution was washed with saturated aqueous sodium carbonate and water, and then dried (anhydrous sodium sulphate). The yield of pyridine oxodiperoxychromium(VI), estimated by the absorbance of the solution at 580 nm (ε 740[6]), was 2.2 g (24% based on chromium trioxide).

A series of alcohols (10 mmole) was oxidised to the corresponding carbonyl compounds by the pyridine complex (approx. 11 mmole); the results of the experiments are summarised in the table. The experimental procedure is illustrated for the preparation of 4-nitrobenzaldehyde. 4-Nitrobenzyl alcohol (3.8 g, 25 mmole) in dichloromethane was added to a solution of pyridine oxodiperoxychromium(VI) (6.6 g, 30 mmole) in dichloromethane (200 ml) and the complex allowed to decompose at room temperature (5 hours). Diethyl ether (750 ml) was added to the reaction mixture which was left for 1 hour, to allow the chromium complexes to separate, and then filtered. The filtrate was concentrated (to 250 ml) and washed with dilute hydrochloric acid, sodium carbonate and water. Removal of the solvent gave p-nitrobenzaldehyde (3.4 g, 90%), m.p. 103-4°, identical to an authentic sample.

The oxidation was followed by t.l.c.; the carbonyl compounds start to form before any oxygen is evolved. Although decomposition of the complex gives a molar equivalent of oxygen in the absence of an alcohol, decomposition of the peroxy compound in the presence of an alcohol yields approximately 0.5 mole of oxygen per mole of complex. If the complex is allowed to decompose completely and the alcohol is added subsequently, only low yields of the carbonyl compounds are obtained. These experiments suggest that the peroxy complex acts as the oxidising agent, rather than a chromium trioxide derivative produced by its initial decomposition. The oxidation takes place under mildly basic conditions and only a slight (1.1) molar excess of the reagent is generally sufficient to effect complete conversion of the alcohol to the carbonyl compound. The aldehydes produced are not significantly oxidised further by the complex; 4-nitrobenzaldehyde was recovered in over 90% yield after treatment with an equimolar amount of the complex. Also attempted oxidation of cinnamaldehyde with the pyridine complex produced only traces of benzaldehyde; benzaldehyde produced in the oxidation of cinnamyl alcohol arises from direct oxidation of the alcohol.

Table

Alcohol	Product	Yield %
4-nitrobenzyl alcohol	4-nitrobenzaldehyde	90
2-nitrobenzyl alcohol	2-nitrobenzaldehyde	69
3,4-dimethoxybenzyl alcohol	3,4-dimethoxybenzaldehyde	80
3-hydroxybenzyl alcohol	3-hydroxybenzaldehyde	20
4-N,N-dimethylaminobenzyl alcohol	4-N,N-dimethylaminobenzaldehyde	22
cinnamyl alcohol	cinnamaldehyde benzaldehyde	80[a,b] 20[a,b]
cyclohexen-3-ol	cyclohex-2-enone	55[a]
4-t-butylcyclohexanol	4-t-butylcyclohexanone	80
borneol	camphor	69
testosterone	androsten-3,17-dione	93
nonan-1-ol	nonanal	64[a]

The total volume of the reaction mixture in each case was approx. 100 ml. Except where otherwise stated, the % yield refers to isolated pure compound. [a] Yield determined by g.l.c. using an internal standard; [b] Yield based on unrecovered starting material.

1,10-Phenanthroline oxodiperoxychromium(VI)[6] is thermally stable relative to the pyridine complex, is much less readily soluble in organic solvents, and a 3-fold excess of the reagent is required to effect complete oxidation of an alcohol; its use required higher temperatures and longer reaction times. The oxidation of alcohols by the complexes may involve intermediate formation of a complex between the alcohol and CrO_5; co-ordination of the alcohol to chromium would be more difficult in competition with the bidentate phenanthroline ligand than in competition with pyridine and this would explain the difference in the properties of the complexes. Pyridine peroxychromium(VI) is a cheap and convenient reagent and usefully extends the range of chromium compounds available for the oxidation of organic compounds;[1] the procedure compares favourably with that of the Collins oxidation[7,8] since it avoids using a large molar excess of the oxidising reagent and the volume of solvent is relatively small.

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