

Isomerization of β -Pinene

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β -Pinene can be converted quantitatively to α -pinene by palladium in the presence of hydrogen. Using an analytical micro sorption method it can be shown that the isomerization is almost always followed by a very slight hydrogenation and a small second isomerization. These secondary reactions occur to about the same extent on treatment of index-homogeneous Δ^3 -carene, *d*-limonene, α -pinene and terpinolene with the catalyst.

The isomerizations can be performed on a half micro scale and, in combination with micro sorption analysis, the method can be used to detect and estimate β -pinene in terpene mixtures.

In the field of terpenes, isomerizations are easily caused by the action of suitable agents. Most of these conversions are such that a complex mixture of products is formed. In the case of liquid terpene hydrocarbons it is very difficult to isolate pure compounds from these mixtures, and especially difficult to determine the quantities of the various compounds formed by isomerization. This can be clearly understood from, *e. g.*, the small boiling range of the terpenes, their ability to undergo further isomerizations during chemical isolation and their lack of evident physical identification properties; *cf.*, however, the work by O'Connor and Goldblatt¹.

Richter and Wolff² have reported the isomerization of β -pinene to α -pinene by palladium-black to be quantitative, but their experimental proofs for such a reaction are not fully convincing. Comparing the physical constants given by Richter and Wolff — the calculated n_D^{25} values are given in Table 1 — with those of terpenes purified to index homogeneity, see Widmark^{3,4}, one can assume most of their isomerized samples to be partly hydrogenated. It is not possible to calculate the extent of hydrogenation from their unanalysed refractive indices, as pinane is known to exist in *cis*- and *trans*-forms and as will be shown in this paper, the isomerization is followed by a second isomerization which forms products of higher refractive indices.

Most of the isomerizations by Richter and Wolff were carried out in ether solution but they have demonstrated the reaction to proceed (at a reduced rate) even without any solvent. Their reactions were performed on a macro scale using about 10 % palladium-black and the isomerization products were

Table 1. Calculated n_D^{25} values from Richter and Wolff's² isomerizations.

Starting material n_D^{25}		After isomerization n_D^{25}			
<i>d</i> - α -Pinene	1.4629 ^a	6 h	8 % Pd		1.4628
<i>d</i> - α -Pinene	1.4631	6 h	7.5 » Pd		1.4615
<i>l</i> - α -Pinene	1.4659	6 h	17.5 » Pd		1.4638
β -Pinene	1.4767 ^b	7 h	8 » Pd		1.4624
β -Pinene	»	6 h	— » Pd		1.4622
β -Pinene	»	1 h ^c	— » Pd		1.4606
β -Pinene	»	— ^c	— » Pd		1.4601

a) Index-homogeneous α -pinene = 1.4632, cf. Widmark³

b) » β -pinene = 1.4763, cf. Widmark⁴

c) by shaking.

distilled at atmospheric pressure. They found the presence of hydrogen necessary — fully in accordance with the findings of the present author — and they introduced the hydrogen by bubbling or in some cases by shaking. Moreover, they found that when the catalyst was saturated first with hydrogen the isomerization could proceed in a nitrogen atmosphere; cf., however, Fig. 1, curve c. As seen in Table 1, there was a more marked hydrogenation in their isomerizations when shaking was employed.

In this investigation it was found most convenient — from an analytical point of view — to isomerize the undiluted terpenes (half micro scale) by shaking and to use about half a percent of palladium on barium carbonate as catalyst. This catalyst can be prepared under more controlled conditions than palladium-black. To minimize hydrogenation, the isomerizations were carried out in small ground-glass stoppered test tubes with a maximum free space of 2 ml of hydrogen gas. Isomerization produced by bubbling hydrogen at a slow rate over the catalyst was found to give irregular results. After the isomerization the terpenes were analysed for purity by a micro sorption method devised by Blohm⁵. From these analyses it is clearly demonstrated that the catalytic isomerization of β -pinene to α -pinene is a quantitative reaction, followed, however, by a small second isomerization.

The activity and the properties of the catalyst were investigated by determination of the time necessary for full conversion of β -pinene and by sorption analysis of the products formed.

ACTION OF THE CATALYST ON TERPENES

α -Pinene. Small samples of α -pinene, purified to index-homogeneity³, were shaken with controlled (see experimental part) Pd-BaCO₃-catalyst under different conditions. On sorption analysis, sorptograms — n_D^{25} plotted against the 5 μ l fraction numbers — were obtained, which showed mostly a slight upward slope in the beginning and a low peak at the end. It has not yet been found possible to calculate the amount of hydrogenation and isomerization products by comparison with sorptograms of mixtures of known composition

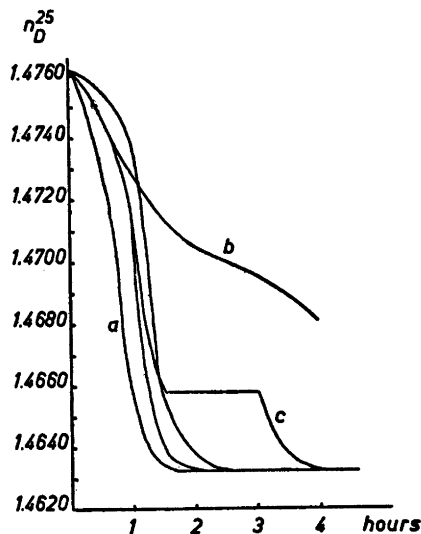


Fig. 1. Rate of isomerization. a) Normal rates using 50 to 200 mg Pd-BaCO₃ or 10–200 mg Pd-black. b) Incomplete isomerization using 2 mg Pd-black. c) Isomerization when the hydrogen was temporarily omitted.

as the peak constituent is unknown and the slope product, very probably pinane, has not yet been prepared in a state of index homogeneity. However, from sorptograms of mixtures of other index-homogeneous terpenes (*cf.* Widmark and Blohm⁶) one can assume the formation of by-products to be not more than a few percent each. Until a more accurate method is found the result of the isomerizations will be deduced from the figure of the sorptograms.

On shaking α -pinene with catalyst for one, four and twelve hours, there was a slight increase in both slopes and peaks. However, the variations caused by different samples of catalyst — prepared in exactly the same way — were almost of the same size.

Similar results were also obtained when the reaction was carried out in ether solution, when palladium-black was used, when the hydrogen was bubbled through the material, or when a freshly oxidized sample with a peak was employed.

β -Pinene. The time for full conversion of β -pinene to α -pinene varied mostly from half an hour to four hours depending on the sample of catalyst employed. Only those samples giving conversion within two hours were considered sufficiently active for use in this investigation. There was some dependency on the amount of catalyst used, but as seen from Fig. 1 very small amounts gave a sufficiently high rate of isomerization. 50 mg 5% Pd-BaCO₃ was found convenient to use for one millilitre samples. Calculated on the amounts of palladium, Pd-BaCO₃ gave a more rapid isomerization than Pd-black when very small amounts of catalyst were used. The presence of hydrogen was found to be essential for isomerization and when a tube was not properly filled with hydrogen no conversion took place (curve c, Fig. 1).

On sorption analysis after isomerization, sorptograms were obtained similar to those from α -pinene after treatment with the catalyst. One can therefore assume the second isomerization product to be formed from α -pinene.

Δ^3 -Carene, *d*-limonene and terpinolene. In a previous communication³ this author has studied the occurrence of β -pinene in Swedish sulfate turpentine. The content of β -pinene was calculated by comparing the sorptograms of isomerized and unisomerized samples, and by determining the amounts of β -pinene necessary to bring the sorptograms up to their original shapes. This analytical method was found useful, but upon isomerization of the last turpentine fractions unusual sorptograms were obtained which were explained by the presence of terpenes other than Δ^3 -carene and α - and β -pinene in the turpentine mixture.

It was therefore of interest to determine the action of the catalyst on other index-homogeneous terpenes, both alone and mixed with β -pinene. It was found that the changes in the sorptograms of Δ^3 -carene, *d*-limonene and terpinolene were almost the same as, or less than, in the case of α -pinene.

On isomerization of two component mixtures of these pure terpenes, with β -pinene as the minor constituent, sorptograms were obtained which resemble — with the exception given above — the ones containing the corresponding amount of α -pinene. On isomerization of a mixture of 17 % β -pinene, 10 % *d*-limonene, and 73 % Δ^3 -carene, a sorptogram was obtained which differed considerably from that of a mixture of 15 % α -pinene, 10 % *d*-limonene, and 75 % Δ^3 -carene. This observation was of interest as the last fractions of sulfate turpentine gave sorptograms, before and after isomerization, which resembled the corresponding ones from the first mixture.

Examination of the use of the catalytic isomerization method as an analytical tool to detect and calculate roughly the amount of β -pinene in turpentine mixtures, reveals that a few percent can be detected in favourable cases, *e. g.* the first fractions in the sulfate turpentine. The limit is set by the slight action of the catalyst on other terpenes. With small contents of β -pinene this action has to be controlled with each sample of catalyst. Presence of limonene seems to hamper the interpretation of the sorptograms. However, it is apparent that the isomerization method could be a good analytical aid, in combination with infra-red determinations, when analysing more complex turpentine mixtures.

EXPERIMENTAL PART

Preparation of the catalysts

Palladium on barium carbonate (5 % Pd). Barium carbonate was prepared from 7.5 ml barium chloride solution (33 g $\text{BaCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow 100$ ml) and 5.5 ml sodium carbonate (40 g $\text{Na}_2\text{CO}_3 \rightarrow 200$ ml). After decanting and washing several times with water 2.9 ml 1 *N* NaOH were added with vigorous shaking to the wet precipitate followed by 1.66 ml palladium chloride solution (5 g $\text{PdCl}_2 + 12.2$ ml conc. HCl $\rightarrow 50$ ml), 3.9 ml 1 *N* NaOH and after a minute, 2 drops of 35 % formaldehyde solution. After shaking for 20 minutes the catalyst was washed several times with water, the water being removed by centrifugation. Finally, the catalyst was filtered off using a sintered glass crucible, dried at 80° C, and stored in a desiccator.

Palladium-black. This catalyst was prepared in lots of 0.5 g according to Wieland⁷.

Sorption method. A micro sorption apparatus (column 250 \times i. d. 1.4 mm), fully conforming to Blohm's instructions, was used. 40.0 μl test samples were displaced with

abs. ethanol through the column and separated into 5 μ fractions. The silica gel (Davison, 922-08-226, through 200 mesh) was activated for 2 hours at 140° and 15 mm Hg. The refractometer, Bellingham & Stanley No. 402330, was calibrated against a standard plate n_D 1.5009. The thermostat was controlled to 25° \pm 0.02°. On reading the refractive indices of the 5 μ fractions, a fresh paper \sim 5 \times 5 mm was used for each determination.

Isomerization of β -pinene.

Samples of index-homogeneous β -pinene were isomerized using the two catalysts (see above) both by shaking in small ground-glass stoppered test tubes (8 \times 50 mm) filled with hydrogen and by bubbling hydrogen at a very slow rate through a narrow capillary over the catalyst. Similar results were obtained in each case, although sometimes the bubbling-method gave irregular results.

One ml samples of β -pinene were isomerized by shaking with different amounts of the two catalysts. The degree of isomerization was determined by reading the refractive indices. There was no marked difference in rate of isomerization using 50 to 200 mg Pd-BaCO₃ (5 % Pd) or 10 to 200 mg Pd-black (Fig. 2, curves a). Two mg Pd-black gave only a slow rate of isomerization (curve b) and if the hydrogen was temporarily omitted, there was no isomerization (curve c). The variations caused by using different amounts of catalyst were of the same order as the variations caused by different samples of catalysts. A few samples of catalysts gave, for some unexplained reason, a very slow rate of isomerization even though they had been prepared exactly according to the given instructions.

One isomerization was performed with a catalyst giving a slow rate of isomerization (23 hours) and samples were removed during the isomerization for sorption analyses. These sorptograms* are given below:

3 h	1.4756 _{US}	1.4738 ₁	1.4749 ₂	1.4754 ₃	1.4759 ₄	1.4761 ₅	1.4762 ₆₋₇	
5 h	1.4733 _{US}	1.4675 ₁	1.4709 ₂	1.4768 ₃	1.4740 ₄	1.4748 ₅	1.4752 ₆	1.4757 ₇
7 h	1.4710 _{US}	1.4642 ₁	1.4673 ₂	1.4700 ₃	1.4718 ₄	1.4730 ₅	1.4740 ₆	1.4749 ₇
9 h	1.4690 _{US}	1.4630 ₁	1.4647 ₂	1.4659 ₃	1.4682 ₄	1.4707 ₅	1.4725 ₆	1.4741 ₇
12 h	1.4657 _{US}	1.4632 ₁₋₃	1.4640 ₄	1.4652 ₅	1.4672 ₆	1.4700 ₇		
16 h	1.4642 _{US}	1.4632 ₁₋₅	1.4643 ₆	1.4654 ₇				
19 h	1.4633 _{US}	1.4632 ₁₋₆	1.4642 ₇					
23 h	1.4632 _{US}	1.4632 ₁₋₆	1.4635 ₇					

Action of the catalysts on α -pinene

The sorptograms of fully isomerized β -pinene resembled closely those obtained from α -pinene after treatment with the catalyst. In nearly every case, a slight slope in the beginning and a small peak at the end of the sorptogram were formed. A few samples of catalysts gave, however, no slope in the beginning of the sorptograms (*cf.* the sorptograms in the preceding paragraph).

Shaking samples (1 ml) of index-homogeneous α -pinene with Pd-BaCO₃ (50 mg) for 1, 2, 4, and 12 hours the following sorptograms were obtained:

1 h	1.4632 _{US}	1.4629 ₁	1.4630 ₂	1.4631 ₃	1.4632 ₄₋₆	1.4637 ₇	
2 h	1.4631 _{US}	1.4626 ₁	1.4629 ₂	1.4630 ₃	1.4631 ₄	1.4632 ₅₋₆	1.4635 ₇
4 h	1.4632 _{US}	1.4629 ₁	1.4631 ₂₋₃	1.4632 ₄₋₆	1.4635 ₇		
12 h	1.4632 _{US}	1.4629 ₁	1.4630 ₂	1.4631 ₃₋₄	1.4632 ₅₋₆	1.4640 ₇	

These sorptograms are similar to the ones using Pd-black, the bubbling method or when the isomerization was performed in ether solution (2 parts of ether). Using freshly oxidized α -pinene or β -pinene as starting material (sorptograms 1.4632₁₋₄, 1.4637₅, 1.4650₆, 1.4686₇, and 1.4762₁₋₆, 1.4770₇, respectively) only a slight increase in the peaks was obtained (1.4625₁, 1.4629₂, 1.4630₃, 1.4631₄₋₅, 1.4632₆, 1.4643₇, and 1.4629₁, 1.4630₂, 1.4631₃, 1.4632₄₋₆, 1.4649₇, respectively).

* Sorptogram = n_D^{25} values plotted against 5 μ fraction number. In order to simplify printing of the sorptograms the n_D^{25} values are given with the fraction number as index. The unadsorbed value is given US as index.

Action of Pd-BaCO₃-catalyst on Δ^3 -carene, *d*-limonene and terpinolene

As Pd-BaCO₃ was found to be the most convenient catalyst for our purpose the following isomerizations were performed with this catalyst using the shaking method. Shaking samples (1 ml) of index-homogeneous Δ^3 -carene, *d*-limonene and terpinolene with 50 mg Pd-BaCO₃ for 1, 4 and 12 hours there was an effect similar to the one obtained with α -pinene although the peaks were smaller.

Sorptograms: Δ^3 -Carene

1 h	1.4700 _{US}	1.4698 ₁	1.4700 ₂₋₇		
4 h	1.4699 _{US}	1.4692 ₁	1.4698 ₂₋₃	1.4700 ₄₋₆	1.4703 ₇
12 h	1.4699 _{US}	1.4693 ₁	1.4697 ₂₋₄	1.4698 ₅	1.4700 ₆₋₇

d-Limonene

1 h	1.4703 _{US}	1.4701 ₁	1.4703 ₂₋₆	1.4704 ₇	
4 h	1.4703 _{US}	1.4700 ₁	1.4701 ₂	1.4703 ₃₋₇	
12 h	1.4701 _{US}	1.4693 ₁	1.4701 ₂	1.4702 ₃₋₄	1.4703 ₅₋₆ 1.4704 ₇

Terpinolene

1 h	1.4863 _{US}	1.4863 ₁₋₆	1.4869 ₇	
4 h	1.4862 _{US}	1.4859 ₁	1.4862 ₂₋₆	1.4864 ₇
12 h	1.4862 _{US}	1.4862 ₁₋₆	1.4865 ₇	

Isomerization of β -pinene mixtures

The index-homogeneous terpenes given above were mixed with small amounts of β -pinene and isomerized. The sorptograms before and after isomerization are given below:

Δ^3 -Carene + 5 % β -pinene.	1.4701 _{US} 1.4700 ₁ 1.4701 ₂₋₅ 1.4702 ₆ 1.4703 ₇ ;
after isomerization	1.4700 _{US} 1.4698 ₁ 1.4701 ₂₋₆ 1.4703 ₇ .
<i>d</i> -Limonene + 5 % β -pinene.	1.4708 _{US} 1.4710 ₁ 1.4708 ₂₋₃ 1.4706 ₄ 1.4703 ₅₋₆ 1.4710 ₇ ;
after isomerization	1.4701 _{US} 1.4679 ₁ 1.4694 ₂ 1.4701 ₃ 1.4702 ₄ 1.4703 ₅₋₆ 1.4704 ₇ .
<i>d</i> -Limonene + 10 % β -pinene.	1.4710 _{US} 1.4718 ₁ 1.4710 ₂ 1.4707 ₃ 1.4705 ₄ 1.4703 ₅₋₆ 1.4705 ₇ ;
after isomerization	1.4700 _{US} 1.4669 ₁ 1.4691 ₂ 1.4701 ₃ 1.4703 ₄₋₆ 1.4704 ₇ .
Terpinolene + 2 % β -pinene.	1.4861 _{US} 1.4854 ₁ 1.4860 ₂ 1.4861 ₃₋₅ 1.4862 ₆₋₇ ;
after isomerization	1.4861 _{US} 1.4852 ₁ 1.4859 ₂ 1.4861 ₃₋₄ 1.4862 ₅₋₆ 1.4867 ₇ .
Terpinolene + 5 % β -pinene.	1.4859 _{US} 1.4843 ₁ 1.4854 ₂ 1.4859 ₃ 1.4860 ₄₋₆ 1.4862 ₇ ;
after isomerization	1.4849 _{US} 1.4817 ₁ 1.4850 ₂ 1.4853 ₃ 1.4856 ₄ 1.4858 ₅ 1.4780 ₆ 1.3970 ₇ .
Terpinolene + 10 % β -pinene.	1.4853 _{US} 1.4822 ₁ 1.4842 ₂ 1.4850 ₃ 1.4854 ₄ 1.4858 ₅ 1.4859 ₆ ;
1.4860 ₇ ;	
after isomerization	1.4834 _{US} 1.4757 ₁ 1.4832 ₂ 1.4846 ₃ 1.4851 ₄ 1.4853 ₅ 1.4856 ₆ 1.4030 ₇ .
Δ^3 -Carene + 10 % limonene + 17 % β -pinene (slightly oxidized).	1.4719 _{US} 1.4708 ₁ ;
1.4705 ₂ 1.7403 ₃ 1.4708 ₄₋₆ 1.4718 ₇ ;	
after isomerization	1.4728 _{US} 1.4703 ₁ 1.4708 ₂ 1.4709 ₃ 1.4710 ₄₋₆ 1.4754 ₇ .
Δ^3 -Carene + 10 % <i>d</i> -limonene + 15 % α -pinene.	1.4682 _{US} 1.4667 ₁ 1.4682 ₂ 1.4690 ₃ ;
1.4691 ₄ 1.4693 ₅ 1.4697 ₆ 1.4701 ₇ .	

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