Pakistan J. Sci. Ind. Res., Vol. 31, No. 8, August 1988

DIRECT ISOMERIZATION AND ESTERIFICATION OF α-PINENE TO BORNYL AND ISOBORNYL ACETATES

M. Riaz, M. Hanif, Mushtaq Ahmed and F.M. Chaudhary

PCSIR Laboratories, Lahore-16

(Received March 30, 1986)

Isomerization of α-pinene to bornyl and isobornyl acetates in the presence of acetic acid and bor-acetic acid anhydride, under different conditions of time, temperature, and concentration of the catalyst have been studied. The optimum conditions were obtained both with boric acid and boron trioxide. The isomerization products were analysed and identified by gas chromatography.

Key words: Esterification, α-pinene, Bornyl/Isobornyl acetates.

INTRODUCTION

α-Pinene and β-pinene constitute about 50% of the Pakistan turpentine oil which is obtained from the oleoresin of *pinus roxburgii* and are the starting materials for the preparation of bornyl and iso-bornyl acetates and a host of other commercially important chemicals. The isomerisation of α-pinene to bornyl and isobornyl acetates has been studied by many workers. Acharya *et al* [1] prepared bornyl acetate first by the dehydrohalogenation of bornyl chloride to camphene followed by a number of steps, when the end product was obtained. Mulany and his co-workers [2] evolved a single step isomerization and esterification of α-pinene to bornyl esters by treating α-pinene with aromatic hydroxy carboxylic acids e.g. salicylic [3] and hydroxy nerphthoic acids. The various other catalysts employed were benzoic acid, oxalic acid [4], inorganic salts [5], activated alumina [6, 7], activated clay [8, 9] and silica gel [10]. The nature of the reaction products obtained depended upon the type of isomerisation catalysts and reaction conditions.

The present studies were undertaken to evolve a single step reaction to produce bornyl and isobornyl acetates from α-pinene because these esters are of commercial importance being the starting material for camphor. The catalytic system employed is bor-acetic anhydride. The reactions were carrried out at a temperature range of 50-150°. The other reaction parameters studied were the reaction time and the catalyst concentrations. The results are being presented in this communication.

EXPERIMENTAL

Materials. Technical grade α-Pinene was purified by steam distillation and the purity was checked by gas chromatography. Glacial acetic acid and acetic anhydride were dried before use. Analytical grade boric acid and boron trioxide (E. Merck) were used.

Procedure. α-pinene (31.5 g, 0.25 mole), glacial acetic acid (30 g, 0.5 mole) acetic anhydride (5.1 g, 0.05 mole) and a boron trioxide (0.557 g, .008 mole) were taken in a 250 ml. round bottom flask, equipped with a magnetic stirrer and condenser. The flask was immersed in an oil bath at the desired temperature. The contents were heated, for the desired reaction times; heating was then discontinued and the contents of the flask were transferred to a 500 ml separating funnel.

Sufficient water was added and the lower acidic layer was drained out and a discarded. The upper oily layer was washed thorougly with water till it was neutral. The oily layer was transferred to a round bottom flask and subjected to steam distillation till it gave no oily drops. The steam distillate was transferred to a separating funnel and the upper oily layer was collected and dried over anhydrous sodium sulphate. Similar experiments were performed by changing various parameters of temperature, time and concentration of the catalyst.

Analysis. The reaction product was analysed on a Pye-Unicam 104 Gas Chromatograph fitted with an 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 split ratio of 1:60 and sample size 0.1 µl. The temperature was programmed as 50° for 4 min. with 4/min increse to 100°, detector temperature 250° and injection temperature 200°.

RESULTS AND DISCUSSION

Isomerization of α-pinene to bornyl and isobornyl acetates has been studied in the presence of acetic acid and bor-acetic acid anhydride. In order to find out the effect on the reaction products, the reaction conditions studied in detail were: (i) Reaction temperature, (ii) Reaction time and (iii) Amount of catalyst used. The results under the varying reaction conditions of temperature, time of reaction and the amount of catalyst have been tabulated in the Table 1-4. These studies have provided full information regarding the optimum conditions for the maximum yield of bornyl and isobornyl acetates.

Effect of temperature. The effect of temperature on the isomerization of α-pinene to bornyl and isobornyl acetates in the presence of bor-acetic acid anhydride (formed by acetic anhydride and boron trioxide) in acetic acid has shown that the isomerization does not occur at 50° (Table 1) but beyond that reaction product starts forming till a maximum conversion is obtained at 110°. (Fig. 1-2). The effect of temperature on the isomerization is gradual till it reaches the maximum and then there is a decline in the formation of the esters. The isomerization of α-pinene to acetates under the influence of reaction temperature has been observed to be directly related to the formation of camphene.

Table 1. Influence of temperature on the isomerization of α-pinene.
α-Pinene = 31.5 g; Acetic acid = 30 g; Acetic anhydride = 5.1 g; B_2O_3 = 0.557 g; Time 20 hours.

S. No.	Recovery %	Temperature °C	(1) α-Pinene	(2) Camphene	(3) α-Terpinene	(4) Limonene	(5) γ-terpinene	(6) p-Cymene	(7) Terpinolene	(8) Fenchol	(9) Bornyl-acetate
1.	88	50	99.34	—	—	—	—	—	—	—	—
2.	97.6	70	24.29	22.96	—	11.49	—	0.81	2.60	6.55	14.66
3.	87.3	90	0.96	16.33	0.84	21.64	0.88	1.85	8.55	8.78	23.36
4.	85.71	110	0.40	14.85	0.63	18.69	0.49	5.51	7.32	8.23	25.04
5.	73	130	0.50	16.38	0.64	20.42	0.79	7.39	8.53	8.20	24.09
6.	68.25	150	0.45	16.58	0.18	20.69	0.40	—	10.65	7.90	23.72

Table 2. Influence of temperature on the isomerization of α-pinene.
α-Pinene = 31.5 g; Acetic acid = 30 g; Acetic anhydride = 5.1 g; Boric acid = 1 g; Time 20 hours.

S. No.	Recovery %	Temperature °C	(1) α-Pinene	(2) Camphene	(3) α-Terpinene	(4) Limonene	(5) γ-terpinene	(6) p-Cymene	(7) Terpinolene	(8) Fenchol	(9) Bornyl-acetate
1.	90.47	50	99.20	—	—	—	—	—	—	—	—
2.	93.65	70	17.02	24.29	0.01	0.08	0.08	3.67	0.13	5.92	9.29
3.	79.36	90	3.56	25.09	0.46	24.69	0.36	2.79	7.50	5.64	15.37
4.	85.71	110	0.50	19.06	2.21	26.73	1.74	2.87	13.43	4.39	16.79
5.	82.50	130	1.79	19.87	0.39	27.34	1.02	0.64	20.30	5.64	21.69
6.	69.84	150	1.42	16.09	0.86	22.17	0.06	0.81	22.17	5.83	17.07

Table 3. Influence of time on the isomerization of α-pinene.
α-Pinene = 31.5 g; Acetic acid = 30 g; Acetic anhydride = 5.1 g; B_2O_3 = 0.557 g; Temperature 110°

S. No.	Times in Hours	Recovery %	(1) α-Pinene	(2) Camphene	(3) α-Terpinene	(4) Limonene	(5) γ-terpinene	(6) p-Cymene	(7) Terpinolene	(8) Fenchol	(9) Bornyl-acetate
1.	5	92	2.15	21.93	0.54	27.43	0.54	0.09	15.33	6.77	21.53
2.	10	92	2.51	19.77	0.32	25.39	1.74	0.32	21.09	6.03	22.29
3.	15	85	2.31	15.84	—	24.36	1.41	—	25.58	6.86	23.13
4.	20	79	2.06	15.54	—	22.97	1.55	—	23.39	7.39	25.41
5.	25	95	1.88	16.31	0.28	21.34	2.16	0.15	18.25	7.20	25.83
6.	30	79	1.37	16.83	1.36	19.01	0.89	4.54	13.49	8.76	28.97
7.	35	70	2.02	16.62	0.57	22.81	1.94	0.84	17.78	5.99	25.36
8.	40	82.5	1.54	20.25	0.30	25.70	1.37	0.75	18.38	5.74	24.48

Table 4. Influence of the amount of catalyst on the isomerization of α-pinene.
α-Pinene = 31.5 g; Acetic acid = 30 g; Acetic anhydride = 5.1 g; Temperature = 110°; Time 20 hours.

S. No.	Amount of Catalyst	Recovery	(1) α-Pinene	(2) Camphene	(3) α-Terpinene	(4) Limonene	(5) γ-Terpinene	(6) p-Cymene	(7) Terpinolene	(8) Fenchol	(9) Bornyl-acetate
1.	0.557 x 2	84	1.79	19.87	0.39	27.34	1.02	0.64	20.31	5.04	21.69
2.	0.557 x 4	82	1.68	20.24	—	26.63	1.42	—	20.74	4.90	20.86
3.	0.557 x 6	92	1.69	20.51	—	26.44	1.74	0.45	21.68	5.24	20.94
4.	0.557 x 8	92	1.61	20.17	—	25.75	1.71	—	21.40	5.24	20.61
5.	0.557 x 10	88.88	1.87	20.59	1.22	25.30	1.79	0.74	17.23	4.27	21.19

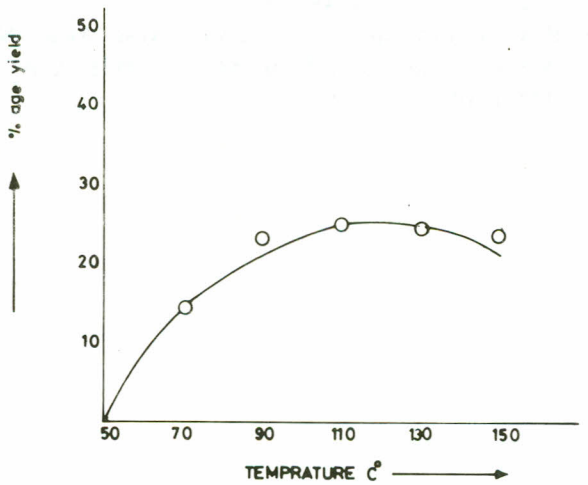


Fig. 1. Effect of temperature on the yield of bornyl and isobornyl acetate in presence of boron trioxide.

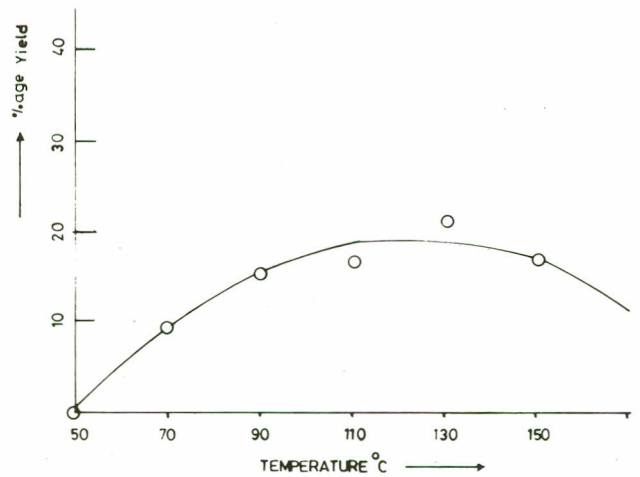
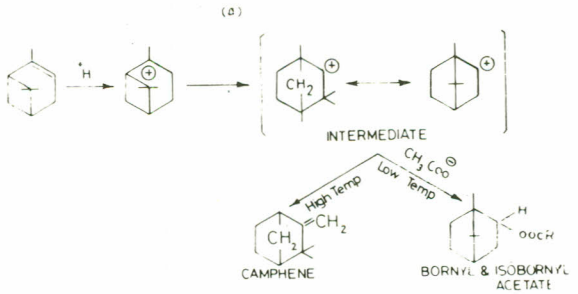


Fig. 2. Effect of temperature on the yield of bornyl & iosobornyl acetate in presence of boric acid.

The yield of camphene decreases with the increase in the temperature and reaches a minimum at 100°, then increses slightly. It is interesting to note that overall yields of these two products over the entire range of temperature remain almost constant. The formation of the products might be explained by postulating that a common intermediate is formed which under the influence of temperature gets converted either to camphene or to esters of borneol and isoborneol.



The other catalyst studied under similar conditions was boric acid, the quantity of which was equivalent to that of boron trioxide. The results of the series of experiments are shown in Table 2.

The conversion of α-pinene to isomerized products in the presence of boric acid has also been found to be maximum at 110°.

Effect of Time. The effect of reaction time on the isomerization reaction was studied at 110°; the temperature at which maximum yield of bornyl and isobornyl acetate is obtained. There is an increase in the reaction product, with the increase in reaction time (Table 3). A maximum yield was obtained after 30 hrs. and then there was a decline in the isomerization product. There is a slight variation in the yield of other by-products like, fenchol, p-cymene and γ-terpinene under all the reaction conditions.

Effect of the Amount of Catalyst Used. The effect of the amount of catalyst on the isomerization of α-pinene has been shown in (Table 4). It is observed that the quantity of the catalyst has no effect on the yield of bornyl and isobornyl acetates. The yields of other by-products like camphene, limonene, α-terpinene p-cymene, γ-terpinolene and fenchol also remain almost uneffected through out the catalyst quantity variation studies.

Even though many catalysts have been employed for the isomerization studies of α-pinene to bornyl and isob-

ornylacetates yet the results found in the case of bor-acetic anhydride in acetic acid have been very promising. The quantity of the catalyst has been calculated on the basis of boron trioxide.

Acknowledgement. Authors are thankful to Mr. Islam-Ud-Din, J. Technician for his help during the studies.

REFERENCES

1. B.G.S. Acharya and T.S. Wheeler, J. Univ. Bombay, **4,** 118 (1935).
2. H.M. Mulany and E.R. Watson, J. Indian Chem. Soc., **3,** 253 (1956).
3. M.S. Kharasch and W.B. Reynolds, J. Org. Chem., **9,** 148 (1944).
4. Saburo Akiyoski, Repts. Imp. Ind. Research Inst., Osaka, Japan **17**(11), 1 (1937); C.A. **31,** 8526[6] (1937).
5. Wm. M. Dehn and Kisly E. Jakson, J. Am. Chem. Soc. **55,** 4284 (1933).
6. Aldo E.A. Mitta and Ildefonso Al-varez, Rep. Argentina, Ministerio ind. y com. nacian, Direc-gen. Ind. Manuf; Inst. Technol, Ser. A. **5,** 3 (1950); C.A., **46,** 100i (1952).
7. Paul Adrien Mulcey, Bull. Inst. Pin., 177-81, 201-6 (1931), C.A. **26,** 718 (1932).
8. M. Nazir, M. Ahmed and F.M. Chaudhary, Pakistan J. Sci. Ind. Res., **19,** 175 (1967).
9. Aldo E.A. Mitta, Industria y quimica (Buenos Aires) **13,** 94 (1951), C.A. **48,** 3309b (1954).
10. B.A. Arbuzov and Z.G. Isaeva, Izvest. Akad. Nauk S.S.S.R., otdel kim Nauk 843-9 (1953)., C.A., **49,** 1654i (1955).