

CHARACTERIZATION SOLUTION OF CRYSTALLIZED TBC AT ROOM TEMPERATURE

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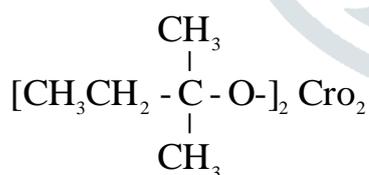
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ABSTRACT

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.

INTRODUCTION

Di-tertiary amyl chromate was first of all used by Dr. G.D. Mishra and R. Thakur²⁴ for the oxidation of aliphatic and aromatic acids. TAC is prepared by mixing tertiary amyl alcohol (2-methyl-2-butanol) and CrO_3 together in definite proportion. The following composition is proposed for TAC,



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 β -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.

EXPERIMENTAL

Di-tertiary alkyl chromates namely di-tertiary butyl chromate and di-tertiary amyl chromates have been extensively used for the oxidation of various classes of organic compounds. A brief survey of previous works has been given below:

OXIDATION OF OLEFINS WITH TBC

In this class Safrole seems to be the only example studied.¹ Its oxidation gives mainly back the starting material along with some allylic bond cleavage products like piperonylic acid, piperonal and 3,4-methylene dioxy cinnamaldehyde.

The percentage of different products depends on the medium (neutral or acidic).

In the class of disubstituted olefins oxidation of isosafrol has been studied¹ in neutral and acidic media. Oxidative cleavage takes place giving piperonal, piperonylic acid and acetic acid.

It was suggested that piperonal and piperonylic acid were formed by further oxidation of methylene dioxy-cinnamaldehyde. Oxidation of the latter compound alone gave piperonal (38%) and piperonylic acid (7%). Cyclic peroxides were proposed as intermediates in the formation of 3,4-methylene dioxy-cinnamaldehyde from safrole.

As an oxidant TBC has a marked selectivity in converting tri-substituted olefins to unsaturated ketones. Thus, oxidation of steroidal-5-enes by TBC constitutes a general method for the preparation of steroidal-5-ene-7-ones, i.e., the oxidation of cholest-5-ene-3-O1-acetate^{2,3,4} cholest-5-ene⁵ and androst-5-ene-3-diol diacetate⁶ to 3-acetoxy-cholest-5-ene-7-ene, cholest-5-ene-7-ene and 3, 17-diacetoxy-androst-5-ene-7-ene respectively. Similar oxidation has been reported in the decaline series.

The reason for the preferential oxidation of the C₇-methylene group in steroidal-5-ones relative to C₄ methylene group may be attributed to steric factors involved in the oxidation reaction. Oxidation of tri-substituted olefins by TBC has been studied extensively in monoterpenes. Oxidation of terpineol⁸ gave 8-hydroxy-carvotan acetone, 8-hydroxy piperitone, the olefinic cleavage product homoterpenyl methyl ketone and acetone in traces.

RESULT AND DISCUSSION

Common chromium containing oxidants such as, Jones reagent ($\text{H}_2\text{CrO}_4 + \text{H}_2\text{SO}_4$), Sarett's reagent ($\text{CrO}_3 + \text{C}_5\text{H}_5\text{N}$), Etard's reagent ($\text{CrO}_2 \text{Cl}_2$), $\text{CrO}_3 + \text{OP} [\text{N} (\text{CH}_3)_2]_3$, CrO_3 , Na_2CrO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ etc., have been used extensively as well as selectively in organic chemistry for producing various products depending upon the nature of the substrates. However, some alkyl chromates have also been used as oxidants in the recent years. Di-tertiary amyl chromate (i.e., TAC) is one of them.

In the present work, we have used TAC for the oxidation of phenolic compounds namely, phenol, catechol, quinol, resorcinol and 2-naphthol in the medium of dioxen as a solvent. Various molar ratios of substrate to oxidant have been used using the same solvent. Oxidation products were isolated in good yields and analysed for carbon hydrogen and chromium. Empirical formula of the oxidation products were determined from the elemental analyses data and their formulations on the basis of infrared spectral analysis. The proposed formulations of the oxidation products were confirmed by TGA.

Oxidation products of phenol, isomeric dihydroxybenzens and 2-naphthol are given in Tables-A, B and C respectively.

An interesting aspect of the present study is that oxidation products obtained from different substrates are isolated as stable solid chromium complexes of varying colour and compositions.

It is evident from the table-A, that phenol on oxidation with TAC of different concentrations gives only oxalic acid which undergoes complexation with different oxidation states of chromium.

Catechol on oxidation with TAC of different concentrations produces different oxidation fragments which form complexes with Cr in its different oxidation states. In the case of quinol, both formic acid and oxalic acid are obtained as oxidation products which get complexed with Cr to form stable complexes of varyig compositions. Resorcinol on oxidation with TAC of higher molar concentrations yields formic acid whereas with lower molar concentrations of TAC, acetic acid is obtained. These two oxidation products also get complexed with different oxidation states of Cr.

The compositions of solid products obtained from 2-naphthol, clearly indicate that in all conditions formic acid is invariably produced. Formic acid serves as ligands and forms stable complexes with chromium.

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