

CHARACTERIZATION OF OXIDATION PRODUCT OF ORGANIC COMPOUND USING UNUSUAL OXIDANT

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ABSTRACT

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 peroxide¹, 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.

INTRODUCTION

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:-

- i) They cause explosion during reaction if not handled carefully,
- ii) they are not very much stable at room temperature.

H. Firouzabadi et al¹, used the commercially available oxidant such as dipyrindine chromium (VI) oxide and pyridine chlorochromate for the oxidation of different classes of organic compounds and found them unsuitable.

As reported by J. C, Collins² et al, the disadvantages with dipyrindine chromium (VI) oxide³ 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 chlorochromate⁴ 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 time⁵. In some cases, it is not effective at all⁶.

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.

EXPERIMENTAL

Preparation of di-tertiary butyl chromate (TBC).

Different Scientists have used different methods for the preparation of TBC.

i) **Takayki Sugga**⁷ prepared TBC by dissolving 163 g of CrO₃ in 325 g of tertiary butyl alcohol (TBA) in small portions with ice-cooling followed by dilution with 1000 g of benzene. The solution was concentrated to 75% of its volume in vacuum and finally mixed with 55 g of glacial acetic acid and 75 g of acetic anhydride.

ii) **Tamon Matsuura, T. Sugga and Takashi Sakao**⁸, prepared the oxidant (TBC) as under : 197 g of CrO₃ was mixed with 394.5 g of TBA and then diluted with 1100 g of benzene. 50 g of glacial acetic acid and 100 g of acetic anhydride was added to it and the solution concentrated to 66% of its original volume.

iii) R. V. Oppenauer and H. obberauch⁹ used the following method for the preparation of TBC. CrO₃ 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_2SO_4 . This reagent does not attack double bonds \square to \square -OH group.

iv) **Albert Leo and F. H. Westheimer**¹⁰ prepared TBC by dissolving 1 g of CrO_3 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.

v) **J.K. Noryonberski**¹¹ used the following procedure for the preparation of TBC. 5 g of CrO_3 was added gradually in small instalments to a well-mixed and colled 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 Na_2SO_4 to give the oxidant.

vi) **Tamon Matsuura and Kajo Fugita**¹² prepared TBC as given below : 73.5 g of 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 Na_2SO_4 . Acetic anhydride was then added to the solution to give TBC.

Di-tertiary butyl chromate as on 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 Obberauch⁹. The oppenauer reaction which employs TBC as an oxidant resembles the internal redox reaction as both are accelerated by pyridine.

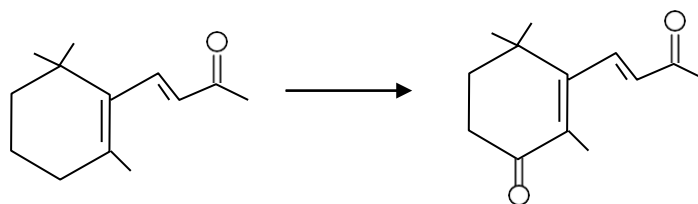
The oxidant, di-tertiary butly chromate prepared by oppenauer and obbersuch was found to oxidize primary alcohols to aldehydes almost quantitatively. If excess of TBA is removed from the reagent by concentration in vacuo, a stronger oxidant results. If a carboxylic acid anhydride is added to the TBC 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

Solvents used in oxidation by TBC

In most of the oxidation reactions using TBC, non- polar solvents such as petroleum ether,^{9,13,14} benzene^{12,15} and carbon tetrachloride^{16,17} have been used. Methyl recinoleate (B.P195-205°C was oxidized by TBC in petroleum ether^{13,14} at 15⁰-30⁰C. The

oxidation product was examined by distillation, paper chromatography and I.R. Cyclohexanol¹⁸ on oxidation with TBC in benzene at 35°C for 48 hours yielded small quantity of adipic acid. d- limonens¹⁹ was oxidized by RBC in benzene in a stream of CO₂



for 36 hours. Steroids¹⁶ have been oxidised

by TBC in the medium of carbon tetrachloride. In some cases anhydrous acetic acid has been used as a solvent. The TBC oxidises β - ionone selectively to 4-oxo-ionone in presence of anhydrous acetic anhydride as solvent β - ionone 4-oxo-ionone. It has also been found that a polar solvent²⁰ like TBA is better for the purpose than the usual non-polar solvents. Oxidation reactions with TBC have been carried out in neutral media^{21,22} as well as in slightly acidic media, oxidation of terpenolene with TBC in the molar ratio (substrate : TBC :: 1:2) was carried out in presence of Ac₂O and AcOH²³ for 45 hours at

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^o-50^oC. 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^oC. A mixture of sulphuric acid and hydrazine has also been used for the decomposition of the oxidant left unused.

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