ON UTILISATION OF INDIAN TURPENTINE OILS

PART II

CONVERSION OF α- AND β- PINENES INTO BORNYL ACETATE BY ACETIC ACID IN PRESENCE OF CATALYSIS

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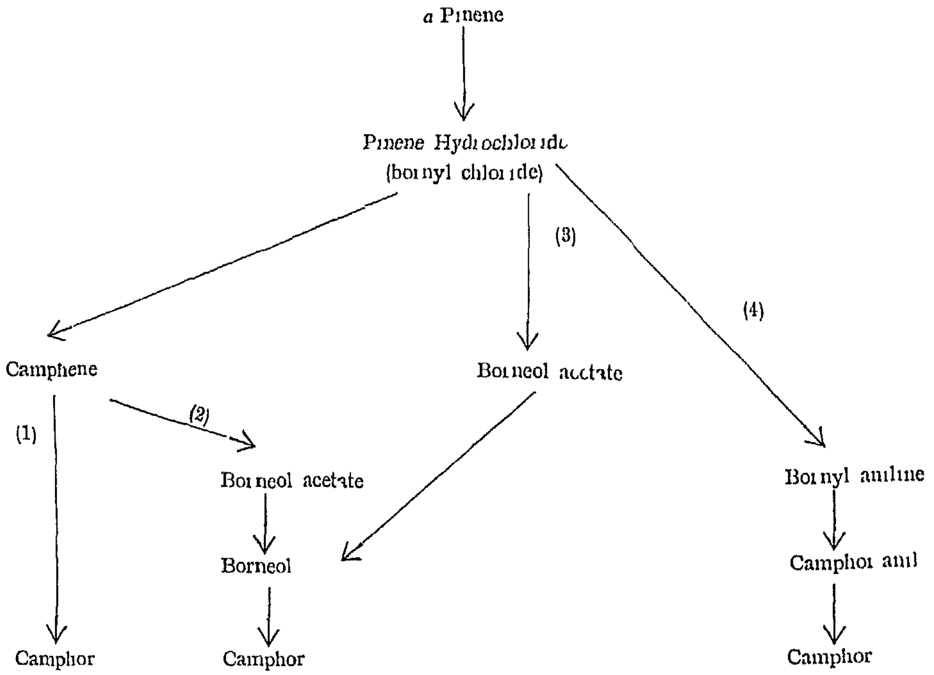
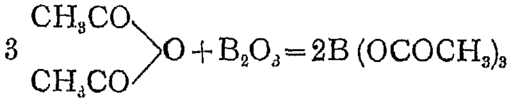
There are several synthetic processes known in literature for the conversion of α-pinene to camphor The first industrial process by which α-pinene can be converted into camphor consists in the initial conversion of pinene into pinene hydrochloride or bornyl chloride From pinene hydrochloride camphor is obtained by the following four different processes as outlined below



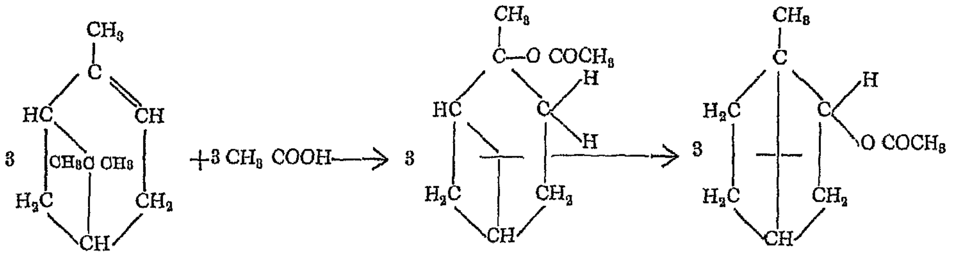
Of the above four methods, the first two are indeed very important and are still in practice in many countries (vide part I). Although to the third method, viz, conversion of pinene hydrochloride directly into isobornyl acetate, is attributed an yield of about 83–85 per cent of bornyl acetate in patent literature (U S.P. 1372382, C.A, 1921, **15**, 1906) the yield of isobornyl acetate at our hand by this method was not, however, satisfactory The fourth method (*Ritter, J Amer Chem Soc*, 1933, **55**, 3322) involving the conversion of pinene hydrochloride into bornyl aniline etc, has not yet been tried industrially, although Ritter claims a yield of camphor as high as 89 per cent by his method

The industrial interest of the modern method of direct conversion of pinenes to borneol-ester by acetic acid or formic acid in presence of catalysts like boric acid, boric trioxide, anhydrous oxalic acid, phosphorus pentoxide, etc, was first aroused by L Schmidt (D R P 406,768, 592,131 (Sch 47731), 589,779 (I 99730), 582,043 (Sch 94897)). Some detailed study of this method with α-pinene has been made by Imoto (*J Soc Chem Ind Japan*, 1938, **41**, 209B, 251B, 375B, 1939, **42**, 183B) with boro-acetic anhydride as catalyst and sulphuric acid as promoting agent By this process, Imoto obtained a yield of 38 9 per cent (theor) of borneol The mechanism of the reaction is explained as follows



$$3\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\!\!>O + B_2O_3 = 2B(OCOCH_3)_3$$

Boro-acetic anhydride acts as a catalyst and the reaction proceeds as.



Of the two general methods viz, hydrochloride method and the catalytic method mentioned above, the success of the first depends on the isolation of the bornyl chloride in good yield As mentioned in part I, in India " One has to depend on *Pinus longifolia* turpentine, as his source of pinene, at least for some time to come, because *Pinus excelsa* turpentine is neither being produced at present nor is there any likelihood of its being produced in the near future" α-Pinene obtained from the turpentine oil of *Pinus longifolia* is always contaminated with small quantities of β-pinene and carene, etc, and it is extremely difficult to isolate the crystalline pinene hydrochloride by this method It is worthwhile mentioning that the catalytic method is applicable to both α-pinene and β-pinene, whereas, in the hydrochloride method only pure α-pinene has to be used because with β-pinene both pinene hydrochloride and dipentene dihydrochloride are formed

With a view to finding out whether the ordinary variety of Indian turpentine oil (*Pinus longifolia*, which is available in India in enormous quantities) can be utilised for the manufacture of camphor, it was considered desirable to study in detail the workability of the catalytic method using α- and β- pinenes obtained from *Pinus longifolia*

In the first series of experiments to be described in this part, the catalytic effect of boric acid anhydride and acetic anhydride has been studied, the yield of borneol being only 17 5% (theor) in the case of α-pinene and 18 8% (theor) in the case of β-pinene With the addition of small amounts of sulphuric acid as reaction promoter (cf M Imoto, *J Soc Chem Ind Japan*, 1939, **42**, 314B) the yield of borneols in the case of α-pinene could be raised to 35 7 of the theory, the yield of borneols in the case of β-pinene under similar condition being 24 7 per cent

EXPERIMENTAL

Conversion of pinenes to borneols with acetic acid in the presence of the catalysts boro-acetic anhydride

Pure α-pinene was obtained from the turpentine oil of the oleo-resin from *Pinus excelsa* It has the following characteristics B P 150–52°/680 mm , $d_{26}^{26} = 0\ 8559$, $n_D^{28} = 1\ 4626$, $(\alpha)_D^{26} = +24\ 59$

In the following experiments boro-acetic anhydride was used as the reaction catalyst Freshly fused boric trioxide was finely powdered and treated with acetic anhydride , acetic acid and pinene were then added to this The mixture was heated on an oil-bath under stirring

TABLE I(a)

Expt	α-Pinene (g.)	Acetic acid (g.)	Acetic anhydride (g.)	B_2O_3 (g.)	Temp (°C.)	Hours of reaction	Yield of borneols on hydrolysis of the ester (g.)
1	136	120	20	2	90–95	25	20·0
2	136	120	20	2	100–105	24	24·5
3	136	120	20	2	110–115	24	25·0
4	136	120	20	2	125–130	20	19·5
5	136	150	30	2	105–110	24	27·0 (17·53% of theory).

After the reaction was over, the product was fractionated at atmospheric pressure (681 mm.) upto 185°C. The higher boiling residue containing mainly the ester was fractionated under reduced pressure.

QUANTITIES OF THE INGREDIENTS COLLECTED AT DIFFERENT TEMPERATURES FROM THE PRODUCTS OF THE ABOVE FIVE EXPERIMENTS

Expt No.	Fraction I Upto 125°	Fraction II 125–175°	Fraction III 175°–185°	Fraction IV 112–130°/30 mm	Residue
	g.	g.	g.	g.	g.
1	117·0	106·0	8·5	25·0	5·0
2	115·5	101·7	10·5	28·5	4·0
3	116·0	103·0	10·0	29·0	5·0
4	118·0	107·0	13·4	22·0	5·5
5	153·0	102·0	8·5	33·5	5·0

The fraction I consisted mainly of acetic acid, fraction II consisted of the mixture of several terpenes α-pinene, dipentene, camphene, terpinene, etc The fraction III was hydrolysed with methyl alcoholic potash The hydrolysed product on fractionation gave a small quantity of borneol (solidified on cooling) and fenchyl alcohol (b p. 196–199°) The fraction IV on hydrolysis gave borneol-isoborneol mixture, and was purified by crystallisation from petroleum ether, m p 198–200°

β-Pinene was separated by repeated careful fractionation of the turpentine oil from *Pinus longifolia* It contained very little α-pinene and carenes It has the following characteristics B P., 157–58°/681 mm , $d_{27}^{27} = 0\ 8581$, $n_D^{27} = 1\ 4679$, $(\alpha)_D^{27} = -14\ 29$

TABLE I(*b*)

Expt	β-Pinene (g)	Acetic acid (g)	Acetic anhydride (g)	B_2O_3 (g)	Temp (°C)	Hours of reaction	Yield of borneols on hydrolysis of the ester (g)
1	136 0	120 0	20 0	2 0	105–110	24	27 0
2	136 0	150 0	30 0	2 0	105–110	24	29 0 (18 8% of theory)
3	136 0	130 0	30 0	2 0	110–120	24	28 0

The reaction product was fractionated as in the case of α-pinene

QUANTITIES OF THE INGREDIENTS COLLECTED AT DIFFERENT TEMPERATURES FROM THE PRODUCTS OF THE ABOVE THREE EXPERIMENTS

Expt No	Fraction I Upto 125° Acetic acid	Fraction II 125–175° Terpenes	Fraction III 175–185° Ester and terpenes	Fraction IV 112–130°/30 mm Ester	Residue
	g	g	g	g	g
1	118 0	93 0	8 5	36 0	6 0
2	154 0	105 0	7 0	39 0	5 0
3	126 0	95 5	7 5	36 5	6·0

Conversion of pinenes to borneols with acetic acid in the presence of the catalyst boro-acetic anhydride and promoter sulphuric acid : α-Pinene to borneols

Treatment of α-pinene with acetic acid in the presence of the catalyst boro-acetic anhydride gave very low yield of borneol This method was therefore modified according to M Imoto (*J Soc Chem Ind. Japan,* 1939, **42,** 183B) The method consists of two stage operations In the present investigation a large number of experiments were performed in order to study the following factors with a view to finding out the optimum condition

1 Initial time of reaction before addition of sulphuric acid (reaction promoter)
2 Quantity and concentration of sulphuric acid
3 Time of reaction after addition of sulphuric acid
4 Temperature of reaction after addition of sulphuric acid

The best yield of bornyl ester was obtained under the following experimental conditions To boric acid anhydride (2 g) dissolved in acetic anhydride (30 g) was added α-pinene (136 g) and acetic acid (130 g) under constant stirring, and the mixture heated at 110–115° for 14 hours The reaction product was cooled to ordinary temperature and 80 per cent sulphuric acid (8 0 g) was added drop by drop, under constant stirring, and heated at 50–55° for another 4 hours Anhydrous sodium acetate was added to convert the sulphuric acid to sodium sulphate as otherwise it causes decomposition during recovery of acetic acid by fractionation The solid sodium sulphate so formed was removed by filteration and the residual liquid fractionally distilled The fraction distilling upto 125° consisted mostly of acetic acid, the fraction collected between 125–175° was a mixture of several terpenes A small amount of bornyl ester distilled between 175–185° along with terpenes The main ester fraction distilled at 105–120°/25 mm A very high boiling polymerised product was left in the flask as residue was not further studied

Hydrolysis of bornyl ester to borneols was carried out with methyl alcoholic potash as described before The yield of borneol was 55 g (35 7% of theory)

In the following three tables are described the results obtained by varying several of the factors referred to above, with α-pinene 136 gm, acetic acid 130 g, acetic anhydride 30 g, and boric anhydride 2 0 g in all the experiments

TABLE II(*a*)

Influence of varying the initial period of reaction before addition of sulphuric acid

Expt No	Initial time of reaction in hours	Reaction time in hrs with sulphuric acid	Amount of sulphuric acid (60%) in grams	Reaction temperature after addition of sulphuric acid (°C)	Yield of borneols on hydrolysis of the ester in grams
1	25	7	15	55–60	30 5
2	20	7	15	55–60	36 5
3	15	7	15	55–60	50 0
4	12	7	15	55–60	48·0

TABLE II(*b*)

Influence of varying (i) *the concentration,* (ii) *the amount of sulphuric acid,* (iii) *the time of reaction, after addition of sulphuric acid*

Expt No	Initial time of reaction in hours	Reaction time in hrs with sulphuric acid	Amount of sulphuric acid in grams	Reaction temperature after addition of sulphuric acid (°C)	Yield of borneols on hydrolysis of the ester in grams
1	15	7	20 (50%)	55–60	40 5
2	15	6	15 (60%)	55–60	48 0
3	15	5	12 (70%)	55–60	50 0
4	15	4	8 (80%)	55–60	52 0
5	15	4	6 (90%)	55–60	49 0
6	15	3 5	4 (98%)	55–60	45 0

The time of reaction (after addition of sulphuric acid) and the amount of sulphuric acid was decreased with the increase of the concentration of the acid as otherwise large amount of polymerised products are formed

TABLE II(*c*)

Influence of varying the reaction temperature after addition of sulphuric acid

Expt No	Initial time of reaction in hours	Reaction time in hrs with sulphuric acid	Amount of sulphuric acid (80%) in grams	Reaction temperature after addition of sulphuric acid (°C)	Yield of borneols on hydrolysis of the ester in grams
1	15	4	8	45–50	50 0
2	15	4	8	50–55	55 0
3	15	4	8	55–60	52 0

It will be noticed that the temperature range of 50–55° is conducive to the best of yields

β-Pinene to borneols

In the case of β-pinene the additional use of sulphuric acid along with the catalyst boro-acetic anhydride does not much improve the yield of borneols. Experimental conditions were identical as in the case of α-pinene β-Pinene is readily attacked by sulphuric acid, resulting in the formation of large amounts of polymerised products. The yield of borneol was improved to 24.7 per cent from 18.8 per cent Results of some experiments are given in the following table.

TABLE III

(β-Pinene 136 g, acetic acid 130 g, acetic anhydride 30 g, Boric anhydride 2 g)

Expt No	Initial time of reaction in hours	Time of reaction in hrs after addition of sulphuric acid	Amount of sulphuric acid in grams	Temperature of reaction after addition of sulphuric acid (°C)	Yield of borneols after hydrolysis of the ester
1	14	6	15 (60%)	50–55	35 0
2	14	5	12 (70%)	50–55	36 5
3	14	4	8 (80%)	45–50	38 0

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