

# Selective dehydrogenation of dipentene (*R*-(+)-limonene) into paracymene on silica supported palladium assisted by $\alpha$ -olefins as hydrogen acceptor

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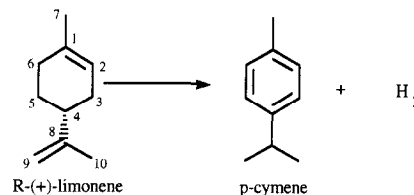
## Abstract

Paracymene is a well known material used in polymers and perfume chemistry. It can be obtained by the dehydrogenation and the aromatization of dipentene (*R*-(+)-limonene). To be useful, this reaction must be fully selective to avoid further purification processes. Dipentene is readily dehydrogenated with a palladium catalyst, but hydrogenation simultaneously takes place leading to *cis* and *trans* paramenthanes which drastically decreases the yield in paracymene. To avoid this hydrogenation which occurs by hydrogen transfer,  $\alpha$ -olefin has been used as hydrogen acceptor. Using silica supported palladium and a hydrogen acceptor (e.g. 1-decene) paracymene is obtained from dipentene with a very high yield (95%) at a moderate temperature (145°C).

**Keywords:** *R*-(+)-limonene; Dehydrogenation; Paracymene; Pd/SiO<sub>2</sub>; Hydrogen transfer reaction

## 1. Introduction

Catalytic dehydrogenation of dipentene (*R*-(+)-limonene) to paracymene (Eq. (1)) is of great interest for the further formation of polymers (synthetic fibers, antiseptics, etc.). Paracymene is also a useful raw material for the synthesis of non-nitrated musks, which nowadays tend to replace nitrated musks.



Paracymene can be obtained by the dehydrogenation of various terpenes. For instance, numerous authors have studied the catalytic dehydrogenation of 3-carene to paracymene [1–10] using acids or metals as catalysts.

This reaction is not selective in paracymene since it also produces metacymene isomers.

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When dehydrogenating  $\alpha$ -pinene,  $\beta$ -pinene or pinane [11–13] selectivity in paracymene is quite good because steric factors prevent formation of orthocymene.

The use of dipentene as a precursor of paracymene is interesting because dipentene already possesses the required skeleton. This dehydrogenation has been described with acidic or basic catalysts [14]. However, to our knowledge, only one result in the patent literature has been reported using metallic catalysts [15]. This patent claims that the dehydrogenation of dipentene to paracymene occurs selectively at 230°C with palladium oxide and sulfur on active carbon.

It has been demonstrated recently that ethylcyclohexane could be transformed into ethylbenzene on carbon supported Pt, Rh or Pd catalysts [16]. Similar results have been obtained starting from cyclohexene or cyclohexane [17]. On the other hand, hydrogen acceptors such as mesityl oxide or oxygen have been used to improve the dehydrogenation rate of various compounds, including terpenes [18–20].

The aim of this paper is to describe a highly selective dehydrogenation reaction of dipentene into paracymene, using palladium on silica as catalyst and a hydrogen acceptor such as an  $\alpha$ -olefin to displace the thermodynamics of the dehydrogenation.

## 2. Experimental

### 2.1. Catalyst preparation

Palladium was impregnated on silica (Degussa Aerosil 200 m<sup>2</sup>/g) by cationic exchange of the tetramine palladium complex [Pd(NH<sub>3</sub>)<sub>4</sub>](OH)<sub>2</sub>. The catalyst was then calcinated in dry air and reduced under a hydrogen flow, both at 450°C. Chemical analysis of the catalyst shows a 1.77% Pd in weight on silica. The volumetric measurement of adsorbed hydrogen at 20°C under 20 mbar gives 0.8 H/Pd. In these conditions, the formation of the  $\beta$  hydride phase is avoided [21]. Assuming a stoi-

chiometry of 1 adsorbed hydrogen atom per surface palladium atom, a dispersion (ratio between surface palladium atoms and total palladium atoms) of 80% is obtained.

### 2.2. Catalytic tests

The dehydrogenation of dipentene was performed in the liquid phase, under an hydrogen atmosphere at a temperature varying from 100 to 180°C. Before each experiment, 0.4 g of Pd/SiO<sub>2</sub> (3.6 mmol of Pd) was reduced at 450°C under a hydrogen flow and transferred in argon into the reactor containing 220 g of dipentene (1.8 mol). In all case, the ratio substrate/catalyst was equal to 500. When the reaction was carried out in the presence of a hydrogen acceptor (e.g. an  $\alpha$ -olefin), the same amount of the desired olefin (1.8 mol) was added into the reactor with the dipentene. Then argon was replaced by hydrogen and the reactor was heated to the desired temperature. The reaction was followed by GC analysis of the liquid phase, using a CP-WAX 57CB column and a flame ionization detector.

## 3. Results and discussion

With palladium on silica, at 100°C and 180°C, dipentene is transformed into paracymene and paramenthane (*cis* and *trans* isomers) (Fig. 1 and Table 1).

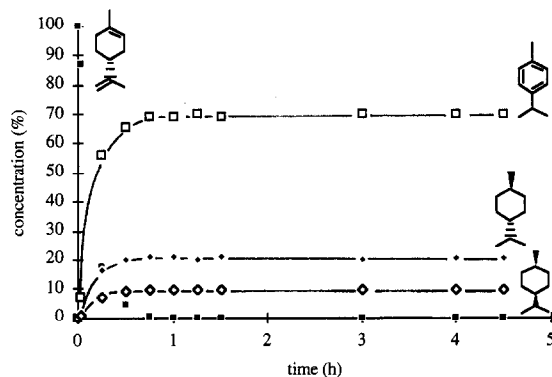



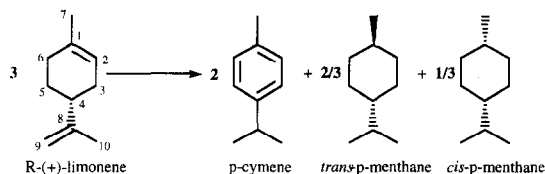


Fig. 1. Dehydrogenation of dipentene at 100°C with Pd/SiO<sub>2</sub>.

Table 1  
Effect of temperature on the amount of paracymene and paramenthane obtained at 100% conversion of dipentene with Pd/SiO<sub>2</sub>

temperature (°C)				t <sub>100</sub>
	(%)	(%)	(%)	(h)
100	70	20	10	1
180	62	25	12	0.5

For three molecules of limonene consumed, about two molecules of paracymene and one molecule of paramenthane are formed. Dehydrogenation of one molecule of limonene into paracymene gives one molecule of hydrogen and two molecules of hydrogen are needed to form paramenthane from limonene. It is clear that this 'disproportionation' of dipentene occurs at 100 and 180°C on Pd/SiO<sub>2</sub>. This is not unexpected as cyclohexene is easily 'disproportionated' on noble metals in such conditions [22–24]. The whole reaction can be illustrated as follows:



*Trans* and *cis* paramenthanes are formed in a 2/1 ratio. The predominance of the *trans* isomer is in agreement with its higher stability due to the equatorial position of the two alkyl groups. In this configuration, 1,4-diaxial interactions are minimal. The difference in energy for the two configurations, calculated using SYBYL<sup>1</sup> as molecular modeling software, is 3.8 kcal/mol. This difference can be noted on the infrared

spectrum, where the  $\delta_{\text{sym}}(\text{CH}_3)$  band is more intense for the *cis* isomer (stronger intramolecular interactions) than for the *trans* one.






Since hydrogen is produced by dehydrogenation of the limonene molecule on the metallic surface and then could hydrogenate an adsorbed limonene molecule into paramenthane, it became evident to try an hydrogen acceptor to achieve a better selectivity for the dehydrogenation process. Several olefins have been tested as hydrogen acceptors: 1-octene, 1-decene, 1-undecene and 1-dodecene. The boiling points of each olefin under 1 atm are respectively 123, 181, 192 and 213°C. In comparison, the boiling point of limonene is 176°C.

The compositions of the products obtained after the complete conversion of limonene (that we shall refer as the time  $t_{100}$  of reaction) and for various hydrogen acceptors and temperatures are reported on Table 2. The best results are obtained with 1-decene and 1-undecene, for which yields in paracymene reach 92%. With 1-decene, the reaction seems to be faster than with 1-undecene. Other olefins do not provide good yields in paracymene as they seem to be less efficient hydrogen acceptors.

To illustrate the results obtained with Pd/SiO<sub>2</sub> and 1-decene at 180°C, simultaneous kinetics of dehydrogenation of limonene (a) and hydrogenation of 1-decene (b) are represented in Fig. 2.

It is interesting to note (Table 2) that with

Table 2  
Composition of the mixture obtained after the reaction of limonene (100% conversion) with Pd/SiO<sub>2</sub> and different terminal olefins

	Temp.						alcene	alcane	t <sub>100</sub>
	(°C)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(h)
1-octene	120	43	5	2	21.3	23.4	50	50	7
1-decene	180	92	6	1.5	0	0	0	100	1
1-decene	140	88	7.5	2.7	1.2	1.4	0	100	1
1-decene	100	75	17	5.5	1.2	1.4	0	100	1.5
1-undecene	180	91	6.7	2.3	0	0	0	100	2
1-dodecene	180	70	4.5	2	9.8	15.3	20	80	4

<sup>1</sup> Tripos Ass., 1699 S. Hanley Rd., Suite 303, St. Louis, MO 63144, USA.

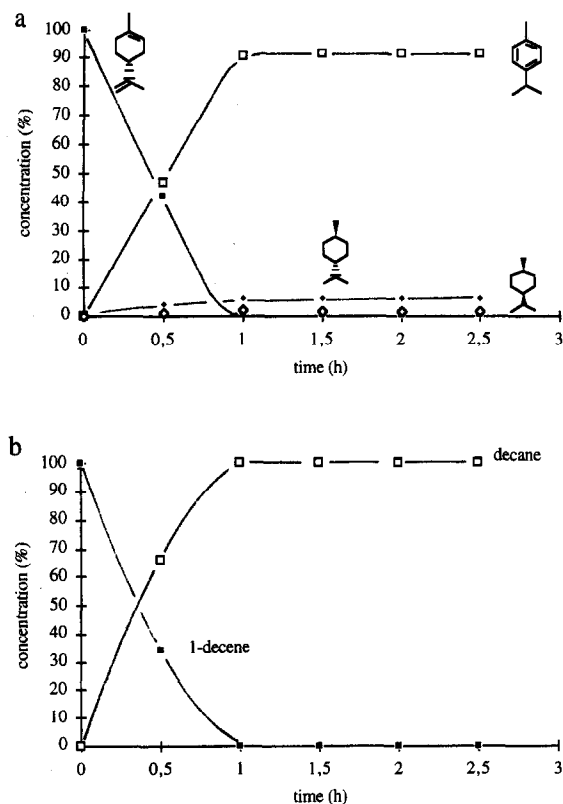


Fig. 2. Simultaneous kinetics of limonene dehydrogenation (a) and 1-decene hydrogenation (b) at 180°C.

1-decene as a hydrogen acceptor, 1-decene is fully hydrogenated to decane and dipentene is selectively dehydrogenated to paracymene at various temperatures (180°C, 140°C, 100°C). The best yield in dehydrogenation is obtained for the highest temperature. However, even at low temperature (e.g. 100°C), it is possible to obtain 75% of paracymene.

The role of 1-decene can be explained simply as follows. Each time a limonene molecule is transformed into paracymene, one molecule of hydrogen is given off. The latter can be used to hydrogenate either limonene into paramenthanes (rate  $r_1$ ), or 1-decene into decane (rate  $r_2$ ). If  $r_2$  is much higher than  $r_1$ , then decane and paracymene are the main products.

The byproducts of these reactions are always a mixture of *cis* and *trans* paramenthanes. Whatever the temperature, the ratio *trans/cis* was nearly constant with a value of about 3. It

should be recalled that this ratio is about 2 when no hydrogen acceptor was used. The reason for such difference of behavior is not clear.

#### 4. Conclusion

When treating limonene in the presence of metallic catalysts such as Pd/SiO<sub>2</sub>, disproportionation of the molecule into paracymene and paramenthane usually occurs. The same results obtained at various temperatures show that the reaction is a real disproportionation and not a thermodynamic equilibrium at a given temperature.

However, dehydrogenation of limonene to paracymene has been achieved selectively by means of  $\alpha$ -olefin as hydrogen acceptor. Among the terminal olefins used to fulfill this aim, 1-decene appears to be the best. Other olefins do not provide the same yields in paracymene, a possible explanation being the physical analogy between limonene and 1-decene: each one possesses ten carbon atoms and their boiling points are quite close (176°C and 181°C, respectively). With 1-decene as a hydrogen acceptor, yield in paracymene reaches 92% at moderate temperatures (180°C) and the formation of paramenthanes is limited to below 8%.

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