

## Microwave assisted synthesis of some Chromium (III) complexes of cyclohexanol with TBC

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**Abstract :** The application of microwave irradiation to organic reaction has shown to enhance significantly the rate of many organic processes. In the present work, the products obtained by the oxidation of cyclohexanol in tetrahydrofuran (THF), 1,4-dioxane and dichloromethane by ditertiary butyl chromate (TBC) in varying molar ratios by microwave dielectric heating conditions are studied. The analysis of compounds was done by chemical as well as instrumental methods including FTIR and DTA/TGA mass loss pattern. The results clearly indicates the advantages of Microwave Assisted Organic Synthesis (MAOS) over conventional synthetic methods with respect to reaction efficiency and product yield, less pollution and higher energy efficiency.

**(Keywords :** Microwave, cyclohexanol, ditertiary butyl chromate (TBC), synthesis tetrahydrofuran (THF), and FTIR spectroscopy)

### Introduction

Microwave Assisted Organic Synthesis (MAOS) and Microwave Induced Organic Reaction (MORE) have gained popularity as a non conventional eco-friendly technique for rapid organic synthesis in conformity with 12 principles of Green chemistry<sup>1</sup>. P. Lidstrom et.al<sup>2</sup> have reported a detailed survey of MAOS and MORE. Percy Spencer in 1947<sup>3</sup> introduced microwave dielectric technique as a source of energy. In 1986 R.Gedye et al.<sup>4,5</sup> applied microwave dielectric heating to organic synthesis and now there are more than 2000 papers that describe the application of this technique for synthesis of new compounds. Keeping in view, the increasing importance of MAOS and MORE in organic

synthesis, the authors have undertaken the oxidation of cyclohexanol in different solvents with ditertiary butyl chromate by microwave heating. TBC has proved to be a potent and versatile oxidant under aqueous and non aqueous media as substantiated by the volumes of work done after its first use in 1949 by R.V. Oppenauer and H. Oeberrauch<sup>6</sup>. The oxidation products of organic substrates formed may serve as ligands to give adducts or complexes of chromium in different oxidation states<sup>7-10</sup>. Cyclohexanol<sup>11</sup> is an alicyclic alcohol exists as colourless liquid with a camphor-like odour. It is important feedstock in the polymer industry, as a precursor to nylons and to various plasticizers. Small amounts are used as a solvent. In this present paper, we have reported the synthesis and study of some complexes of chromium in lower oxidation states with cyclohexanol by oxidizing it with TBC to explore the versatility of oxidising agent and expand the horizon of cyclohexanol chemistry.

### Experimental:

The chemicals used in the present work were of A.R. grade obtained from commercial sources. The chemical used were cyclohexanol, tetrahydrofuran (THF), dichloromethane, 1,4-dioxane, tertiary butyl alcohol (TBC), acetone, chromium (VI) oxide, silver nitrate, potassium persulphate, ammonium iron(II) sulphate (Mohr's salt), potassium dichromate, barium diphenylamine -4-sulphonate.

TBC which has been used as the oxidant in the present work, was prepared in situ by

dissolving a weighed amount of chromium (VI) oxide in 10 ml tertiary butyl alcohol. Weighed amount of cyclohexanol was dissolved in 10 ml of solvents i.e., THF, 1,4-dioxane and dichloromethane in clean and dry beaker with constant stirring. The substrate: oxidant ratios used were 1:1, 2:1 and 3:1; cyclohexanol was found to be freely soluble in all the three selected solvents. Oxidation of this substrate with TBC was performed in three sets, each for the three solvents. The two solutions were mixed together to prepare a homogeneous reaction mixture, stirred continuously for a considerable time using a magnetic stirrer [REMI RS-12 Rotatory Shaker] and any change in consistency was noted. The mixture was then heated in an LG MG-3937C 20-Litre, 2450 MHz 800W Microwave Oven (MW irradiation 160W, variable oxidation time). Initial and final temperature of the reaction mixture was recorded to specify the exothermic/ endothermic nature of the reaction under investigation. The reactions were found to be exothermic, in general, except for those in 1,4-dioxane in which they were endothermic as indicated by a drop in temperature of the reaction mixture. The nine products formed in each of these cases were washed with acetone, dried and weighed, bottled and labeled as 111CHOL, 121CHOL, 131CHOL, 211CHOL, 221CHOL, 231CHOL, 311CHOL, 321CHOL, 331CHOL and used for further analysis and characterization. Percentage composition of C, H and O was determined using EuroEA Elemental Analyser while the chromium content in this sample was estimated volumetrically using  $K_2S_2O_8$  (excess), 0.1 N  $K_2Cr_2O_7$  solution and 0.1 N Mohr's salt solution. The oxygen content was found out by subtraction of percentage of C, H & Cr from 100. Empirical formula of these complexes was then deduced. The IR spectrum of products was recorded on a "Fourier Transform Infra Red Spectrophotometer-4700type A". The thermogravimetric and differential thermal analysis (TG-DTA) of the compounds were carried out on "Thermal Analysis System –Perkin Elmer Diamond TG/DTA." The samples were heated at the rate of 10<sup>0</sup> C/min. in the temperature range of room

temperature to 700<sup>0</sup>C. The recorded details have been summarised in Table 1 and Table 2.

## Results and Discussion

\* The nine complexes obtained after the oxidation of cyclohexanol with TBC in different solvents had different physical properties, like colour, solubility, etc.

\* Table-2 shows that the common oxidation products i.e. formic acid, acetic acid, acrylic acid & crotonic acid are formed during the process along with water.

\* The reactions performed in 1,4-dioxane was found to be endothermic, while those performed in other solvents were exothermic. Comparing the reaction time and corresponding yield of products, it can be concluded that 1,4-dioxane serves as the most efficient solvent and the compound sample 111CHOL, 211CHOL, 221CHOL and 311CHOL was most efficiently prepared sample of cyclohexanol with low time of formation and good yield.

\* The substrate oxidant ratio also affects the nature and characteristics of the products formed. With increase in molar concentration of the oxidant for each reaction set intensification of the colour of the products was observed and this may be indicative of the increase percentage of chromium in the sample. This was confirmed from the elemental analysis of the samples as evident from the empirical formula of the compound. It may be due to different oxidation states of chromium in different products.

\* The extent of oxidation of the substrate increases as the ratio of the oxidant increases.

\* In case of 111CHOL, 211CHOL and 311CHOL, when the ratio of oxidant is maximum, the most stable oxidant state i.e., III is observed in the form of  $Cr_2O_3$ . In other cases oxidation states of chromium are less than III.

\* The oxidation is more efficient in 1,4-dioxane than in THF and dichloromethane as supported by the presence of less oxidized product in 321CHOL and 331CHOL. There are no such products in 211CHOL, 221CHOL and 231CHOL where the solvent is dioxane.

**Table -1**  
**Preliminary characteristics of the products of cyclohexanol with TBC**

| Sample | Label    | Solvent                         | Substrate/<br>Oxidant<br>Molar ratio | MW<br>Irradiatio<br>n time in<br>sec, 160W | Yield<br>in g | Colour      | Solubility in<br>water |
|--------|----------|---------------------------------|--------------------------------------|--------------------------------------------|---------------|-------------|------------------------|
| 1.     | 111CHOL  | THF                             | 2.0ml /2.0 g;1:1                     | 25s                                        | 2.21g         | Dark Brown  | Insoluble              |
| 2.     | 121 CHOL | THF                             | 2.0ml/1.0 g;2:1                      | 40s                                        | 1.08g         | Light Brown | Insoluble              |
| 3.     | 131CHOL  | THF                             | 2.0ml/0.67g;3:1                      | 60s                                        | 0.85          | Light Brown | Partially Soluble      |
| 4.     | 211CHOL  | 1,4- dioxane                    | 2.0ml /2.0 g;1:1                     | 20s                                        | 2.39g         | Dark Brown  | insoluble              |
| 5.     | 221CHOL  | 1,4-dioxane                     | 2.0ml/1.0 g;2:1                      | 22s                                        | 1.74g         | Dark Brown  | Partially soluble      |
| 6.     | 231CHOL  | 1,4- dioxane                    | 2.0ml/0.67g;3:1                      | 30s                                        | 1.71g         | Dark Brown  | Insoluble              |
| 7.     | 311CHOL  | CH <sub>2</sub> Cl <sub>2</sub> | 2.0ml /2.0 g;1:1                     | 35s                                        | 1.63g         | Brown       | Insoluble              |
| 8.     | 321CHOL  | CH <sub>2</sub> Cl <sub>2</sub> | 2.0ml/1.0 g;2:1                      | 40s                                        | 1.12g         | Light Brown | Insoluble              |
| 9.     | 331CHOL  | CH <sub>2</sub> Cl <sub>2</sub> | 2.0ml/0.67g;3:1                      | 45s                                        | 0.67g         | Light Brown | Partially soluble      |

**Table -2 (Products)**

| Sample | Label    | Empirical Formula                                              | Formulation                                                                                                                   |
|--------|----------|----------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------|
| 1.     | 111CHOL  | Cr <sub>2</sub> C <sub>6</sub> H <sub>16</sub> O <sub>10</sub> | Cr <sub>2</sub> O <sub>3</sub> (CH <sub>3</sub> COOH)(CH <sub>3</sub> CH=CHCOOH)(H <sub>2</sub> O) <sub>3</sub>               |
| 2.     | 121 CHOL | CrC <sub>6</sub> H <sub>16</sub> O <sub>10</sub>               | CrO(CH <sub>3</sub> COOH)(HCOOH)(CH <sub>2</sub> =CHCOOH)(H <sub>2</sub> O) <sub>3</sub>                                      |
| 3.     | 131CHOL  | CrC <sub>7</sub> H <sub>18</sub> O <sub>11</sub>               | CrO <sub>2</sub> (CH <sub>3</sub> COOH) <sub>2</sub> (CH <sub>2</sub> =CHCOOH)(H <sub>2</sub> O) <sub>3</sub>                 |
| 4.     | 211CHOL  | Cr <sub>2</sub> C <sub>6</sub> H <sub>14</sub> O <sub>9</sub>  | Cr <sub>2</sub> O <sub>3</sub> (CH <sub>3</sub> COOH)(CH <sub>3</sub> CH <sub>2</sub> =CHCOOH)(H <sub>2</sub> O) <sub>2</sub> |
| 5.     | 221CHOL  | CrC <sub>8</sub> H <sub>18</sub> O <sub>9</sub>                | CrO(CH <sub>3</sub> COOH) <sub>2</sub> (CH <sub>3</sub> CH=CHCOOH)(H <sub>2</sub> O) <sub>2</sub>                             |
| 6.     | 231CHOL  | CrC <sub>6</sub> H <sub>14</sub> O <sub>7</sub>                | CrO(CH <sub>3</sub> COOH) (CH <sub>3</sub> CH=CHCOOH)(H <sub>2</sub> O) <sub>2</sub>                                          |
| 7.     | 311CHOL  | Cr <sub>2</sub> C <sub>6</sub> H <sub>18</sub> O <sub>11</sub> | Cr <sub>2</sub> O <sub>3</sub> (CH <sub>3</sub> COOH)(CH <sub>3</sub> CH=CHCOOH)(H <sub>2</sub> O) <sub>4</sub>               |
| 8.     | 321CHOL  | CrC <sub>6</sub> H <sub>16</sub> O <sub>11</sub>               | CrO <sub>2</sub> (CH <sub>3</sub> COOH)(HCOOH)(CH <sub>2</sub> =CHCOOH)(H <sub>2</sub> O) <sub>3</sub>                        |
| 9.     | 331CHOL  | CrC <sub>6</sub> H <sub>14</sub> O <sub>8</sub>                | CrO <sub>2</sub> (CH <sub>3</sub> COOH)(CH <sub>3</sub> CH=CH <sub>2</sub> COOH)(H <sub>2</sub> O) <sub>2</sub>               |

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