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MICROWAVE-ASSISTED α-PINENE ACIDIC CATALYTIC ISOMERISATION

József Zsolt SZÜCS-BALÁZS,[a] Maria COROŞ,[a] Diana MOLNAR[a] and Mircea VLASSA[b*]

[a] "Raluca-Ripan" Institute of Chemistry Research, Babeş-Bolyai University, 30 Fântânele, 400294, Cluj-Napoca, Roumania
[b] Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University, 11 Arany János, 400028, Cluj-Napoca, Roumania

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A comparative study of microwave assisted α-pinene acidic catalytic isomerisation reactions with near-critical water procedure under microwave irradiation is presented. This study can be performed because in both cases the mechanism is similar, namely an acidic-catalyzed rearrangement. The non-critical method technique is milder using a lower temperature and pressure and a shorter reaction time than near-critical water conditions. The general aspect of the selectivity of the reaction products is changed, being higher for α-terpinolene and γ-terpinolene and lower for limonene and camphene compared to the non-critical conditions.

INTRODUCTION

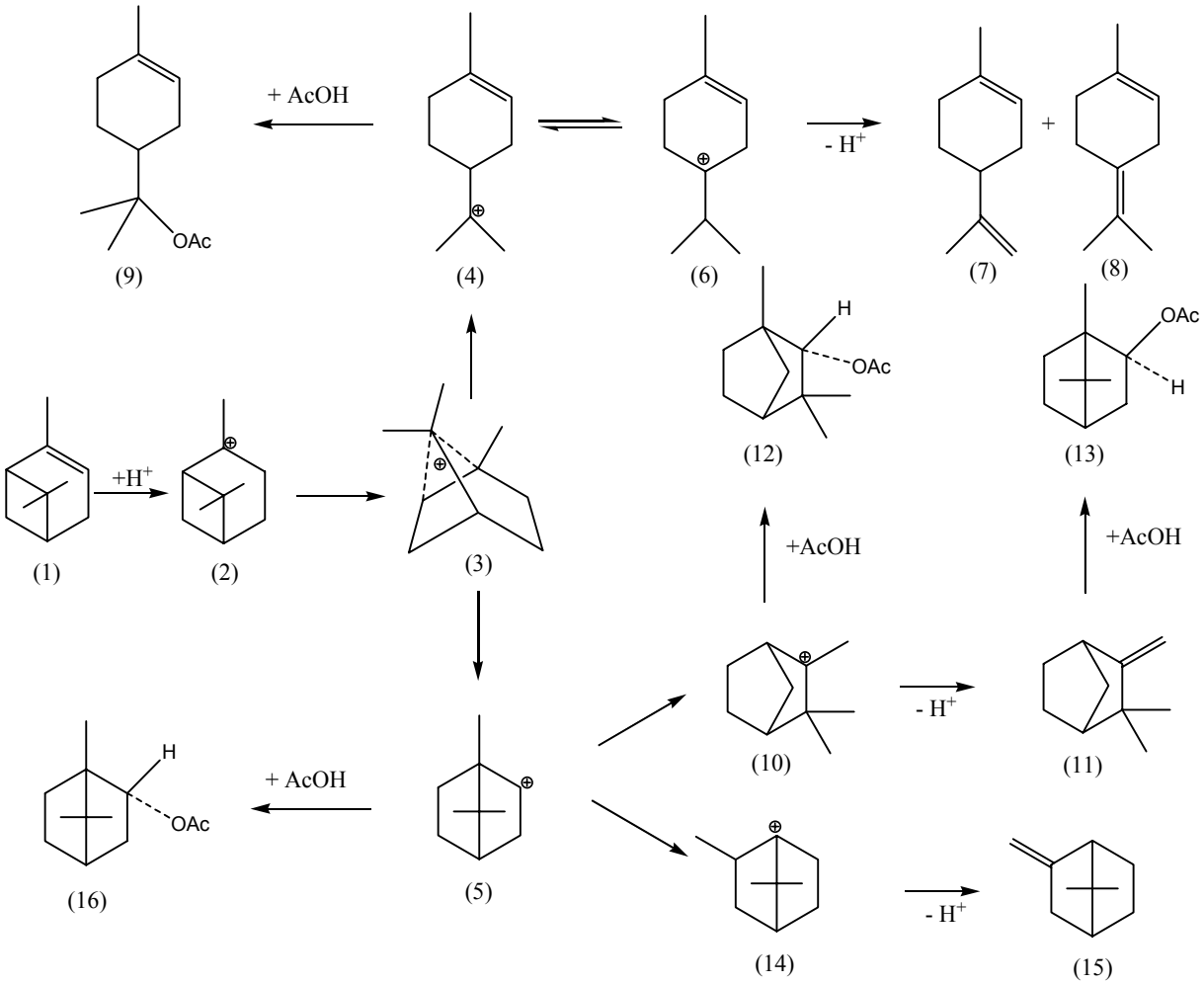
Because of its use as a fragrance intermediate and for technical applications, α-pinene **(1)** is a key compound among industrially used terpenes.[1] From the reaction of α-pinene with acetic acid two series of products can be obtained (see Scheme 1): esters - bornyl- **(16)**, fenchyl- **(12)** and α-terpinyl-acetate **(9)** and compounds with the p-menthadiene structure, resulted by isomerisation reactions such as camphene **(11)**, limonene **(7)**, terpinolene **(8)**, α-terpinene, γ-terpinene, *p*-cymene and α-phellandrene.

The esters usually are prepared in two steps (first step, the treatment of α-pinene with liquid mineral acid and second step, the esterification with acetic anhydride in the presence of liquid mineral acids),[2,3] but this method shows the disadvantage of too large amount of catalysts, corrosion of equipments, complicated technique and serious environmental pollution. From these reasons, many researches[2-8] have been done to develop a clean process with a high selectivity towards the esterification products starting directly from α-pinene. Compared with the current two-step process, this direct process is more convenient for the preparation of esters. A lot of studies are dedicated to enhance the selectivity of products and the conversion of the reagents.[4-8]

In the case of isomerisation reactions the yields of the products strongly depend on the acidity and on the pore structure of catalyst, the nature of the acidic sites (Brønsted or Lewis) and the operating conditions.[9,10]

During the last two decades there has been a great interest in the application of microwave energy as a means of rate enhancement in synthesis,[11] due to the fact that the chemical reactions are affected by overheating, polarization, dielectric properties, solvent sensitivity, spin alignment and (partially) nuclear spin rotation produced by microwave irradiation. This framework represents the major effects of microwaves, which are not always equally important. In this field many reviews[12-17] or books[18-21] have been published. In the terpene chemistry microwaves were applied for solvent free microwave distillation[22] and very seldom in the synthesis of these compounds.[23]

* Corresponding author: mvlasa@chem.ubbcluj.ro



Scheme 1

Stolle[23] achieved the isomerisation of α- and β-pinene in near-critical water and supercritical lower aliphatic alcohols. Generally, two pathways occur – pyrolysis, when supercritical alcohols were used, or acidolysis, when supercritical water was employed. The different behavior in function of the solvent used can be explained by increased availability of the protons in near-critical water (heated at 270°C and at 80 bar) when the autoprotolysis of the water is enhanced. In this case, the main products of the reaction were from the p-menthadiene series. When supercritical alcohols were used thermal pyrolysis took place, due to the formation of radical reaction intermediates.

We achieved a comparative study of the acidic catalytic reactions of α-pinene with microwave activation with the reaction in near-critical water conditions assisted by microwave irradiation, in order to examine, working in milder conditions, the differences that appear in the reaction yields and the selectivity of the products.

RESULTS AND DISCUSSIONS

Experiments were conducted in order to study the behavior of α-pinene in acetic acid with or without different acidic catalysts. After cooling the mixture to ambient temperature the conversion of α-pinene was found to be almost quantitative in all reactions.

Taking into consideration the fact that we used acetic acid as solvent and as catalyst, both acidolysis and esters products were obtained (see Table 1).

Examining the results (Table 1) we can see that for the preparation of bornyl and fenchyl acetate the best method is to work only in the presence of acetic acid, for iso-bornyl acetate is recommended to use acetic acid in the presence of *para*-toluenesulfonic acid and for terpenyl acetate boric acid is the best choice.

The results obtained under microwave irradiation in the presence of the acidic catalyst were compared with those obtained in near-critical water method by Stolle (see Table 2).[23] This fact is

possible because these authors sustain that by using near-critical water the availability of protons is enhanced, the main products of the reaction being from the p-menthane series. This behavior can be attributed to proton-catalyzed rearrangement mechanism, and the addition of other acids-catalyzing reactants like mineral acids, zeolites or heteropolyacids is not necessary.

In the case of rearrangement of **(1)** in near-critical water under microwave irradiation the majority of products originated from the acidolysis reaction pathway, as in case of our experiments. This can be explained by the fact that from the two competitive reactions, namely the pyrolitic ring cleavage and reaction via carbocations (produced by addition of a proton to the double bond) the first one has a higher activation energy. Stolle[23] worked at 270°C and this temperature was not high enough to pyrolyze great amounts of **(1)**, and, as a result, only small quantities of pyrolytic products were formed (see Table 2).

Table 1

Conversion and selectivity of the products formed by isomerisation of α-pinene using acetic acid and other acidic catalysts under microwave irradiation

No	Catalyst	C (%)	Selectivity (%)										
			Isomerisation products						Ester products				Unknown
			Bicyclic terpenes		Monocyclic terpenes								
			Fen	Cf	α-T	Lim	γ-T	T	Fac	Bac	iso-Bac	Tac	
1	A.A.	99	4.2	11	1.6	39.7	1.4	11.4	9.3	15.4	1	2	3
2	A.A.+$B(OAc)_3$	98	4.3	14.7	1.9	32.9	1.9	12.8	6.6	12	1.2	7.4	4.3
3	A.A.+H_3BO_3	98	4.1	13.5	09	32.4	1.6	11.6	6.6	11.6	0.7	9.1	8.6
4	A.A.+B_2O_3	97	4.3	14.5	4.4	32.5	3.3	17.7	4.8	10.1	2.2	2	4.6
5	A.A.+APTS	100	1.1	10.2	0.1	17.9	5.3	9.9	3.2	4.6	14.3	2.1	31.3

A.A. = Acetic acid, Fen = Fenchene; Cf = Camphene; T = Terpinolene; α-, γ-T = α-, γ-Terpinene; Lim = Limonene; Fac = Fenchyl acetate; Bac = Bornyl acetate; iso- Bac = iso-Bornyl acetate; Tac = Terpenyl acetate; C = Conversion, APTS = *para*-Toluenesulfonic acid.

Table 2

Results of rearrangement of α-pinene in near-critical water, with 100% conversion, according to Stolle and coworkers [23*]

Compound	Yield (%)	Reaction type
Limonene	14	P,A
Alloocimene	9	P
Pyronene	4	P
Terpinolene	20	A
γ-Terpinene	24	A
α-Terpinene	12	A
α-Phellandrene	2	A
p-Cymene	5	A
Camphene	3	A
Unknown	7	?

*Reaction conditions: 250 µl α-pinene, 15 ml 0.03 M NaCl solution, 80 ml quartz vessel, heating 10 min, reaction time 60 min, cooling 20 min, P_{max}: 1.2 kW, microwave Synton 3000. A = Acidolysis, P = Pyrolysis.

Working in milder conditions than Stolle,[23] in our case the pyrolitic reactions did not occur, and as a result alloocimene and pyronene were not formed (Tables 1 and 2). Also the general aspect of the product yields is dramatically changed. Thus, in the case of our reaction conditions the higher yields were obtained in the case of limonene (39.7% in presence of acetic acid compared to 14% in near-critical water method) and of camphene (14.7% in boric acetate in acetic acid compared to 3% in near-critical water procedure). For terpinolene the yields are approximately the same (17.7% in presence of boric oxide compared to 20% in near-critical water). For α-terpinene and γ-terpinene the yields are better in near-critical water method (12% and 24%, respectively, compared to only 4.4% in the presence of boric oxide in acetic acid and 5.3% in the presence of *para*-toluenesulfonic acid in acetic acid, respectively, in our method). We cannot identify α-phellandrene and

p-cymene, products that appear in traces in near-critical water method (2% and 5%, respectively). *p*-Cymene can be formed as a side reaction of the endocyclic α-terpinene and γ-terpinene isomers due to their tendency to form the thermodynamic stable aromatic compounds. The reason that we could not observe the formation of p-cymene consisted in a very low yield of α-terpinene and γ-terpinene isomers obtained in our case.

The isomerisation products/ester products ratio is in favor of the isomerisation one (see Table 3). Both products of the reactions have the same starting mechanism, namely addition of the proton to a double bond. By the addition of acetic acid to the resulted carbocations the esters are formed; the isomerisation products appear by a rearrangement of the carbocations. According to these observations, to name the formation of bornyl-, isobornyl-, terpenyl-, and fenchyl-acetate an esterification reaction, as sometimes appear in literature,[8] is incorrect.

Table 3

Isomerisation products/esterification products ratio

No	Catalyst	Selectivity (%)		Isomerisation products/ esterification products
		Isomerisation products	Esterification products	
1	A.A.	69.4	27.7	2.5
2	A.A.+$B(OAc)_3$	68.4	27.1	2.5
3	A.A.+H_3BO_3	64.1	28.1	2.3
4	A.A.+B_2O_3	77.0	19.2	4.0
5	A.A.+APTS	44.6	24.2	1.8

A.A= Acetic acid

EXPERIMENTAL

The microwave reactions were carried out in a CEM Discovery Labmate microwave oven with irradiation powder of 300 W; with continuous irradiation on all power range in 1W steps. The power of the microwave irradiation could be controlled via a pressure-, temperature-, or power-regulated program. The temperature of all vessels was controlled by IR-sensor. The feedback control of the pressure was made by pressure sensor Discovery IntrelliVent and pressure attenuator Discover IntrelliVent. In this case, the power input was limited by temperature T_{lim}= 150°C, pressure p_{lim}= 17 bar and power = 0.1 kW. For heating up to T_{lim} 6 min and for cooling down 20 min were used. The 10 ml glass vessels were used and were filled with maxim 5 ml of solution.

The GC analysis was carried out using a Hewlett Packard 5890 series II instrument. SPB^{TM} capillary column (60m x 0.32mmx0.25μm film thickness) and SUPELCOWAX^{TM} 10 capillary column (60 m x 0.32 mm x 0.5μm film thickness) were used with H_2 as carrier gas (0.2 ml/min). The second capillary column is more polar than the first one and both were used for analysis of all reaction products. Both capillaries were used for analysis of each compound. FID detector temperature was 270°C. GC oven temperature was kept at 60°C for 3 min and programmed to 210°C at a rate of 4°C/min, and kept constant at 210°C for 20 min; split ratio was adjusted to 80:1. The injector temperature was set to 260°C. The qualitative and quantitative analysis of the mixtures of reactions was made using internal standards.

Reaction of α-pinene with acetic acid, solid acidic catalysts under microwave conditions

The mixture of α-pinene (6 g, 0.043 mmol), acetic acid (7.92 g, 0.132 mmol) and catalyst (0.06 g) was heated into microwave oven at 150°C. Microwave power was 100 W and pressure was 6 bars. The reaction mixtures were analyzed in all methods by GC.

CONCLUSIONS

In conclusion, compared to near-critical water method, the procedure that uses microwave assisted of α-pinene acidic catalysis isomerisation reactions in non-critical conditions is milder, using a lower temperature (150°C compared to 270°C), a lower pressure (6 bar compared to 80 bar) and a shorter reaction time (45 min compared to 90 min). The general aspect of the reaction selectivity is changed, being higher for limonene and camphene and lower for α-terpinene and γ-terpinene than in near-critical water procedure.

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