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# Flash Vacuum Thermolysis of Terpenic Compounds in the Pínane Series

Laurent Lemée<sup>a</sup>, Max Ratier<sup>b</sup>, Jean-Georges Duboudin<sup>c</sup> & Bernard Delmond<sup>b</sup>

<sup>a</sup> Institut du Pin, Université Bordeaux I, 351, cours de la Libération , 33405, Talence Cedex, FRANCE

<sup>b</sup> Laboratoire de Chimie Organique et Organométallique (URA 35 CNRS), Université Bordeaux I, 351, cours de la Libération, 33405, Talence Cedex, FRANCE

<sup>c</sup> Ecole Nationale Supérieure de Chimie et de Physique de Bordeaux, 351, cours de la Libération, 33405, Talence Cedex, FRANCE Published online: 23 Sep 2006.

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# FLASH VACUUM THERMOLYSIS OF TERPENIC COMPOUNDS IN THE PINANE SERIES

# Laurent Lemée<sup>a</sup>, Max Ratier<sup>b</sup>, Jean-Georges Duboudin<sup>c</sup> and Bernard Delmond<sup>\*b</sup>

a) Institut du Pin, Université Bordeaux I, 351, cours de la Libération 33405 - TALENCE CEDEX (FRANCE)
b) Laboratoire de Chimie Organique et Organométallique (URA 35 CNRS) Université Bordeaux I, 351, cours de la Libération 33405 - TALENCE CEDEX (FRANCE)
c) Ecole Nationale Supérieure de Chimie et de Physique de Bordeaux, 351, cours de la Libération, 33405 - TALENCE CEDEX (FRANCE)

Abstract : The flash pyrolysis of various derivatives (hydrocarbons and oxygenated compounds) in the pinane series has been studied. We observed a high degree of conversion and good selectivity.

Thermal isomerization has been used for many years to perform the opening of the cyclobutane ring, specific to the pinane serie derivatives<sup>1</sup>, and leading to aliphatic terpenoïds.

In many cases<sup>2-6</sup>, a complex mixture was obtained ; however, only the pyrolysis of  $\beta$ -pinene constituted an industrial process<sup>7</sup> to myrcene, a versatile precursor of perfumery chemicals.

Hence, we have examined the behaviour of some pinane derivatives under flash vacuum pyrolysis conditions<sup>8,9</sup>, to increase the selectivity of the

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<sup>\*</sup> To whom correspondence should be addressed.

fragmentation and to obtain the more useful raw materials for the perfume industry.

Flash vacuum thermolysis is a process allowing the fragmentation, according to a monomolecular way, of compounds with a sensitive structure. The use of high temperatures and low contact times under reduced pressure, avoids intermolecular secondary reactions in the oven.

These particular conditions are suited to terpenic structures as on the pinane series, in which some works 10,11 have already been performed.

During this present study, we have used a flash pyrolysis unit under reduced pressure (5.10<sup>-2</sup> mm Hg) and variable temperatures (until 900°C). We report the results of the pyrolysis of  $\beta$ -pinene 1,  $\alpha$ -pinene 2, cis-pinane 3, 2,10-epoxy pinane 4 and 2,10-dihydroxy pinane 5.

For each of the compounds, we have determined optimum conditions (temperature, pressure, contact time); the crude mixture has been analyzed by gas chromatography-mass spectrometry coupling.

# Discussion

The flash pyrolysis of  $\beta$ -pinene **1** (scheme 1) at 900°C gave with a high ratio transformation (R.T. : 90%) a major product (87%), myrcene **6**.

This compound is a very important industrial raw material for both the perfume and vitamin industries.



In similar conditions, the pyrolysis of  $\alpha$ -pinene 2 (scheme 2) gave (yields 85%) a crude product mixture. From gas chromatography analysis we observed the presence of dipentene 7 (42%), allo-ocimenes 2 (32%), ocimene 10 (4%) and isomer pyronenes 11 (22%).





The decrease in oven temperature (750°C) allowed us to increase the ocimene/allo-ocimene ratio, however a high yields of starting material was recovered. To avoid this drawback we used a silica filled tube, increasing the contact time of  $\alpha$ -pinene in the oven. The degree of conversion became convenient (95%) but we observed total disparition of ocimene and isomerization of acyclic hydrocarbons to pyronenes.

During the pyrolysis of cis-pinane  $\underline{3}$  (scheme 3) the thermolysis tube was packed with silica to improve the conversion of cis-pinane. The 2,6-dimethyloctadiene (dihydromyrcene)  $\underline{12}$  was obtained as main product (82%) with good yields (85%).



The flash pyrolysis of oxygenated compounds  $\underline{4}$  and  $\underline{5}$  (scheme 4) prepared from  $\beta$ -pinene by epoxidation ( $\underline{4}$ ) then acid hydrolysis ( $\underline{5}$ ) gave a crude mixture, in which the major component was myrtenal  $\underline{14}$  (58-78%), the primary product from thermal isomerization. Further pyrolysis led to perillaldehyde  $\underline{15}$  and acyclic aldehyde  $\underline{16}$ .



#### Conclusion

From this study, the flash vacuum pyrolysis of pinane derivatives appears to be a particularly efficient process to realize the fragmentation of the cyclobutane ring with a good selectivity. In the most cases yields and degree of conversion were convenient to obtain useful intermediates (myrcene, dihydromyrcene, myrtanal,...) for perfume industry.

## **Experimental section**

Gas-chromatography was performed with a DELSI IGC 121 FL (capillary column BP 20; 1 = 25 m; id = 0.22 mm). Starting materials ( $\alpha$ -pinene,  $\beta$ -pinene, cis-pinane, 1,2-epoxy-pinane) were commercial products.

### Apparatus

The reaction apparatus was an all-glass assembly, linked to a vacuum pump ( $5-10^{-2}$  mmHg), and consisting of a charging flask, preheater, reaction tube (quartz), backed up by a liquid-nitrogen trap and a receiver.

#### Procedure

Pyrolysis reactions were run on preparative scales by placing the starting materials in the charging flask, outside the thermolysis apparatus. Reactions were carried out at 650 to 900°C in the main oven and 250-300°C in the sublimation oven with pressures of  $10^{-2}$  mm. In practice, one has to pack the main oven with broken porcelain to increase the contact time; pyrolysis without the packing resulted in decreasing yields. The given temperatures have been shown to be most suitable for optimal conversion.

The pyrolyzate was analyzed by gas-chromatography (BP 20) and the products were identified by gas-chromatography (VARIAN 3300) coupled with a mass spectrometry (VG Micromass 16 F).

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