IJCRT.ORG ISSN : 2320-2882

INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)

An International Open Access, Peer-reviewed, Refereed Journal

# THE STUDY OF THE OXIDATION PRODUCT OBTAINED BY THE OXIDATION OF ORGANIC COMPOUNDS

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## ABSTRACT

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.

## INTRODUCTION

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 oxidatior 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.

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[24] for the oxidation of aliphatic and aromat acids. TAC is prepared by mixing tertiary amyl alcohol (2-methyl-2-butanol) and $Cro_3$ together in definite proportion.

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**

The reaction products obtained in this case also are a result of the oxidation of either of the double bonds, shown above. The oxidation has been reported in conjugated as well as non-conjugat ketones.

These two axamples represent, what we may call, the most important applicaiton of TBC oxidation, i.e., the synthesis of absisic acid. Oxidation of - ionone with TBC in tert-butyl-alcohol gave 1-hydroxy-4-keto- -ionone along with 4-keto--ionone.

In this case, besides the usual oxidation of the allylic methylene group to a ketone group, the doubly activated methene proton is also oxidised to give the allylic alcohol. The formation of such an allylic alcohol proved to be very useful from the point of view of the synthesis of absisic acid.

**B) OXIDATION OF AICOHOLS WITH TBC**

**a) Oxidation of primary Aliphatic Alcohols:**

Oxidation of primary aliphatic alcohol was done by Takayuki Sugga keiichkihara and Tamon Matsuura. A benzene solution of terti-butyl chromate (from one part of $Cro_3$ and two parts of tert-butyl alcohol) was added over 0.5 hour to a well stirred solution of an

equimolecular amount of the alcohol in benzene at 1-2$^0$C. The mixture was then stirred at the temperature and for the period given in the table and the products separated.

**TABLE**

**Percentage of the reaction products formed**

| Alcohol ($RCH_2OH$) | Temp OC | Time | R.CHO | R.COOH | $R.COOCH_2R$ |
|---|---|---|---|---|---|
| n-Lauryly (a,b) | 25 | 2 days | 3 | 53 | 28 |
| n-Lauryl | 1-2 | 6 hrs. | 38 | 23 | 38 |
| n-Hexyl | 1-2 | 6 hrs. | 25 | 37 | 34 |
| n-Butyl | 1-2 | 6 hrs. | 29 | 32 | 35 |
| Ethyl | 1-2 | 6 hrs. | 17 | 20 | 23 |
| n-Amyl | 1-2 | 6 hrs. | 43 | 17 | 20 |
| Iso-amyl | 1-2 | 6 hrs. | 31 | 29 | 34 |
| Neo-pantyl (c) | 1-2 | 6 hrs. | 36 | 5 | 13 |
| Geraniol (d) | 1-2 | 6 hrs. | 77 | 2 | - |
| Isobutyl | 1-2 | 6 hrs. | 17 | 26 | 29 |
| Isobutyl (e) | 15 | 66 hrs. | 5 | 18 | 43 |

a- 2.5 moles reagant used.

b- Solvent was petroleum ether.

c- 2-methyl-2-hept-6-one(3x) was isolated.

d- Acetone was isolated.

e- 1.5 moles of reagent used.

In contrast to saturated alcohol all of which give the corresponding aldehyde geraniol with an oleffinic double bond adjacent tot he hydroxymethyl group produces a high yield of citral but the ester was not isolated.

**b) Oxidation of alicylic alcohole with TBC:**

Oxidation of alicylic alcohols with TBC was done experimentally by Takayuki Sugga and Tamon Matsuura. The oxidation of 1:1 molar solution of cyclohexyl carbinol with TBC in benzene at 1-2$^0$C for 6 hrs., gave the corresponding aldehyde, acid and ester in 48%, 28% and 19% yield respectively.

Oxidation of 1:3 molar ratio of cyclohexanol and TBC at $35^0$C for 6 hrs., prodcued only 85% cyclohexanone but oxidation for 48 hrs., gave 7% adipic acid together with 68% of katone. Cyclohexane-trans-1, 2-diol at $35^0$C for 3.5 hrs., gave no diketone but 57% adipic acid and 7% trans-1,2-adipoxycyclohexane whereas p-menthane-trans-1, 3 diol at $30^0$C for 2.5, 4.5 and 8.5 hrs., gave hydroxy ketone in 47, 60 and 63% yield respectively.

Oxidation of primary aromatic alcohols was done by Takayuki Sugga, keiichikihara and Temon Matsuura. Oxidation with TBC had been carried out with benzyl alcohol, its para-substituted derivaties and trans-cinnamyl alcohol and also with -phenyl ethyl alcohol. In the first three alcohols the corresponding aldehydes were obtained as the main products, but no estar was formed. However, the last, with a methylene group next to the -OH group, gave the corresponding esteer aldehyde and acid as would a saturated primary aliphatic alcohol. Oxidation of p-alcohols with tert-butylcromate (IV) was done by Takayuki Sugga and Tamon Matsura. Primary alcohols without a -electron system on the carbon - to the-$CH_2OH$ group i.e., n-butyl alcohol and n-$C_6H_{11}OH$ was stuided with TBC. On oxidation with TBC they afforded the corresponding acid, aldehyde and ester in comparable yields. Likewise a cyclic - glycol with two secondary hydroxy groups yielded the corresponding cyclic ester along with the groups fission products. The yield and the nature of the ester formed remained unaffected by the continuous removal of the acid from the reaction mixture during the course of reaction. Not only this but the addition of a second acid to the system also failed to affect the nature or the yield of the ester formed. However, when a second aldehyde was added to the system, a second ester was found among the reaction products. These observation indicated that the formation of the ester does not result from the direct esterification of the alcohols with the acid formed from it by oxidaiton. Rather the ester is formed by oxidation of a hemiacatal intermediate formed by the reaction of alcohol and aldehyde. The special studies of the mxtures of alcohols and aldehydes revealed bonds characteristics of hemiacetal formation. Unsaturated alcohols such as $PhCH_2OH$ and trans-cinnamyl alcohol yielded only the corresponding aldehyde on oxidation with TBC. In this, there was no IR spectral evidence for hemiacetal formation in the reaction mixtures.

Information on the oxidation of primary and secondary alcohols by TBC available till 1959 reviewed by Matruura and Sugga. In general the oxidaiton of a primary aliphatic alcohol[2] give a mixture of the corresponding aldehyde, acid and the ester of the acid formed and the starting alcohol:

$RCH_2OH$ R-C- OH + R-CH + R-C - O-R

A primary alcohol aromatic like benzyl alcohol gives a mixutre of Benzaldehyde and benzoic acid but no ester is formed in these reactions. Oxidation of benzyl alcohol in presence of small amount of pyridine by TBC in benzene gives 70% yield of benzaldehyde in 45 minutes. The same reaction in the absence of pyridine gives only 55% yield of benzaldehyde after three hrs., of reaction.

The presence of an electron withdrawing or electron releasing group in the aromatic ring does not affect the course of oxidation. On the other hand, alcohols like - phenylethyl alcohol gives the corresponding ester and other oxidation products such as phenylethyl acetate (46%) - phenyl acetal-dehyde (3%) - phenyl acetic acid (3%) accompanied by other oxidation products such as benzaldehyde (2%) and benzoic acid (7%). Besides these products, a resinous material is obtained in about 10% yield.

**RESULT AND DISCUSSION**

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 eveident 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.

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