



# CHEMICAL CHARACTERIZATION OF SOME ORGANIC COMPOUNDS USING UNUSUAL OXIDANT OF OXIDATION PRODUCT

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## Abstract

The use of di-isopropyl chromate as an oxidant is discouraged on the ground that the reaction takes a long time for completion and it is very difficult to isolate and analyse the reaction products.

Di-tertiary alkyl chromates such as di-tertiary butyl chromate (abbreviated as TBC) and di-tertiary amyl chromate (abbreviated as TAC) have been used extensively as oxidants in organic chemistry.

## Introduction

A few of the many oxidants which are commonly used in organic chemistry are : potassium permanganate, potassium dichromate, nitric acid, chromic oxide, osmium tetroxide, hydrogen peroxide, selenium dioxide, ozone, etc. However, search for efficient and uncommon oxidants to be used in neutral medium has been an interesting field for the organic chemists. With this aim in view, different researchers have widely studied some Cr (VI) based oxidants such as chromium peroxide etherate, pyridine chromium peroxide, 2, 2'- bipyridyl chromium peroxide<sup>1</sup>, di- isopropyl chromate di-tertiary alkyl chromate etc. These oxidants find use in the oxidation of various classes of organic compounds, and their merits and demerits have been extensively studied.

Among the peroxy compounds of Cr (VI), only 2,2'- bipyridyl chromium peroxide and

pyridine chromium peroxide were reported to be successful oxidants. However, they have some limitations as given below:- They cause explosion during reaction if not handled carefully,

i) they are not very much stable at room temperature.

Firouzabadi et al<sup>1</sup>, used the commercially available oxidant such as dipyridine chromium (VI) oxide and pyridine chlorochromate for the oxidation of different classes of organic compounds and found them unsuitable.

As reported by J. C, Collins<sup>2</sup> et al, the disadvantages with dipyridine chromium (VI) oxide<sup>3</sup> are:-

- i) It should be used in large excess,
- ii) It is also unstable and highly hygroscopic,
- iii) It shows poor selectivity in the oxidation of primary alcohol to aldehyde,
- iv) It is not prepared by convenient method and it can ignite spontaneously.

Pyridine chlorochromate<sup>4</sup> is another widely used and commercially available oxidant but it poses the following difficulties:-

- i) It is not suitable for the acid-sensitive compounds,
- ii) It is hygroscopic,
- iii) It takes a long reaction time<sup>5</sup>. In some cases, it is not effective at all<sup>6</sup>.

## Experimental

R. V. Oppenauer and H. Obberaich<sup>9</sup> used the following method for the preparation of TBC. CrO<sub>3</sub> was added to an excess of TBA (tertiary butyl alcohol) and the mixture cooled whereby reddish yellow crystals (m.p 7-8°C) separated out. This was dissolved in non-polar organic solvent and dehydrated with anhydrous Na<sub>2</sub>SO<sub>4</sub>. This reagent does not attack double bonds or -OH group.

i) **Albert Leo and F. H. Westheimer**<sup>10</sup> prepared TBC by dissolving 1 g of CrO<sub>3</sub> in 1.5 g of TBA containing 50 ml of purified ligroin. The solution was decanted into anhydrous calcium chloride, filtered and cooled in dry ice.

ii) **J.K. Noryonberski**<sup>11</sup> used the following procedure for the preparation of TBC. 5 g of CrO<sub>3</sub> was added gradually in small instalments to a well-mixed and cooled solution mixture consisting of 10 ml of TBA and 10 ml of carbon tetrachloride. The mixture was

diluted with 65 ml of carbon tetrachloride and filtered through a layer of anhydrous  $\text{Na}_2\text{SO}_4$  to give the oxidant.

iii) **Tamon Matsuura and Kajo Fugita**<sup>12</sup> prepared TBC as given below : 73.5 g of  $\text{CrO}_3$  was added to 110 g of TBA and the mixture cooled whereby reddish yellow crystals separated out. This was dissolved in 200 ml of benzene and dehydrated with anhydrous  $\text{Na}_2\text{SO}_4$ . Acetic anhydride was then added to the solution to give TBC.

### **Di-tertiary butyl chromate as an oxidant**

Di-tertiary butyl chromate (TBC) has been shown to be highly useful and suitable oxidant. Oxidation of olefins and alcohols by TBC was first reported by Oppenauer and Obberauch. The Oppenauer reaction which employs TBC as an oxidant resembles the internal redox reaction as both are accelerated by pyridine.

The oxidant, di-tertiary butyl chromate prepared by Oppenauer and Obbersuch was found to oxidize primary alcohols to aldehydes almost quantitatively. If excess of TBA is removed from the reagent by concentration in vacuo, a stronger oxidant results. If a carboxylic acid anhydride is added to the TBC solution, a more powerful oxidant is formed. This oxidant oxidizes primary alcohol with almost explosive rapidity. It also exoduses methylene group ( $-\text{CH}_2-$ ) activated by a vicinal double bond to a carbonyl group.

## **Result and Discussion**

### **Oxidation by TBC**

In normal practices the oxidation procedure involves stirring the mixture of the substrate and TBC in presence of a suitable solvent at room temperature or  $40^\circ\text{C}$ - $50^\circ\text{C}$ . Sometimes refluxing of the reaction mixture becomes essential. The reaction time depends on the nature of the substrate and the concentration of the oxidant.

Methods have also been devised to decompose the excess of oxidant left after the completion of reaction. In some cases the excess of oxidant is decomposed with oxalic acid at  $0^\circ\text{C}$ . A mixture of sulphuric acid and hydrazine has also been used for the decomposition of the oxidant left unused.

The solution of crystallized TBC at room temperature in pure and dry benzene is fairly and sufficiently stable and requires several days for its decomposition. However, in presence of a trace (0.005 mole/litre) of water, the ester (TBC) is rapidly hydrolysed. The hydrolysis is

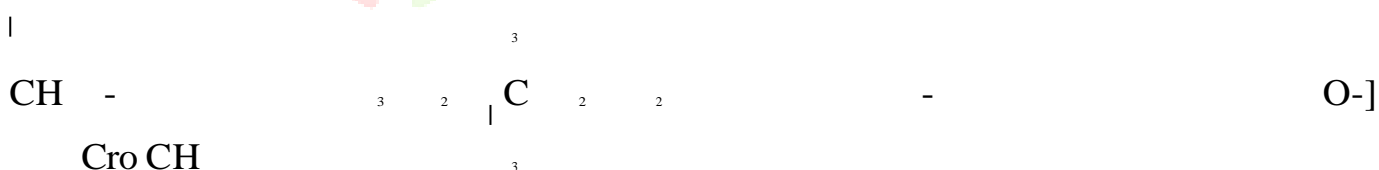
catalysed by pyridine. Di-tertiary butyl chromate (TBC) has been exhaustively used by Dr. G.D. Mishra and co-workers for various selective oxidation and degradation of organic compounds- such as substituted alkenes, alcohols, saturated and unsaturated fatty acids, amines, esters, ethers, phenols, carbohydrates etc., under different reaction condition. The detailed survey of their works and some other works has been given in Chapter II of this thesis.

In our present work we have used di-tertiary amyl chromate (abbreviated as TAC) which resembles TBC in many respects. The characteristics of TAC may be summarized as under :

- i) It is stable at room temperature.
- ii) Its preparation does not pose any difficulty.
- iii) Its reaction time is short.
- iv) The yield of the oxidation product is satisfactory.
- v) The oxidation reactions do not require high proportion of the oxidant.

Di-tertiary amyl chromate was first of all used by Dr. G.D. Mishra and R. Thakur<sup>24</sup> for the oxidation of aliphatic and aromatic acids. TAC is prepared by mixing tertiary amyl alcohol (2-methyl-2-butanol) and  $\text{CrO}_3$  together in definite proportion. The following composition is proposed for TAC,

[CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>]



The present work deals with the study of the oxidation product obtained by the oxidation of organic compounds such as phenol, catechol, quinol, resorcinol and naphthol with TAC in various molar ratios in presence of dioxan as solvent.

Elements were estimated instrumentally whereas chromium present. In the complexed oxidation products was determined volumetrically. The possible formulations for the oxidation products were composed on the basis of their empirical formulae and I.R. spectra.

On the basis of the methods adopted in this thesis it is also possible to throw light on the

mechanism of oxidation because the complexation of the oxidation products with Cr in different molar ratios taken place at different stages of oxidation.

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