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STUDIES ON THE OXIDATION OF CAMPHENE TO CAMPHOR

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Acid catalysed oxidation of camphene to camphor with the dichromates of sodium, potassium and ammonium in aquous medium at 155-120° has been studied. The effect of variation in reaction time and sulphuric acid concentration has also been studied. The oxidation products were analysed and identified by gas chromatography.

Key words: Diohromates, Camphene, Camphor.

INTRODUCTION

The oxidation of camphene to camphor, an industrially important chemical with dichromates in the presence of glacial acetic acid and sulphuric acid was first of all studied by Acharya and Wheeler [1] In another studies [2], they omitted glacial acetic acid and reported better yields. Davankov and co-workers [3,4] studied the oxidation of camphene to camphor with potassium dichromate, sulphuric acid and water mixture employing different activating agents such as hydrogen peroxide, nitric acid, perchromic acid, sodium nitrite and nitrate. The use of activating agents reportedly reduced the reaction time and increased the yields of camphor. Davankov *et al* [5]. In another study reported the use of napthalene-sulphonic acid as emulsifier and the same oxidation mixture. Nguyen and Phi [6] using sodium and potassium dichromates as oxidising agent have claimed above 80% yields of camphor but no experimental details were given.

The conversion of camphene to camphor has been postulated to proceed as follows (Fig. 1).

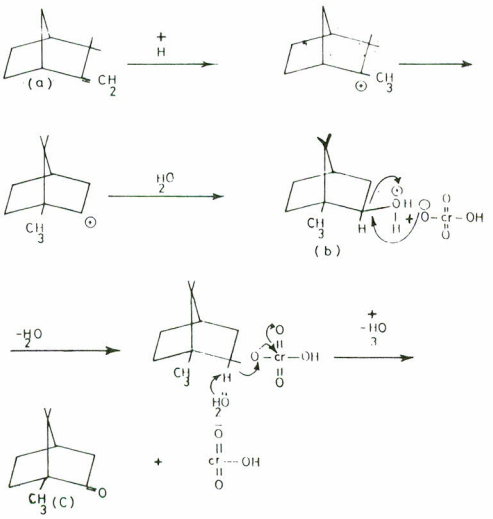

Fig. 1

(1) Hydration of double bond with water in the presence of acid (formation of secondary alcohol via Wagnerf Meerveen rearrangement (a to b).

(2) Conversion of secondary alcohol to ketone (oxidation with chromic acid (b to c).

The present investigations were undertaken to evolve single step oxidation of camphene to camphor without the use of activating agents and emulsifiers. Accordingly the acid catalysed oxidation of camphene to camphor with the dichromates of sodium, potassium and ammonium at 115-120° has been investigated. Studies with ammonium dichromate are being reported for the first time. The effect of variation in reaction time and sulphuric acid concentration has been studied.

EXPERIMENTAL

Materials. Technical grade camphene (Riedal de Haen AG, Camphene, 80% and tricyclene 20% as checked by GLC) was used. Sulphuric acid and dichromate salts were of analytical grade.

Procedure. Camphene (20, 7g, 0.152 mole) was taken in a 500 ml. round bottom flask equipped with a magnetic stirrer and a condenser. To it was then added potassium dichromate (13.76g. 0.0466 mole) dissolved in 200 ml. water and sulphuric acid (30g. 0.3 mole). The flask was immersed in an oil bath maintained at 115-120° and the contents of the flask were heated for the desired reaction time. Heating was then discontinued and the contents of the flask were poured into cold water. The supernatent liquid was separated, washed thoroughly with cold water till neutral and dried over sodium sulphate and weighed.

Similar experiments were performed using other dichromate salts.

In another set of experiments the concentration of sulphuric acid was varied.

Analysis. The reaction product dissolved in diethyl ether was analysed on a Pye-unicam 104 gas chromato-

graph fitted with a F.I. detector using a 25 m WCOT SP – 1000 column. Hydrogen was used as the carrier gas with a flow velocity of 67.75 cm/sec and a split ratio of 1:60 and sample size 0.1 μl. The temperature was programmed as 50° for 4 min., with 4°/min to 100° while detector and injection temperatures were 250° and 200° respectively. Various components were identified by their retention times and by Co-injection of standard samples. Percentage composition of individual components was calculated on the basis of peak area using SP 4100 (spectra physics) computing integrator.

RESULTS AND DISCUSSION

Oxidation of camphene to camphor has been studied in the presence of dichromates of potassium, sodium and ammonium in the aquous medium at 115-120°. In order to find out the variations in the reaction products the reaction conditions studied in detail were:

1. Reaction time.
2. Oxidants (dichromate salts).
3. Concentration of sulphuric acid.

The results obtained under varying conditions of time, dichromate salts and concentration of sulphuric acid are given in Table 1, Fig. 2 and 3. These studies have afforded useful information regarding optimum conditions required for obtaining maximum yields of camphor.

Table 1. Oxidation of camphene to camphor with potassium dichromate influence of concentration of sulphuric acid

Camphene = 20.7 g H_2O = 200 ml
Time = 40 hours Temperature = 115-120°

S. No.	Concentration of H_2SO_4/moles	Recovery %	Camphene %	Camphor %	Isoborneol %
1.	0.24	86.9	37.9	49.1	–
2.	0.28	86.5	32.1	55.5	0.36
3.	0.32	91.7	26.7	64.7	–
4.	0.36	83.5	23.5	65.5	0.3
5.	0.4	96.0	20.2	69.4	–

The recovery values reported in the Table 1 are the percentage weight of the reaction product (camphene and camphor, isoborneol etc.) based on the weight of camphene employed in these reactions.

Effect of reaction time. The effect of reaction time on the oxidation of camphene to camphor with dichromates of potassium, sodium and ammonium, keeping temperature constant is shown in Fig. 2 and 3.

In case of oxidation with potassium dichromate, it was observed, that with increase in reaction time the percentage of camphor increased and that of unreacted camphene decreased. When the reaction mixture was analysed after 50 hrs. the yield of camphor increased to (70.5%) and the percentage of unreacted camphene dropped to (18.1%) Fig. 2 and 3.

In case of oxidation with sodium dichromate, it was observed, that with increase in reaction time the percentage of camphor increased and that of unreacted camphene decreased (Fig. 2 and 3). After 40 hrs. the yield of camphor was less as compared to oxidation with potassium dichromate.

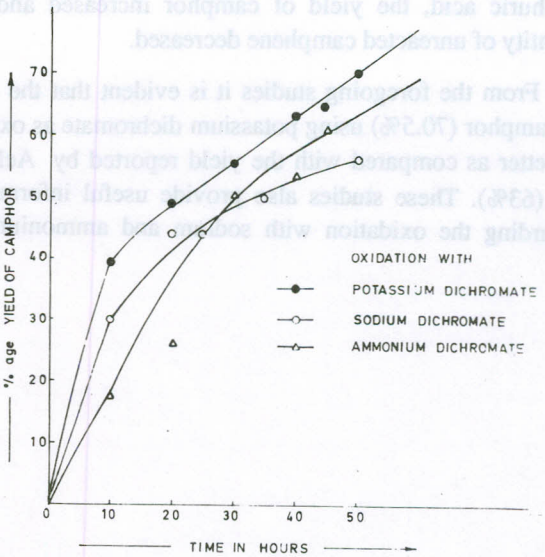

Fig. 2

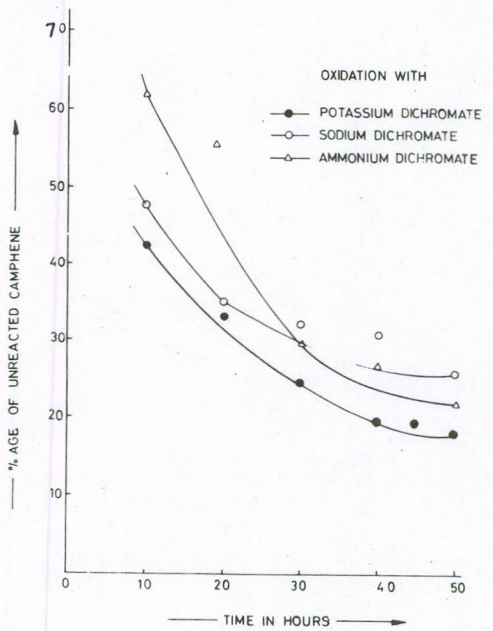

Fig. 3

In case of oxidation with ammonium dichromate, the yield of camphor increased with increase in reaction time (Fig. 2) in all these cases the conversion of camphene to isoborneol varied from 3 to 6%. It is assumed that the standard reaction governing the formation of camphor proceeds in the fashion indicated in Fig. 1.

Concentration of sulphuric acid. The effect of concentration of sulphuric acid in oxidation of camphene to camphor with potassium dichromate has been shown in Table 1 . Both reaction time and temperature were kept constant. It was observed that with the increase in concentration of sulphuric acid, the yield of camphor increased and the quantity of unreacted camphene decreased.

From the foregoing studies it is evident that the yield of camphor (70.5%) using potassium dichromate as oxident is better as compared with the yield reported by Acharya [2] (63%). These studies also provide useful information regarding the oxidation with sodium and ammonium dichromates, as no data is available regarding the oxidation with ammonium dichromate.

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